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APPLICATION OF OIL INDUSTRY WASTES (SLUDGES AND SULFUR) IN RUBBER PRODUCTION

Abstract. The important scientific direction of petrochemistry is manufacture of plasticizers, softeners, vulcanizing agents, fillers on the basis of industrial wastes. This allows to expand the raw-material base, use heavy stocks of refinery wastes, reduce environmental pressure on the nature and solve the problem of manufacture of import-substituting softeners for the rubber-processing industry of Kazakhstan. Besides, the feature of Kazakhstan petroleum crude oils is high concentration of sulfur compounds, in consequence of which much wastes are formed. Optimization of developed rubber compounds for manufacture of a wear-resistant chafer strip of passenger car tires was carried 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. With a view 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: organic share of oil sludge, oil sludge, softeners, vulcanizing agent, Tengiz sulfur, vulcanizing system, rubber compound, chafer strip.

Introduction. Rubber industry of 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 to expand the raw-material base, use heavy stocks of refinery wastes, reduce environmental pressure on the nature and solve the problem of manufacture of import-substituting softeners and vulcanizing agents for the rubber-processing industry of Kazakhstan. Besides, the feature of Kazakhstan petroleum crude oils is high concentration of sulfur compounds, in consequence of which much sulfuric wastes are formed [1-4].

Experimental part

The generally accepted is application of organic and inorganic low-molecular compounds in the receipts of rubber compounds. By the efficacy, 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 production. 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.

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 [5-8].

Result and its discussion

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 [9, 10].

Optimization of developed rubber compounds for manufacture of a wear-resistant chafer strip of passenger car tires was carried 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 [11-13].

With a view 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 [14-17]. 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 the chafer strip of the passenger car tires.

Table 1 – Receipt of the optimal rubber compound for the rubberizing of the wear-resistant chafer strip

Ingredients	Per 100 mass shares of the rubber substance							
	Control variant	Studied variant						
SKI-3	40,0	40,0	40,0	40,0	40,0	40,0	40,0	40,0
SKMS-30 ARK	60,0	60,0	60,0	60,0	60,0	60,0	60,0	60,0
Tengiz sulfur	2,4	2,4	2,4	2,4	2,4	2,4	2,4	2,4
Sulfonamide "M"	1,2	1,2	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	0,4	0,4
Zinc oxide	5,0	5,0	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	2,0	2,0
Pine rosin EM-3	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0
Softener ASMG	4,0	–	–	–	–	–	–	–
Organic share of the oil sludge	–	4,0	4,5	5,0	5,5	6,0	6,5	7,0
Oil PN-6SH	4,0	4,0	4,0	4,0	4,0	4,0	4,0	4,0
Protective wax ZVP	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0
Acetone anil R	2,0	2,0	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	2,0	2,0
Technical carbon P-514	40,0	40,0	40,0	40,0	40,0	40,0	40,0	40,0
Technical carbon P-234	30,0	30,0	30,0	30,0	30,0	30,0	30,0	30,0
Mineral share of the oil sludge	10,00	10,0	10,0	10,0	10,0	10,0	10,0	10,0

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 system. This reduction is directly proportional to the percentage composition of the organic share of the oil sludge [18-20].

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 rubberizing of the wear-resistant chafer strip. Analysis of the rubber compounds' vulcanometric curves shows that optimal time for attaining the vulcanizing of the rubber compound for the rubber compound of the chafer strip consists 19 minutes.

Physical-mechanical tests of the rubbers 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 wear-resistant chafer strip vulcanizing, 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 vulcanizing of the wear-resistant chafer strip. Dependencies of the main physical-mechanical indicators of the vulcanizates from the softeners' dosage are given in Table 2.

Table 2 – Properties of the rubber compounds and vulcanizates on the basis of rubber substances of general purpose for the vulcanizing of the wear-resistant chafer 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	6-v	7-v
Nominal tensile strength, kgf/cm^2, no less	90	108	105	110	110	112	107	107
Nominal modulus at 300%, kgf/cm^2	70	72	72,5	74	74,5	74	73	73
Relative tensile elongation, %, no less	280	270	300	310	310	290	292	290
Shore hardness, c.u.	73	75	77	77	78	75	75	75

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 macromolecules by the same token reducing the rubber substance macromolecules' intermolecular interaction. Application of Tengiz sulfur allowed to keep the vulcanizing kinetics, which could be reduced when using the organic share of the oil sludge.

Conclusion. 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. 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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ТЕХНИКАЛЫҚ РЕЗИНАДА ӨНЕРКӘСІБІНДЕ МҰНАЙ ҚАЛДЫҚТАРЫН (ШЛАМ МЕН КҮКІРТ) ҚОЛДАНУ

Аннотация. Осы жұмыста мұнай өндеу қалдықтарының – 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. Тенгизде күкірт көлемді қатты блоктар түрінде әдейі жабдықталған алаңшықтарда, басқаша айтканда – "күкірттің карталары", сақталады. Күкірттің шығырларда сақталуы – Канада, Мексика, Нидерландия, Польша және АҚШ сияқты елдерде қолданылатын бірденбір әдіс.

Күкірт, техникалық 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 резеңке сапасының көтерілуіне алып келеді. Полимерлік күкірттің қолданысы, өндіріліп алынатын резеңкелердің икемділік қасиеттерін реттеуге мүмкіндік береді.

Мұнай қалдықтарынан шығатын күкірттің қолданысы, мұнай өнеркәсібінің қалдықтарын кәдеге жарату экологиялық мәселесін шешеді және дөңгелек резеңкелерінің физикалық-механикалық касиеттерін жақсартады.

Түйін сөздер: күкірт, полимерлі күкірт, теңіз күкірті, күкіртті қосылыстар, химиялық қосылыстар, күкірт шаңы, сульфид күкірті, каучук, резеңке бұйымдар, вулканизаттар, вулканизация агенті

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ПРИМЕНЕНИЕ ОТХОДОВ НЕФТЯНОЙ ПРОМЫШЛЕННОСТИ (ШЛАМОВ И СЕРЫ) В ПРОИЗВОДСТВЕ 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 экологическую нагрузку на природу и решить проблему производства импортозамещающих мягчителей для резиновой промышленности Казахстана. Также особенностью казахстанских нефтей является повышенной содержание соединений серы, вследствие чего образуется много серных отходов. Путем последовательного изучения влияния на свойства резин содержания каждого из компонентов в отдельности (серы и нефтешлама) при фиксированных количествах других ингредиентов была проведена оптимизация разработанных резиновых смесей для изготовления износостойкой бортовой ленты легковых шин. С целью выявления оптимального количества органической части нефтешлама 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, бортовая лента.