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Zh.U. Myrkhalykov¹, T.S. Bazhirov¹, A.F. Kemalov²,
R.A. Kemalov², L.Kh. Fokeyeva², K.K. Syrmanova¹, Ye.T. Botashev¹

¹M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan

²Kazan Federal University, Kazan, Russian Federation.

E-mail: tynlybek.bazhirov@gmail.com

ASSESSMENT OF INHIBITIVE PROPERTY OF SULFUR AS A FILLER OF POLYMER MATERIALS WITH A VIEW TO REDUCE TECHNOGENIC IMPACT ON ECOLOGY

Abstract. According to modern representations bitumen polymer compositions (BPC) are dispersions of polymers with bitumens. The important stage of creation of durable insulating materials is their inhibition in consequence of oxidation processes in conditions of their application. In this connection the most acceptable substance is sulfur-containing compounds, which effectively performs this role. Currently sulfur production is sharply marked from the number of other extractive industries that from the ecological point of view the most important problem is not achievement of sustained development condition by the sulfur production, but solution of problems of safe storage or even disposal of extracted sulfur. As against other extractive industries, which main efforts are focused on the search of more effective methods of production of required component against its decreasing world reserves, leading companies in sulfur industries worried first of all by the search of new ways for safe management by extracted by them resource.

Keywords: oil dispersed systems (ODS), film-forming substances, petro chemistry, thermoplastic resins (TPR), sulfur, pigments, physical-mechanical, insulating properties of coatings.

Introduction. According to modern representations bitumen polymer compositions (BPC) are solution of polymer in bitumen. On this basis, large, branched polymer molecules, equally distributing along the mass of bitumen, as if reinforce it, give bitumen elasticity and resilience, as well as thermal resistance, which appear only at some optimal amount of polymer molecules, apparently when their concentration forms continuous net structure.

Preparation of the film-former [1-3], i.e. combination of special bitumen with components was carried out in two stages: a) preparation of polymer solution consisting of thermal polymer resins (TPR) sample, polymer plasticizer and aromatic solvent (o-xylene); b) combination of polymer solution with sample of special bitumen.

Research methods. Bitumen-insulating materials (BIM) were prepared for evaluation of protective properties of such polymers as divinyl-styrene thermoplastic elastomers (DSTE), low molecular sevilenes (LMS), polycyclopentadienes (PCPD), atactic polypropylenes (APP) [4]. It should be noted that the polymers were introduced in amount from 2 to 6 mass percent, after their distribution in the solvent they were applied to the substrates. Electrochemical studies, given in Table 1, were carried out on the fifth day.

Data of Table 1 show that LMS and DSTE polymers with critical concentration of structuring (CCS) 2 and 2-2,5 mass percent respectively have the most effective inhibiting characteristics. Special attention should be paid to the protective barrier that occurs when introducing 8 mass percent TPR, namely at 5 and 7 hour exposure in the electrolyte solution, when passivation of the substrate surface, isolated by bitumen-polymer film-former, occurs.

Table 1 – Change in the metal potential towards standard hydrogen electrode from time

Polymers / mass concentration		0 point	1 hour	3 hours	5 hours	7 hours
DSTE	2%	-325	-252	-178	-273	-169
	4%	-178	-153	-50	-148	-150
LMS	2%	-358	-283	-78	-103	-68
	4%	-313	-188	-62	-88	-158
PCPD	2%	-130	-138	-53	-118	-91
	4%	-178	-205	-120	-161	-148
APP	2%	-220	-194	-155	-168	-161
	4%	-228	-228	-168	-253	-252
TPR	2%	-214	-188	-133	-146	-129
TPR	4%	-225	-158	-160	-178	-158
	6%	-338	-183	-146	-123	-119

Research results

Influence of elemental sulfur as a plasticizer on inhibition of the bitumen-polymer film-former.

When studying physical and mechanical properties of the bitumen-insulating materials (BIM), namely their adhesion-strength properties, it is possible to conclude about the need for their physicochemical modification for the purpose of plasticization and elimination of oxidative degradation, i.e. premature aging. Plasticizers introduced into the composition of BIM weaken the energies of intermolecular interactions in macroassociates of bitumen, significant part of which is destroyed and included according to the principle of intramicellar or supramycellular solubilization into the micellar structure of the inhibitor. Introduction of plasticizer into the composition of BIM, as a rule, slightly reduces strength and hardness of the film, but considerably improves its uniformity and elasticity, increases its elongation at break, increases its frost-resistance, i.e. reduces brittleness at low temperatures, but the main thing is that it improves insulation properties of polymer compounds. Mechanism of action of plasticizers consists in increasing the mobility of individual molecules or segments of macromolecules of polymers which are in the stable state of static, semi-rolled coil, by weakening their molecular interactions, or by increasing the mobility of associates (packets) of macromolecules due to weakening of interphase interactions or lowering the degree of crystallinity.

When choosing BIM's modifying component, we based on the fact that the agent should have both plasticizing effect and should stand against thermal oxidative breakdown, i.e. function as inhibitor-ageing retarder in exploitation of the bitumen material filled with a pigment. Elemental sulfur has these properties and requirements which correspond to GOST 126-79.

Sulfur content may form spatial structures in its certain, conjugated with available particles of the dispersed phase, due to formation of complex structural units (CSU) [5]. In this case, BIM's properties will be determined by this new spatial conjugate structure. Already at low concentrations this additive can have a structuring effect, and at large – plasticizing and vice versa; at low concentrations the effect will be plasticizing, and at large – the structuring effect. In the first case, obviously, this should be due to the fact that if the content is higher than the determined one, the additive cannot be distributed in the dispersion medium, and it will play the role of hinges in the shear. In the second case, with its certain content, it will be sufficient to form independent or spatial structure conjugate with the particles of the dispersed phase of the given system.

According to studies [4], it was shown that sulfur-containing compounds capable to decompose hydroperoxides are introduced to exclude the oxidative degradation of bitumen-polymer compositions (BPC). This leads to plasticization of BPC. Increase in the interplanar distance, characterized by the packing density of the condensed aromatic structures, was detected by X-ray diffraction analysis. Thus, the use of sulfur as a plasticizing agent of bitumen-polymer BIM significantly expands possibilities of their use under different conditions. It is well known that in aromatic and paraffin-naphthenic hydrocarbons, aromatic components oxidize much faster. Thermo-oxidative transformations of sulphurous oil residues proceed in the inhibited oxidation regime. The role of the inhibitor of oxidation of aromatic

hydrocarbons is performed by sulphide-type sulfide compounds, which destroy the intermediate oxidation products – hydroperoxides, and the oxidation process proceeds along the degenerate branching mechanism. Confirmation of the elemental sulfur's inhibitory effect is study of iodine numbers (Table 2).

It should be noted that the iodine number is the number of grams of iodine joining to 100 grams of the product. The procedure to determine the iodine number is given.

Table 2 – Polymer solutions iodine numbers indicators

Polymer solution composition		Iodine number, ml/g
1	OPR-8%, APP-2%	19,05
	OPR-8%, APP -2% + Sulfur 1,5%	2,8713
2	OPR-8%, DSTE-2%	19,177
	OPR-8%, DSTE-2% + Sulfur 2%	5,9266
3	OPR-8%, LMS-2%	20,701
	OPR-8%, LMS-2% + Sulfur 2,5%	2,8575
4	OPR-8%, LMS-4%	17,5683
	OPR-8%, LMS-4% + Sulfur 2 %	2,7214
5	OPR-8%, PCPD-2%	18,542
	OPR-8%, PCPD-2%+ Sulfur 2 %	1,1641
6	OPR-8%, PCPD-2%	18,542
	OPR-8%, PCPD-2%+ Sulfur 1%	2,6554

Analysis of Table 2 shows effect of the elemental sulfur on the iodine numbers indications in the polymer solutions. Thus, the sulfur interacts with double bonds of polymers, and will also interact with free bonds and radicals, contained in the bitumen and formed during thermal and solar irradiation, under chemical and mechanical action.

Coatings were prepared to evaluate protective properties that the sulfur impacts when combined with BIM. It should be noted that the sulfur was introduced in amount of 0,5 to 3 mass percent. After its distribution in the polymer solution, it was applied to the substrates, then electrochemical studies were carried out on the 5th day, their results are given in Table 3.

Table 3 – Change in the metal potential towards the standard hydrogen electrode from time

Name		0 point	1 hour	3 hours	5 hours	7 hours
DSTE	S-0,5%	-208	-167	-43	-18	-58
	S-1%	-124	-265	-103	-58	-25
	S-1,5%	-213	-103	-93	-10	-71
	S-2%	-288	-128	-83	-18	-48
	S-2,5%	-204	-175	-88	-78	-95
	S-3%	-148	-98	-98	-53	-93
APP	S-0,5%	-155	-68	-158	-115	-126
	S-1%	-138	-53	-63	-118	-162
	S-1,5%	-171	-143	-88	-158	-165
	S-2%	-198	-148	-188	-195	-176
	S-2,5%	-224	-118	-118	-142	-133
	S-3%	-170	-185	-148	-110	-105
LMS	S-0,5%	-313	-178	-53	-87	-88
	S-1%	-223	-158	-163	-153	-150
	S-1,5%	-108	-228	-203	-193	-191
	S-2%	-268	-157	-101	-163	-146
	S-2,5%	-228	-68	-138	-128	-133
	S-3%	-123	-63	-168	-168	-167
PCPD	S-0,5%	-338	-168	-158	-147	-131
	S-1%	-243	-128	-168	-158	-143
	S-1,5%	-308	-163	-158	-126	-145
	S-2%	-288	-152	-126	-126	-188
	S-2,5%	-218	-133	-108	-156	-103
	S-3%	-215	-151	-198	-174	-160

Based on the carried out complex studies, the most optimal concentration of the elemental sulfur in the film-forming agents is 2,5 mass percent.

Development of physical and chemical technology of pigmentation of bitumen-polymer materials. Presence of pigments and fillers in organic polymer compounds causes significant change in deformation-strength properties. Thus pigmentation of BIM along with increase in optical properties of the polymer compounds leads to increase in the insulating capacity, internal stresses, modulus of elasticity, and also adhesion-strength properties. Thus, we prepare composition of the pigmented BIM of the modified DSTE, which include estimated amount of worked chromium-containing pigment IM-2201 and film former.

Amount of the pigment and film former is calculated by method [6].

The prepared suspensions are pigmented in a dispersant, reaching dispersion value of 30 μm .

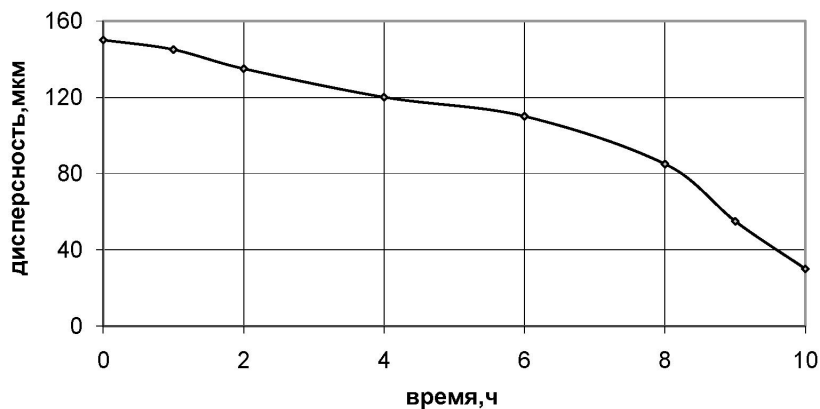


Figure 1 – Time – dispersion relationship graph (suspension 2)

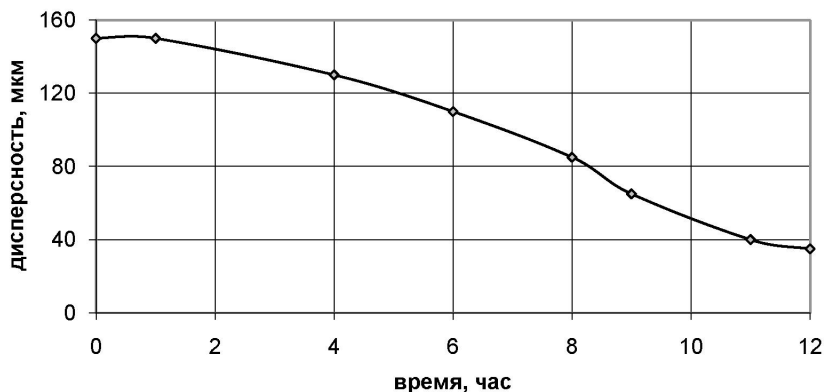


Figure 2 – Time – dispersion relationship graph (suspension 3)

Analysis of the physical and mechanical properties, pigmented BIM is presented in Tables 4–6.

Tables 4 – Analysis of the physical and mechanical properties, pigmented BIM of the modified DSTE (curing time is 3 days)

OPC	Hardness according to ME-3, c.u.	Bending, points	Hardness according to ISO 15184, points	Adhesion, points
0,69	0,2626	2	0	1
0,56	0,2953	1	1	1
0,4	0,3209	1	2	1
0,24	0,3256	1	2	1
0,12	0,3674	1	2,5	1

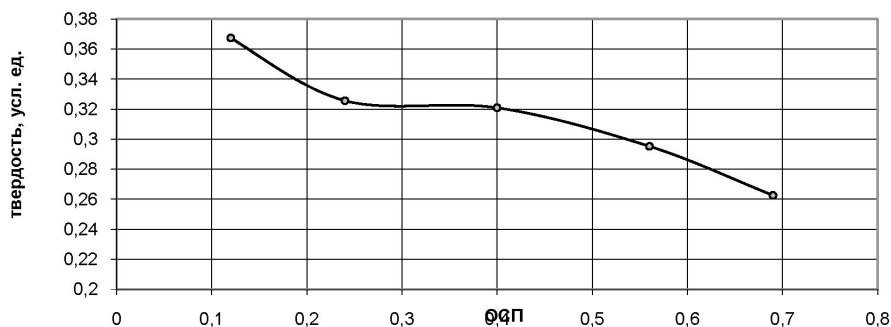


Figure 3 – Change in the coating hardness on the pigment content in it

Tables 5 – Analysis of the physical and mechanical properties, pigmented BIM of the modified DSTE (curing time is 7 days)

OPC	Hardness according to ME-3, c.u.	Adhesion according to ISO 4624, kgf/cm ²	Hardness according to ISO 15184, points	Adhesion, points
0,69	0,3050	2	0	1
0,56	0,3125	3	1	1
0,4	0,3546	5	2	1
0,24	0,3121	7	2	1
0,12	0,3807	9	2,5	1

Tables 6 – Analysis of the physical and mechanical properties, pigmented BIM of the modified LMS (curing time is 3 days)

OPC	Hardness according to ME-3, c.u.	Bending, points	Hardness according to ISO 15184, points	Adhesion, points
0,69	0,3659	3	0	1
0,59	0,5193	2	1	1
0,46	0,5080	1	2	1
0,31	0,4625	1	2	1
0,2	0,2920	1	3	1

Conclusions. It should be noted that the smaller the pigment, metal-containing powder of high aggregative resistance to fracture during dispersion and, thus, the smaller the OPC, the lower the hardness and the higher the adhesion-plastic properties of the polymer compounds.

According to the physical and mechanical studies of the pigmented BIM modified by the polymers, it can be seen that the polymers are important component of the bituminous film former, as the hardness and adhesion of the coatings increase significantly.

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**Ж. У. Мырхальков¹, Т. С. Бажиров¹, А. Ф. Кемалов²,
Р. А. Кемалов², Л. Х. Фокеева², К. К. Сырманова¹, Е. Т. Боташев¹**

¹М. Әуезов атындағы Оңтүстік Қазақстан мемлекеттік университеті, Шымкент, Қазақстан,
²Казан федералдық университеті, Ресей

**ЭКОЛОГИЯҒА ТЕХНОГЕНДІК ӘСЕРІН ТӨМЕНДЕТУ МАҚСАТЫНДА ПОЛИМЕРЛІ
МАТЕРИАЛДАРДЫ ТОЛЫҚТЫРҒЫШ РӨЛІНДЕГІ КҮКІРТТІҢ БАЯУЛАТҚЫШ
ҚАБІЛЕТТІЛІГІН БАҒАЛАУ**

Аннотация. Замануи түсінікте битум полимерлі композиция (БПК) – полимерлердің битуммен дисперсиясы. Төзімді оқшаулау материалдарын жасаудағы маңызды кезең оларды қолдану жағдайында ағымдағы тотығу процестері салдарынан оларды баяулату болып табылады. Осыған байланысты жарамды зат болып табылатын бұл рөлді тиімді атқарушы, күкірт құрамды байланыстарды қолдану тиімді болып табылады. Қазіргі уақытта күкірт өндірісінің басқа кен игеру салаларынан, экологиялық көзқараста маңызды мәселе күкірт өндірісін тұрақты дамытуға қол жеткізу емес, өндірілетін күкіртті қауіпсіз сақтау немесе көміп тастау мәселелерін шешуде болып табылатыныменерекшеленеді. Дүниежүзілік қорлардың азаюы аясында негізгі күштерін қажет компоненттерді алудың тиімді әдістерін іздеуге бағытталған, басқа кен игеру салаларынан, күкірт өндіру саласындағы алдыңғы қатардағы компаниялар ең алдымен олармен алынған ресурстарды қауіпсіз қолданудың жаңа жолдарын іздеумен ерекшеленеді.

Түйін сөздер: мұнай дисперстік жүйелері (МДЖ), қабыршақ түзуші заттар, мұнай химиясы, термoplastикалық шайырлар (ТПШ), күкірт, пигменттер, жабындардың физика-механикалық, оқшаулағыш қасиеттері.

**Ж. У. Мырхальков¹, Т. С. Бажиров¹, А. Ф. Кемалов²,
Р. А. Кемалов², Л. Х. Фокеева², К. К. Сырманова¹, Е. Т. Боташев¹**

¹Южно-Казахстанский государственный университет им. М. Ауэзова, Шымкент, Казахстан,
²Казанский федеральный университет, Казань, Россия

**ОЦЕНКА ИНГИБИРУЮЩЕЙ СПОСОБНОСТИ СЕРЫ В РОЛИ НАПОЛНИТЕЛЯ
ПОЛИМЕРНЫХ МАТЕРИАЛОВ С ЦЕЛЬЮ УМЕНЬШЕНИЯ
ТЕХНОГЕННОГО ВЛИЯНИЯ НА ЭКОЛОГИЮ**

Аннотация. Согласно современным представлениям битум полимерные композиции (БПК) – дисперсии полимеров с битумами. Важным этапом создания долговечных изоляционных материалов является их ингибирование в следствие протекающих окислительных процессов в условиях их применения. В этой связи наиболее приемлемым веществом является серосодержащие соединения, которые эффективно выполняют эту роль. В настоящее время производство серы резко выделяется из числа других добывающих отраслей тем, что с экологической точки зрения более важной проблемой является не достижение серной промышленностью состояния устойчивого развития, а решение вопросов безопасного хранения или даже захоронения добываемой серы. В отличие от других отраслей добывающей промышленности, где основные усилия направлены на поиск более эффективных методов получения требуемого компонента на фоне сокращающихся его мировых запасов, ведущие компании серной отрасли озабочены, прежде всего поиском новых путей безопасного обращения с добытым ими ресурсом.

Ключевые слова: нефтяные дисперсные системы (НДС), пленкообразующие вещества, нефтехимия, термoplastичные смолы (ТПС), сера, пигменты, физико- механические, изолирующие характеристики покрытий.