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STUDY OF MIXTURES OF AMIDES OF SOAPSTOCK WITH POLYETHYLENE POLYAMINE AND SUNFLOWER OIL ACIDS WITH HEXAMETHYLENEDIAMINE IN DIFFERENT PROPORTIONS AS ADDITIVES TO BITUMEN USING GRAVEL

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ABSTRACT
Amides were synthesized by mixing soapstock, which is a waste of cottonseed oil, and polyethylene polyamine in different mass ratios. The reaction was carried out by stirring for 4 hours at a temperature of 140-145°C in a beaker equipped with a mixer, heater and thermometer. After obtaining the amide, the reaction product was cooled to 80°C, the necessary amount of heavy phlegm was added to it and mixed well, then it was collected in closed containers for use. At the same time, sunflower oil acid was obtained by hydrolysis, amide was synthesized with hexamethylenediamine in a mol ratio of 2:1, and the reaction was carried out in a three-necked flask equipped with a mixer, heater and thermometer. For this purpose, sunflower oil acid was first filled into a three-necked flask, a mixer and a heater were turned on, the required amount of hexamethylenediamine was added and the temperature was raised to 140°C, and the reaction was continued at this temperature for 4 hours. Compositions in three mass ratios (1:1, 1:2, 2:1) were prepared by mixing amides synthesized on the basis of soapstock polyethylene polyamine and acid of sunflower oil hexamethylenediamine. These compositions were added as an additive to bitumen using gravel in quantities of 0.4 and 0.6% and its effect on quality indicators was studied. It has been established that the quality indicators of bitumen improve significantly after the introduction of the additive. So, after adding these compounds to bitumen using gravel, its adhesive ability increases to 1 point, whereas it is 3 points. Brittleness decreases from -18 to -26, while penetration increases from 48 to 55 and tensile strength from 75 cm to 100 cm.
Keywords: soapstock, hexamethylenediamine, polyethylenepolyamine, fragility temperature, adhesion, penetration, tensile.

Introduction

Bitumens are complex mixtures that remain in the cube during the distillation of oil. It is used in civil construction, as well as in many other areas of industry as a binder, anti-corrosion material, as well as waterproofing and radiation protection. Bitumen is an irreplaceable material in the construction of roads. Bitumen is used in the construction of airports, industrial and civil buildings [1-5].

One of the main properties of bitumen is the ability of adhesion, which plays a key role in laying asphalt concrete. The adhesiveness of bitumen characterizes the adhesion to the material. Various supplements are recommended to improve this. Acidic amines, organic acids, their

calcium salts, various polymers, esteromers belong to this family [6-8].

For several years, various additives have been synthesized and added to bitumen in order to improve the quality of road bitumen at the Y.H. Mammadaliyev Institute of Petrochemical Processes [9-13].

The main goal of the presented work is to improve the quality indicators of road bitumen produced at the Baku Oil Refinery named after Heydar Aliyev. For this purpose, amides were obtained from cotton oil waste soapstock and polyethylene polyamine and sunflower oil acids and hexamethylenediamine, and compositions were prepared by mixing these amides in different mass ratios (1:1, 1:2, and 2:1). These compositions were added to road bitumen in amounts of 0.4 and 0.6%, and the effect on its quality indicators was studied.

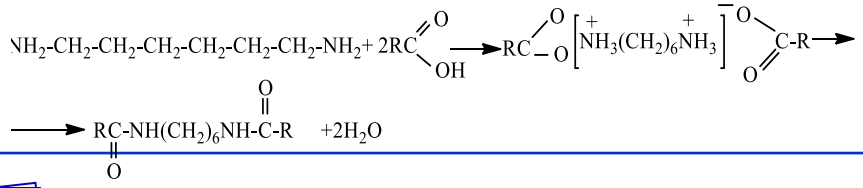
Experimental part

First, the amides of cottonseed oil waste soapstock with PEPA in different mass ratios were synthesized. For this purpose, the required amount of soapstock is poured into a glass equipped with a mixer and a heater. The heater is turned on, the temperature is raised to 60-70^{0}C. At this temperature, the required amount of PEPA is added to the mixing glass and the temperature is raised to 140-145^{0}C and mixed for 4 hours. After obtaining the amide, the reaction product is cooled to 80^{0}C, the necessary amount of heavy phlegm is added to it and collected in closed containers. The amount of substances taken is given in table 1.

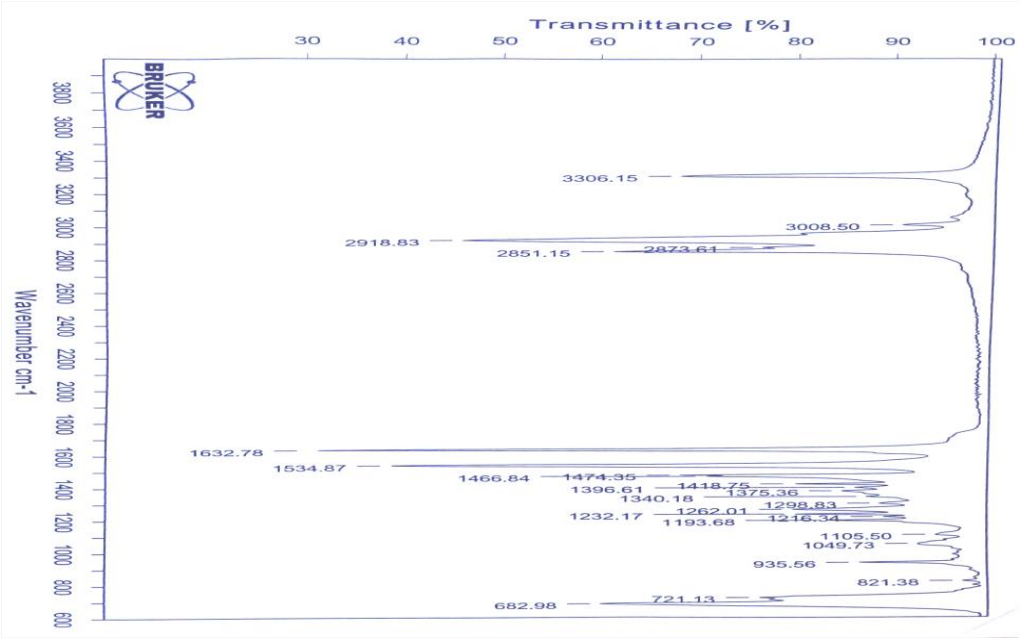
Tablel 1. Synthesis of amides of soapstock with PEPA at different mass ratios.

Number of experiments	Reagents used in the reaction		Heavy phlegm (grams)
	Soapstok, (grams)	PEPA (grams)	
A1	100	20	10
A2	100	20	15
A3	100	20	20
A4	100	25	10
A5	100	25	15
A6	100	25	20
A7	100	30	10
A8	100	30	15
A9	100	30	20
A10	100	15	10
A11	100	15	15
A12	100	15	20

Then hexamethylenediamine (HMDA) amide is synthesized with sunflower oil acids obtained by hydrolysis of sunflower oil. The reaction is carried out in a 3-necked flask equipped with a mixer, a heater and a thermometer. For this purpose, 2 moles of acid are filled into the flask and the heater and mixer are turned on. Then the temperature is raised to 60^{0}C and 1 mol (HMDA) is added to the acid, the temperature is raised to 140^{0}C, and it is mixed at this temperature for 4 hours. The course of the reaction is as follows:



The IR spectra of the synthesized amide were recorded on the ,,ALFA" IR-Fourier spectrometer belonging to the German company Bruker in the wavenumber range of 400-4000 cm^{-1} (figure 1) and it was determined that the following absorption bands of the synthesized amide are present:



721 cm^{-1} - mathematical vibration of the C-H bond of the CH_2 group;
682 cm^{-1} - deformation vibration of NH bond;
1049, 1105, 1193, 1216, 1230 cm^{-1} - valence vibration of the C-N bond:
1534, 1632 cm^{-1} deformation vibration of the NH bond of the NH_2 group:
1375, 1396, 1418, 1474, 1466 cm^{-1} – deformation vibration of CH bond of CH_2 and CH_3 groups;
3008 cm^{-1}- Valence vibration of the C-H bond of the C= C group.

Compositions were prepared from amides obtained by mixing soapstock with PEPA in different mass ratios and amide obtained from the interaction of sunflower oil acid with hexamethylenediamine (table 2).

Table 2. Content of compositions prepared on the basis of soapstock with PEPA and amides of sunflower oil acids with hexamethylenediamine.

Number of compositions	Content of compositions	
	Amide, grams (on the basis of soapstok+PEPA)	Amide, grams (on the basis of acid of sunflower oil + hexamethylenediamine)
1	**2**	**3**
№ 1	A1-2	2
№ 2	A1-2	4
№ 3	A1-4	2
№4	A2-2	2
№5	A2-2	4
№6	A2-4	2

№7	A3-2	2
1	**2**	**3**
№8	A3-2	4
№9	A3-4	2
№10	A4-2	2
№11	A4-2	4
№12	A4-4	2
№ 13	A5-2	2
№14	A5-2	4
№ 15	A5-4	2
№ 16	A6-2	2
№ 17	A6-2	4
№ 18	A6-4	2
№ 19	A7-2	2
№ 20	A7-2	4
№ 21	A7-4	2
№ 22	A8-2	2
№ 23	A 8-2	4
№24	A 8-4	2
№ 25	A9-2	2
№ 26	A9-2	4
№ 27	A 9-4	2
№ 28	A10-2	2
№ 29	A10-2	4
№ 30	A10-4	2
№ 31	A11-2	2
№ 32	A11-2	4
№ 33	A11-4	2
№34	A12-2	2
№ 35	A12-2	4
№ 36	A13-4	2

These prepared compositions were added to bitumen in the amount of 0.4 and 0.6% with the presence of gravel, and the effect on the quality indicators of bitumen was studied. The obtained results are given in table 3.

Table 3. The results of the effect of compositions added to bitumen with the presence of gravel on the quality indicators of bitumen.

Content of added compositoins, grams	**Added compositoin, %**	**$T_{boiling}$, ^0C**	**P_{25} · 0,1 MM**	**D_{25}, sm**	**$T_{brittleness}$, ^0C**	**Adhesion**
		1	**2**	**3**	**4**	**5**
1	**2**	**3**	**4**	**5**	**6**	**7**
A road bitumen (Azerbaijan)	0,4 0,6	48.5	48	75	-18	3 2
Sample 1 Experiment 1-2 (S.O.A.+HMDA)-2	0,4 0,6	47.8 47.6	52 52	74 78	-22 -24	2 2
Sample 2 Experiment 1-2 (S.O.A +amine)-4	0,4 0,6	47.4 47.2	52 52	76 81	-18 -22	1 1

1	2	3	4	5	6	7
Sample 3 Experiment 1-4 (S.O.A +amine)-2	0,4 0,6	47.3 47.5	52 52	80 72	-19 -22	1 1
Sample 4 Experiment 2-2 (S.O.A +amine)-2	0,4 0,6	47.5 47.2	52 52	66 58	-23 -21	2 2
Sample 5 Experiment 2-2 (S.O.A + amine)-4	0,4 0,6	46.4 46.2	53 53	74 77	-18 -19	2 2
Sample 6 Experiment 2-4 (S.O.A +amine)-2	0,4 0,6	46.2 46	53 53	75 78	-24 -22	1 1
Sample 7 Experiment 2-3 (S.O.A +amine)-2	0,4 0,6	47.8 47.6	52 52	76 78	-19 -20	1 1
Sample 8 Experiment 3-4 (S.O.A +amine)-4	0,4 0,6	47.4 47.1	52 52	92 83	-19 -20	1 1
Sample 9 Experiment 3-4 (S.O.A +amine)-2	0,4 0,6	46.3 46	53 53	65 75	-20 -22	1 1
Sample 10 Experiment 4-2 (S.O.A +amine)-2	0,4 0,6	47 46.6	53 53	58 70	-18 -18	2 1
Sample 11 Experiment 4-4 (S.O.A +amine)-4	0,4 0,6	45.8 45.6	55 55	74 83	-22 -20	1 2
Sample 12 Experiment 4-4 (S.O.A +amine)-2	0,4 0,6	46.5 46.1	54 55	66 85	-21 -20	2 2
Sample 13 Experiment 5-2 (S.O.A.+amine)-2	0,4 0,6	46.6 46.2	55 55	68 83	-18 -18	1 2
Sample 14 Experiment 5-4 (S.O.A +amine)-4	0,4 0,6	46 45.6	55 55	84 100	-21 -19	2 2
Sample 15 Experiment 5-4 (S.O.A +amine)-2	0,4 0,6	46.8 46.5	55 55	84 68	-18 -16	3 2
Sample 16 Experiment 6-2 (S.O.A +amine)-2	0,4 0,6	45.6 45.2	56 56	100 75	-18 -20	2 1
Sample 17 Experiment 6-2 (S.O.A +amine)-4	0,4 0,6	45.8 45.6	56 56	71 92	-17 -16	1 2
Sample 18 Experiment 6-4 (G.Y.T+amin)-2	0,4 0,6	46 45.6	56 56	84 77	-18 -16	1 1
Sample 19 Experiment 7-2 (S.O.A +amine)-2	0,4 0,6	46.8 46	53 53	91 72	-18 -20	1 2

1	2	3	4	5	6	7
Sample 20 Experiment 7-2 (S.O.A+amine)-4	0,4 0,6	44.4 44.2	58 58	93 100	-20 -24	2 2
Sample 21 Experiment 7-4 (S.O.A+amine)-2	0,4 0,6	46.9 46.1	53 53	84 100	-21 -19	1 1
Sample 22 Experiment 8-2 (S.O.A +amine)-2	0,4 0,6	46.8 46.3	53 53	90 100	-20 -22	2 2
Sample 23 Experiment 8-2 (S.O.A +amine)-2	0,4 0,6	44.5 44	58 58	78 88	-21 -17	2 2
Sample 24 Experiment 8-4 (S.O.A +amine)-2	0,4 0,6	45.6 45	56 57	70 86	-20 -18	1 1
Sample 25 Experiment 9-2 (S.O.A +amine)-2	0,4 0,6	46.4 46.8	57 58	75 81	-20 -23	1 1
Sample 26 Experiment 9-4 (S.O.A +amine)-2	0,4 0,6	46.2 45	58 62	92 76	-21 -22	1 1
Sample 27 Experiment 9-2 (S.O.A +amine)-4	0,4 0,6	45.1 45.6	59 59	81 71	-13 -21	1 1
Sample 28 Experiment 10-2 (S.O.A +amine)-2	0,4 0,6	47 46.8	60 60	66 75	-15 -21	2 2
Sample 29 Experiment 10-2 (S.O.A +amine)-4	0,4 0,6	46.2 46	62 62	76 70	-21 -22	1 2
Sample 30 Experiment 10-4 (S.O.A +amine)-2	0,4 0,6	47.3 47	54 56	92 100	-23 -18	3 2
Sample 31 Experiment 11-2 (S.O.A +amine)-2	0,4 0,6	46.8 46.6	56 53	78 73	-17 -22	2 2
Sample 32 Experiment 11-2 (S.O.A +amine)-4	0,4 0,6	46.2 46	54 56	83 70	-22 -24	3 3
Nümunə 33 Təcrübə 11-4 (S.O.A +amine)-2	0,4 0,6	46.5 46.4	54 56	95 61	-23 -19	2 1
Nümunə 34 Təcrübə 12-2 (S.O.A +amine)-2	0,4 0,6	46.3 46.1	54 56	84 100	-25 -22	1 1
Sample 35 Experiment 12-2 (S.O.A +amine)-4	0,4 0,6	46.6 45.6	56 56	65 100	-16 -19	3 2
Sample 36 Experiment 11-4 (S.O.A +amine)-2	0,4 0,6	47.4 47.1	54 56	100 79	-20 -22	1 1

It can be seen from the table that after adding the additive, the quality indicators of gravel-mixed bitumen improved significantly, the adhesion to gravel increased from 3 points to 1 point, the brittleness temperature dropped from -18 to -24, penetration increases from 48 to 58, tensile strength increases from 75 cm to 100 cm.

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SABUNUN AMİD TURŞUSU İLƏ POLİETİLEN POLİAMİNİN VƏ GÜNƏBAXAN YAĞ TURŞULARININ HEKSAMETİLENDİAMİNLƏ QARIŞIQLARININ MÜXTƏLİF NİSBƏTLƏRDƏ ÇINQILDAN İSTİFADƏ ETMƏKLƏ BİTUM ƏLAVƏSİ KİMİ ÖYRƏNİLMƏSİ

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XÜLASƏ

Amidlər pambıq yağı tullantıları olan sabun ehtiyatı ilə polietilen poliaminin müxtəlif kütlə nisbətində qarışdırılması ilə sintez edilmişdir. Reaksiya mikser, qızdırıcı və termometrlə təchiz edilmiş stəkanda 140-145°C temperaturda 4 saat qarışdırılaraq aparılmışdır.
Amid alındıqdan sonra reaksiya məhsulu 80°C-yə qədər soyudulur, ona lazımi miqdarda ağır bəlğəm əlavə edilir və yaxşıca qarışdırılır, sonra istifadə üçün bağlı qablara yığılır. Eyni zamanda hidroliz yolu ilə günəbaxan yağının turşusu alınmış, amid heksametilendiaminlə 2:1 mol nisbətində sintez edilmiş və reaksiya qarışdırıcı, qızdırıcı və termometrlə təchiz edilmiş üç boğazlı kolbada aparılmışdır. Bunun üçün ilk öncə günəbaxan yağı turşusu üç boğazlı kolbaya doldurulmuş, qarışdırıcı və qızdırıcı işə salınmış, lazımi miqdarda heksametilendiamin əlavə edilərək temperatur 140°C-yə qaldırılmış və reaksiya bu şəraitdə 4 saat davam etdirilmişdir. Üç kütlə nisbətində (1:1, 1:2, 2:1) kompozisiyalar soapstock ilə polietilen poliamin əsasında sintez edilmiş amidlərlə günəbaxan yağının heksametilendiamin turşusunu qarışdırmaqla hazırlanmışdır. Bu kompozisiyalar bituma əlavə olaraq 0,4 və 0,6% miqdarda çınqıldan istifadə edilərək əlavə edilmiş və keyfiyyət göstəricilərinə təsiri öyrənilmişdir.
Müəyyən edilmişdir ki, aşqarın tətbiqindən sonra bitumun keyfiyyət göstəriciləri xeyli yaxşılaşır. Belə ki, bu birləşmələri çınqıldan istifadə edərək bituma əlavə etdikdən sonra onun yapışma qabiliyyəti 3 bal olduğu halda, 1 bala qədər artır. Kövrəklik -18-dən -26-ya qədər azalır, penetrasiya isə 48-dən 55-ə və dartılmada davamlılığı 75 sm-dən 100 sm-ə qədər artır.
Açar sözlər: soapstock, heksametilendiamin, polietilenpoliamin, kövrəklik temperaturu, yapışma, penetrasiya, dartılma.

ИЗУЧЕНИЕ СМЕСИ АМИДОВ МЫЛА С ПОЛИЭТИЛЕНПОЛИАМИНОМ И КИСЛОТ ПОДСОЛНЕЧНОГО МАСЛА С ГЕКСАМЕТИЛЕНДИАМИНОМ В РАЗНЫХ СООТНОШЕНИЯХ КАК ДОБАВОК К БИТУМУ С ИСПОЛЬЗОВАНИЕМ ГРАВИЯ

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РЕЗЮМЕ
Амиды были синтезированы путем смешивания соапстока (отхода хлопкового масла) и полиэтиленполиамина в различных массовых соотношениях. Реакцию проводили при перемешивании в течение 4 часов при температуре 140-145°C в стакане, снабженном мешалкой, нагревателем и термометром.
После получения амида продукт реакции охлаждали до 80°C, добавляли к нему

необходимое количество тяжелой флегмы и хорошо перемешивали, затем собирали в закрытые емкости для использования. При этом гидролизом получали подсолнечную масляную кислоту, синтезировали амид с гексаметилендиамином в мольном соотношении 2:1 и реакцию проводили в трехгорлой колбе, снабженной мешалкой, нагревателем и термометром. Для этого в трехгорлую колбу сначала заливали подсолнечную масляную кислоту, включали мешалку и нагреватель, добавляли необходимое количество гексаметилендиамина и повышали температуру до 140°C и продолжали реакцию при этой температуре. температура в течение 4 часов. Композиции в трех массовых соотношениях (1:1, 1:2, 2:1) готовили смешением амидов, синтезированных на основе соапстока полиэтиленполиамина и кислоты гексаметилендиамина подсолнечного масла. Данные составы добавляли в качестве добавки к битуму с использованием гравия в количествах 0,4 и 0,6% и изучали ее влияние на качественные показатели.

Установлено, что качественные показатели битума существенно улучшаются после введения добавки. Так, после добавления этих составов в битум с использованием гравия его адгезионная способность увеличивается до 1 балла, тогда как она составляет 3 балла. Хрупкость снижается с -18 до -26, проникающая способность увеличивается с 48 до 55, а прочность на разрыв с 75 см до 100 см.

Ключевые слова: соапсток, гексаметилендиамин, полиэтиленполиамин, температура хрупкости, адгезия, проникновение, растяжение

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DITHIOPHOSPHORIC ACIDS DERIVATIVES AS EP AND ANTI-WEAR ADDITIVES FOR TRANSMISSION OILS

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ABSTRACT

The article is devoted to a current problem - the synthesis of new compounds and their study as anti-wear and proto-pressure additives for lubricating oils. The purpose of this work is to obtain sulfur-phosphorus-containing compounds that could have tribological properties. Based on literature data and experience in this field, the authors synthesized derivatives of dithiophosphoric acids, which were further studied as extreme pressure and anti-wear additives for lubricating oils. The synthon for the synthesis of compounds was the sodium salt of diisopropyl and allyl dithiophosphoric acids, obtained by reacting the corresponding dithiophosphoric acids with a 40% solution of sodium hydroxide. By reacting the sodium salt of diisopropyl, sodium allyl dithiophosphate with toluene sulfonamide, obtained by reacting toluene sulfonamide with 5-phosphorus chloride, toluene sulfonisopropyl and allyl dithiophosphates were obtained. The resulting compounds have high extreme pressure properties. It has been shown that the extreme pressure properties of the compound depend on the structure of the fragments included in the compound. You should pay attention to the calculated indicator scuff index (Si), which indicates the effectiveness of extreme pressure properties; the higher this indicator, the higher the extreme pressure properties. 4-phenoxycarbonyl methyl ester of diispropyl dithiophosphoric acid was obtained by reacting the sodium salt of diisopropyl dithiophosphoric acid with phenyl chloroacetate; similarly, by adding 5-methyl-2-hydroxy-γ-chloroacetophenone to the diisopropyl dithiophosphate salt, 5-methyl-2-hydroxyphenylcarbonyl methyl ester of diisopropyl dithiophosphoric acid was obtained. These compounds also have high extreme pressure properties; in addition, they are superior to toluene sulfonic acid derivatives of dithiphosphoric acids in anti-wear properties, which is fully explained by the large amount of sulfur in the composition of the latter. The structure of all synthesized compounds was proven by IR spectral analysis, the study of physicochemical properties and elemental analysis. Extreme pressure and anti-wear properties were studied on a four-ball friction machine (FFM-1). The evaluation of extreme pressure properties was carried out according to the load wear index (LWI), according to the critical load (CL) and according to the welding load (WL), anti-wear properties by the diameter of the wear scar (Wd).

Keywords: sulfur-phosphorus-containing compounds, tribological properties, allyl dithiophosphate, anti-wear

Introduction

In connection with progress in the development of sectors of the national economy,

including mechanical engineering, every year there is a need for high-quality lubricants. The author believes that to obtain high-quality lubricants it is enough to use good raw materials, as well as high technologies [1]. However, this is not enough; Many modern base oils contain additives that improve their quality. At the same time, a significant part of such oils is not able to fully satisfy all the requirements for oils for various purposes. In this regard, individual compounds (additives) are added to their composition.

Some of the most popular oils are transmission oils used for lubrication of parts, car engines, gearboxes, brakes, etc. The main requirement for these oils is high anti-wear and extreme pressure properties.

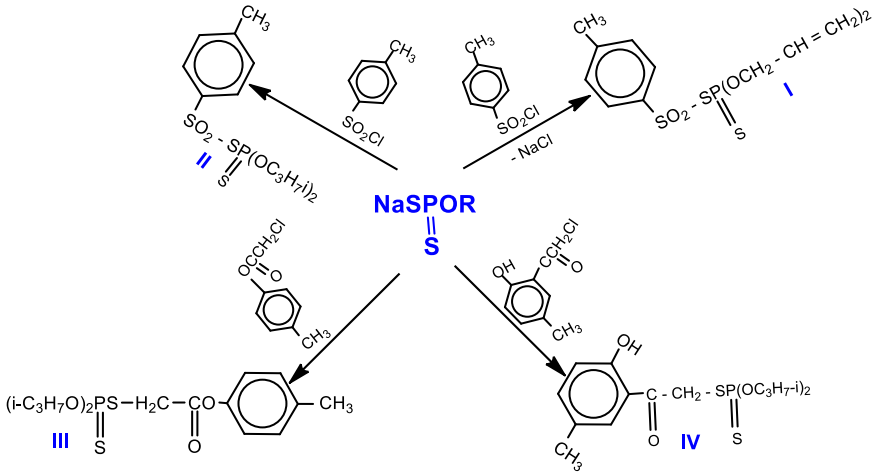
Anti-wear additives protect the metal surface from wear at low loads, and extreme pressure additives prevent the appearance of scuffing on the metal surface at high temperatures and loads. Despite the use of a significant amount of additives in lubricating oils, the mechanism of action, in particular anti-wear and extreme pressure additives, has not been sufficiently studied. However, many experts involved in this issue believe that the lubricating effects of surface-active additives are based on the formation of strong adsorption layers of obstructing, rubbing surfaces, which can explain the anti-wear properties of additives.

Extreme pressure additives are chemically active substances that, under severe conditions (temperature, pressure), disintegrate atoms and small fragments during a chemical reaction with the metal to form chemically modified layers that prevent contact of rubbing metal surfaces [2].

Compounds with high reactivity are used as extreme pressure additives, which during decomposition in most cases contain mainly four elements or functional groups [3].

Some of the highly effective oil additives are derivatives of dithiophosphoric acids, which can be confirmed both by the work carried out by the Institute of Chemistry of Additives of Azerbaijan and by foreign specialists working in the field of oil additives [3-7].

The authors of this work synthesized a number of dithiophosphates of various structures according to the following schemes:



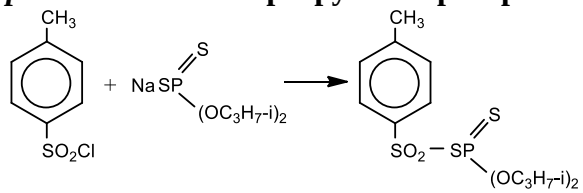
where, R = i-C_3H_7O; CH_2=CH–CH_2–

p-Toluenesulfodiallyl dithiophosphate (I); *p*-toluenesulfodizopropyl dithiophosphate (II); 4-methylphenoxycarbonylmethyldiisopropyldithiophosphate (III); 2-hydroxy-5-methylcarbonylmethyldiisopropyl dithiophosphate (IV).

Experimental part

This section of the article presents the synthesis of the starting compounds, as well as additives obtained on their basis.

***p*-Toluenesulfodizopropyldithiophosphate:**



Example. To a stirred reaction flask, 21.43g (0.1 mol) of diisopropyl dithiophosphate is added to 10g of a 40% aqueous NaOH solution and stirred for 3 hours at 50°C. Then 19.1g (0.1 mol) of toluenesulfonyl chloride was added to the reaction flask. The reaction was continued for 5 hours at 70°C. The resulting product was extracted with benzene, washed with water, and benzene was distilled off. A crystalline product was obtained. Yield 27.6g (75%). T_{mt}. 70-72 °C.

Elemental composition:

$C_{13}H_{21}O_4S_3P$: Found, %: C– 46.51; H – 6.18; S – 28.35; P – 9.16

Calculated, %: C – 46.43; H – 6.25; S – 28.57; P – 9.23

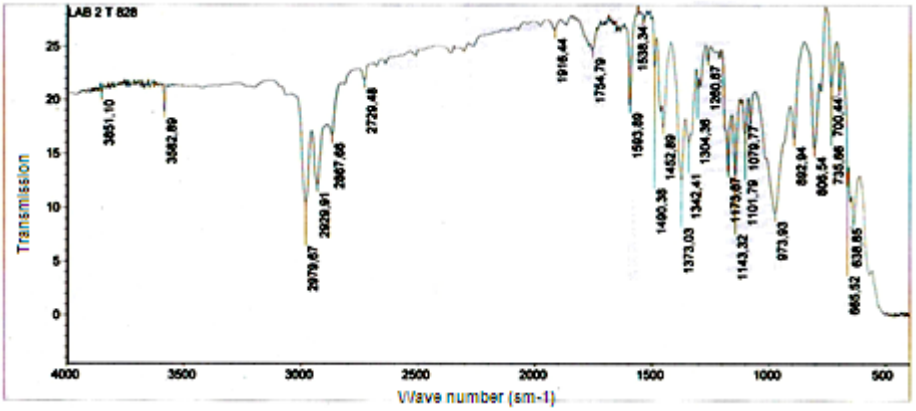
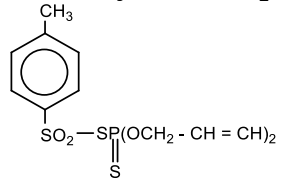


Fig.1. IR spectrum p-toluene sulfodiisopropyl dithiophosphate

In the IR spectrum of the compound, the absorption band of stretching vibrations (the most characteristic) of the fragment –P–O–C_3H_7– is observed in the region of 1079.77, 973.93 cm^{-1}, the P=S bond corresponds to absorption bands in the region of 806.54-638.85 cm^{-1}, stretching vibrations of the fragment –C=C corresponds to bands at 1593.89-1538.34 cm^{-1}, stretching vibrations of the SO_2 group correspond to bands at 1373.03-1173.87 cm^{-1}.

Similarly received *p*-толuenesulfodiallyldithiophosphate:



Physico-chemical constants:

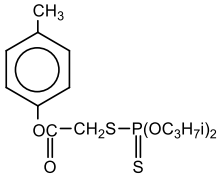
n_{20}^{D}= 1.5540, d_{20}^{4}= 1.2560; M_{RD} found = 94.2, M_{RD} calculated = 93.3

Elemental composition:

$C_{13}H_{17}O_4S_3P$: Found, %: C – 42.72; H – 4.58; S – 26.21; P – 8.48

Calculated. %: C – 42.86; H – 4.70; S – 26.37; P – 8.52

4-Methylphenoxycarbonylmethyldiisopropyldithiophosphate:



Example. 10g of 40% sodium hydroxide are added to a mixture of 21.43g (0.1 mol) of diispropyldithiphosic acid, and the mixture is stirred for 3 hours at 50°C. 16.6g (0.1 mol) of phenyl chloroacetate was then added. The reaction mass was stirred for 5 hours at 70°C. The resulting product was washed with a 5% sodium carbonate solution. After washing with water, the product was subjected to vacuum nitrogen distillation. Yield 33.5g (96%).

Physico-chemical constants:

n_{20}^{D}= 1.58310, d_{20}^{4}= 1.1776; M_{RD} found = 91.54, M_{RD} calculated. = 91.82

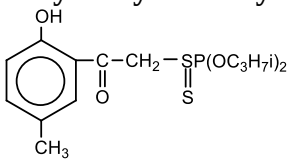
Elemental composition:

$C_{14}H_{21}O_4S_2P$: Found, %: C – 48.43; H – 5.93; S – 18.29; P – 8.66

Calculated, %: C – 48.26; H – 6.08; S – 18.41; P – 8.89

In the IR spectrum of 4-methylphenoxycarbonylmethyldiisopropyl dithiophosphate, absorption bands of the P–S– group are observed at 768 cm^{-1} and at 535 cm^{-1}, characterizing the P=S group, respectively. A strong intensity band corresponding to the carbonyl group is observed at 1753 cm^{-1}.

2-Hydroxy-5-methylcarbonylmethyldiisopropyl dithiophosphate:



Example. 23.6g (0.1 mol) of sodium diispropyldithiphosphate was added to a mixture of 18.46g (0.1 mol) of 5-methyl-2-hydroxy-γ-chloroacetephenone in 20 ml of benzene. Stirring of the reaction mixture continues for 5 hours at 70°C. The organic layer was extracted with hexane and washed with water until neutral. The product was isolated by liquid column chromatography. Yield 29g (8%), the product is a crystalline substance. T_{mt}. 16-17°C.

Elemental composition:

$C_{15}H_{23}O_4S_2P$: Found, %: C – 49.59; H – 6.52; S – 17.58; P – 8.48

Calculated, %: C – 49.71; H – 6.40; S – 17.69; P – 8.55

In the IR spectrum of 2-hydroxy-5-methylcarbonylmethyldiisopropyl dithiophosphate there is an absorption band at 770 cm^{-1}, corresponding to the P=S group. Bands with a frequency of 1470 cm^{-1} and 3030 cm^{-1}, characteristic of aromatic compounds, are also observed, corresponding to the C=O and C–H groups.

Results and its discussion

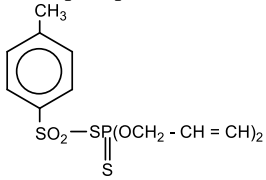
As follows from the test results presented in the table, all synthesized compounds have high extreme pressure and anti-wear properties.

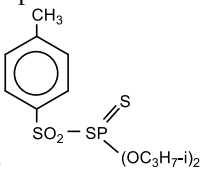
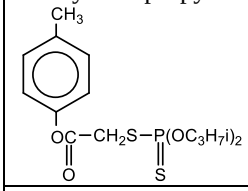
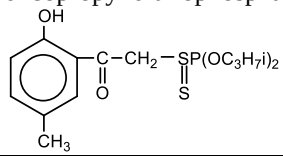
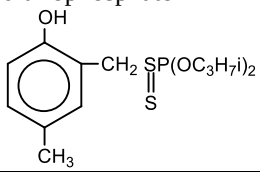
The high extreme pressure efficiency of 4-methylphenoxycarbonylmethyldiisopropyldithiophosphate and 2-hydroxy-5-methylcarbonylmethyldiisopropyldithiophosphate is explained by the presence in the molecules of the carbonyl group C(O), in which the double bond is highly polarized due to a shift in electron density to a more electronegative oxygen atom, which increases its reactivity, due to which increases the anti-seize properties of the connection. This is confirmed by analysis of the results of the tribological properties of the compounds presented in the table.

Thus, the author believes that when dialkyldithiophosphates and triaryl phosphorothionates interact with the metal surface, no phosphites are formed. Additives form a monomolecular layer and initiate polymolecular physical adsorption of hydrocarbon components of the oil on the metal surface [8]. The P=S bond of dithiophosphate additives under moderate loads is considered to be quite strong, which explains the effectiveness of the anti-wear properties of the compounds. According to the authors, the anti-wear properties of compounds increase with increasing their thermal stability. In the area of high loads, on the contrary, less thermally stable compounds are the most effective [9]. Thus, it can be stated that dithiophosphates have effective anti-wear properties at moderate loads, and extreme pressure properties at high loads and temperatures.

You should pay attention to the load wear index (LW_I) of *p*-toluenesulfodialyl dithiophosphate; this indicator, which determines the extreme pressure efficiency of the joint in the range from the critical load (C_l) to the welding load (W_l), is the highest, which means the high efficiency of the joint. This is explained by the presence in the molecule of an allyl group, in which the C–H bond is quite labile, and is easily broken, followed by the disintegration of the molecule into atoms and small fragments, which in turn form protective layers, consisting mainly of metal sulfides and oxides.

Table. Tribological characteristics of synthesized compounds

Compounds	Concentration of samples in oil, %	Tribological characteristics GOST 9490-75			
		Load wear index, LW_I, N	Critical load, CL, N	Welding load, WL, N	Wear spot diameter, Wd, mm
MS-20 oil	–	330	794	1568	0,85
MS-20+p-Toluenesulfodiallyl-dithiophosphate 	1,5	640	1382	3097	0,45

MS-20 + p-Toluenesulfodizopropyl-dithiophosphate 	1,5	560	1235	3097	0,50
MS-20+4-methylphenoxycarbonyl-methyldiisopropyldithiophosphate 	5	598	1382	3685	0,41
MS-20+2-Hydroxy-5-methylcarbonyl-methyldiisopropyl dithiophosphate 	5	529	1382	2930	0,39
2-Hydroxy-5-methyl-diisopropyl dithiophosphate 	5	490	1235	2450	0,35

Conclusions

– New derivatives of diisopropyl and allyl dithiophosphoric acids have been synthesized.

– Their high anti-wear and extreme pressure efficiency has been shown.

– The dependence of the extreme pressure properties of the compound on the polarity of the substituents was revealed.

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DİTİOFOSFOR TURŞUŞLARI TÖRƏMƏLƏRİ EP VƏ TRANSMİSİYA YAĞLAR ÜÇÜN AŞINMAYA QARŞI ƏLAVƏ KİMİ

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XÜLASƏ
Məqalə aktual problemə - yeni birləşmələrin sintezinə və onların sürtkü yağları üçün aşınmaya qarşı və proto-təzyiq əlavələri kimi öyrənilməsinə həsr edilmişdir. Bu işin məqsədi triboloji xassələrə malik ola bilən kükürd-fosfor tərkibli birləşmələri əldə etməkdir. Ədəbiyyat məlumatlarına və bu sahədəki təcrübəyə əsaslanaraq, müəlliflər ditiofosfor turşularının törəmələrini sintez etmişlər, onlar daha sonra sürtkü yağları üçün həddindən artıq təzyiq və aşınmaya qarşı əlavələr kimi tədqiq edilmişdir. Birləşmələrin sintezi üçün sinton, müvafiq ditiofosfor turşularının 40% natrium hidroksid məhlulu ilə reaksiya verməsi nəticəsində əldə edilən diizopropil və allil ditiofosfor turşularının natrium duzu idi. Diizopropilin natrium duzunu toluol sulfonamidlə reaksiyaya salmaqla toluol sulfonamidin 5-fosfor xlorid, toluol sulfonizopropil və allil ditiofosfatlarla reaksiya verməsi nəticəsində əldə edilən natrium allil ditiofosfat əldə edilmişdir. Yaranan birləşmələr yüksək həddindən artıq təzyiq xüsusiyyətlərinə malikdir. Göstərilmişdir ki, birləşmənin həddindən artıq təzyiq xüsusiyyətləri birləşməyə daxil olan fraqmentlərin quruluşundan asılıdır. Həddindən artıq təzyiq xüsusiyyətlərinin effektivliyini göstərən hesablanmış göstərici scuff indeksinə (Si) diqqət yetirməlisiniz; bu göstərici nə qədər yüksəkdirsə, həddindən artıq təzyiq xüsusiyyətləri bir o qədər yüksəkdir. diizpropil ditiofosfor turşusunun 4-fenoksikarbonilmetil efiri diizopropil ditiofosfor turşusunun natrium duzunu fenilxloroasetatla reaksiyaya verməklə alınmışdır; analoji olaraq, diizopropil ditiofosfat duzuna 5-metil-2-hidroksi-γ-xloroasetofenonu əlavə etməklə diizopropil ditiofosfor turşusunun 5-metil-2-hidroksifenilkarbonil metil efiri əldə edilmişdir. Bu birləşmələr də yüksək həddindən artıq təzyiq xüsusiyyətlərinə malikdir; bundan əlavə, onlar aşınmaya qarşı xassələrə görə ditifosfor turşularının toluol sulfon turşusu törəmələrindən üstündürlər ki, bu da sonuncunun tərkibində

çoxlu miqdarda kükürdün olması ilə tam izah olunur. Bütün sintez edilmiş birləşmələrin strukturu İQ-spektral analiz, fiziki-kimyəvi xassələrin öyrənilməsi və elementar analizlə sübut edilmişdir. Həddindən artıq təzyiq və aşınmaya qarşı xüsusiyyətlər dörd tip sürtünmə maşınında (FFM-1) öyrənilmişdir. Həddindən artıq təzyiq xüsusiyyətlərinin qiymətləndirilməsi yükün aşınma indeksinə (LWI), kritik yükə (CL) görə və qaynaq yükünə (WL) görə, aşınma çapığının diametrinə (Wd) görə aşınmaya qarşı xüsusiyyətlərə görə aparılmışdır.

Açar sözlər: kükürd-fosfor tərkibli birləşmələr, triboloji xassələr, allil ditiofosfor turşusu

ПРОИЗВОДНЫЕ ДИТИОФОСФОРНОЙ КИСЛОТЫ КАК ЕР И ПРОТИВОИЗНОСНЫЕ ПРИСАДКИ ДЛЯ ТРАНСМИССИОННЫХ МАСЕЛ

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РЕЗЮМЕ
Статья посвящена актуальной проблеме - синтезу новых соединений и их исследованию в качестве противоизносных и протодавленных присадок к смазочным маслам. Целью данной работы является получение серофосфорсодержащих соединений, обладающих трибологическими свойствами. На основе литературных данных и опыта в этой области авторами синтезированы производные дитиофосфорных кислот, которые в дальнейшем изучались в качестве противозадирных и противоизносных присадок к смазочным маслам. Синтоном для синтеза соединений послужили натриевые соли диизопропиловой и аллилдитиофосфорной кислот, полученные взаимодействием соответствующих дитиофосфорных кислот с 40% раствором гидроксида натрия. Реакцией натриевой соли диизопропила, аллилдитиофосфата натрия с толуолсульфонамидом, полученным при взаимодействии толуолсульфонамида с 5-хлоридом фосфора, были получены толуолсульфонизопропил и аллилдитиофосфаты. Полученные соединения обладают высокими противозадирными свойствами. Показано, что противозадирные свойства соединения зависят от строения входящих в него фрагментов. Следует обратить внимание на рассчитываемый показатель индекса задира (Si), который свидетельствует об эффективности противозадирных свойств; чем выше этот показатель, тем выше противозадирные свойства. 4-феноксикарбонилметиловый эфир диизопропилдитиофосфорной кислоты получали взаимодействием натриевой соли диизопропилдитиофосфорной кислоты с фенилхлорацетатом; аналогично, путем добавления 5-метил-2-гидрокси-γ-хлорацетофенона к диизопропилдитиофосфатной соли получали 5-метил-2-гидроксифенилкарбонилметиловый эфир диизопропилдитиофосфорной кислоты. Эти соединения также обладают высокими противозадирными свойствами; кроме того, они превосходят толуолсульфопроизводные дитифосфорных кислот по противоизносным свойствам, что вполне объясняется большим количеством серы в составе последних. Строение всех синтезированных соединений

подтверждено методами ИК-спектрального анализа, изучения физико-химических свойств и элементного анализа. Противозадирные и противоизносные свойства исследовались на четырехшариковой машине трения (ФФМ-1). Оценку противозадирных свойств проводили по индексу износа под нагрузкой (LWI), по критической нагрузке (CL) и по сварочной нагрузке (WL), противоизносные свойства по диаметру пятна износа (Wd).
Ключевые слова: серофосфорсодержащих соединений, трибологическими свойства, производные дитиофосфорных кислот, противоизносных