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Wright-Patterson Air Force Base, Ohio

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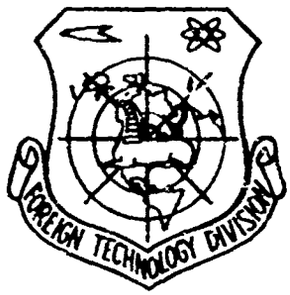
by

A. M. Kuliyev, A. M. Levshina, et al.



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13. ABSTRACT

Sulfur and P contg. polyfunctional additives for motor oils were prepd. by a reaction of polyisobutylene (of mol wt. 700-2,000) or isobutylene styrene copolymer (I) at 235-40 degrees followed by neutralization of the products with MgO, CaO, BaO or the resp. bases, at 80-135 degrees. The additive prepd. contained 1.18-1.85% S and 1.45-1.77% P, and were superior anticorrosive agents and oxidn. inhibitors. Of the additive tested, IKhP-388 additive (a product of I and P_2S_5 neutralized with MgO and mixed with alkylphenol) prove to be the most effective additive for D-11 oil. Other P, S, N, and B contg. additives e.g., IKhP-361 additive were prepd. by treating the hydrolyzed product of I and P_2S_5 with ethylenediamine or ethanolamine and H_3BO_3. [AT1200036]

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Lubricant Additive						
Organic Sulfur Compound						
Organic Phosphorus Compound/(U)IKhP 388 - Lubricant Additive						
(U)IKhP 361 Lubricant Additive						
(U)D11 Lubricating Oil						

EDITED TRANSLATION

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By: A. M. Kuliyev, A. M. Levshina, et al.

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З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

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RESULTS OF STUDIES INVOLVING THE SYNTHESIS OF SULFUR AND PHOSPHORUS CONTAINING POLYMERIC MULTIFUNCTIONAL ADDITIVES

A. M. Kuliyev, A. M. Levshina, V. M. Farzaliyev, L. Ya. Vedeneyeva, I. I. Namazov, and Sh. A. Mkhitaryan

Recently different polymer compounds have been used as effective additives to lubricant oils [1-6].

Synthesis of polymer additives reduces to the introduction of functional polar groups into macromolecules of polymer compounds, which creates polar polymers and copolymers possessing very high operational properties when added to the different oils. Introduction of functional groups into a macromolecule of a polymer is achieved either by polymerization and copolymerization of monomers containing these groups, or by treating the macromolecules of the polymer by different reagents.

High wetting and dispersing properties are characteristic for polymer additives. However, they may also reduce the freezing point, improve the temperature-viscosity, antioxidant, anticorrosion and other properties of lubricating oils, i.e., possess multifunctional properties.

The authors conducted a broad study of the synthesis and application of the different polymer additives, among which the

sulfur- and phosphorus-containing polymer multifunctional additives are especially important.

The sulfur- and phosphorus-containing polymer multifunctional additives were created by treating the initial polymer compounds by phosphorus pentasulfide and neutralizing the obtained acid reaction products by different compounds. Low-molecular (mol. wt. 700-2000) polyisobutylene or a copolymer of isobutylene with styrol were used as the initial polymer compounds.

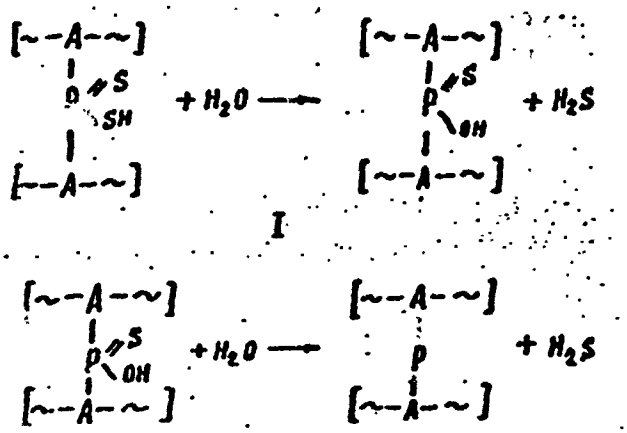
The reaction between the phosphorus pentasulfide and the polymer compound went at 235-240°C and consumed 15.5% of the phosphorus pentasulfide.

On the basis of available published data [7] and the results of our studies it can be considered that the main products from the reaction of phosphorus pentasulfide with polymer compounds is a disubstituted dithiophosphinic acid

$$4\left[\sim\!\!-\underset{\underset{H}{|}}{A}\!\!-\sim\right] + P_2S_5 \longrightarrow 2\begin{array}{c}\left[\sim\!\!-A\!\!-\sim\right]\\ |\\ P\!\!<^{S}_{SH}\\ |\\ \left[\sim\!\!-A\!\!-\sim\right]\end{array} + H_2S\ ,$$

where $\left[\sim\!\!-\underset{\underset{H}{|}}{A}\!\!-\sim\right]$ – macromolecule of polymer compound.

The product was washed with hot water to remove the low-molecular phosphoric acids which formed during the reaction. An emulsion was separated by adding isopropyl alcohol. In certain cases the reaction product of phosphorus pentasulfide with the polymer compound was subjected to hydrolysis by water vapor, after which it was also flushed with water. It may be assumed that the hydrolysis of the product goes as follows [8]:



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The studies showed that when the reaction product of phosphorus pentasulfide with the polymer compound is washed with water the hydrolysis of the thiol group (diagram I) causes the derivative dithiophosphinic acids to pass almost completely into derivative thiophosphinic acids, and the hydrolysis by water vapor forms a mixture of derivative thiophosphinic and phosphonic acids (diagrams I and II).

The additives obtained on the basis of the reaction product of the polymer compound with phosphorus pentasulfide differ mainly by the means of neutralization. Depending upon the neutralizing compound ash (metal-containing), low-ash and no-ash additives may be obtained.

The authors obtained the metal-containing polymer multifunctional additives on the basis of the reaction products of the polymer compounds with phosphorus pentasulfide after neutralizing the latter by oxides or hydrates of acids of alkali-earth metals in the presence of different promotors [9]. In a number of cases the reaction product of the polymer compound with phosphorus pentasulfide was neutralized together with other compounds – alkylphenol, naphthenic sulfonic acid etc.

The reaction product of the polymer compound with phosphorus pentasulfide was neutralized by acids of alkali-earth metals in

the presence of water and ethyl alcohol. The reaction was first carried out at 80-85°C, and then at 135°C.

Carbonic acid was passed through the reaction medium (carbonating) in order to obtain an additive with a high metal content during the neutralization.

Table 1 gives the analysis of the metal-containing polymer additives obtained by neutralizing the acid alkali-earth metals of the phosphorus pentasulfide-polyisobutylene reaction product. We see from the data that all the synthesized additives contain from 1.2 to 1.8% sulfur, from 1.5 to 1.7% phosphorus and have an ash content of from 12 to 34%.

Table 1. Analysis of salts of the alkali-earth metals from the reaction product of phosphorus pentasulfide with polyisobutylene.

(1) Наименование солей	(2) Зольность, %	(3) Содержание, %	
		серы (4)	фосфора (5)
Магниевая	12,1	1,18	1,45
Кальциевая	11,8	1,58	1,65
Бариевая	33,8	1,82	1,77

KEY: (1) Salt; (2) Ash content, %; (3) Content, %; (4) sulfur; (5) phosphorus; (6) Magnesium; (7) Calcium; (8) Barium.

Study of D-11 oil quality with synthesized additives showed that all the obtained additives possess high detergent, anti-corrosive and antioxidant properties (Table 2) and lie near one another in terms of effectiveness.

The reaction product of the polymer compound with phosphorus pentasulfide was also neutralized together with other compounds.

Table 2. Oil qualities of D-11 with salts of alkali-earth metals of the reaction product of phosphorus pentasulfide with polyisobutylene.

Наименование показателей (1) / Наименование масла и присадок (2)	(3) Зольность, %	(4) Вязкость при 100°С сст	Коррозия свинцовой пластинки, г/м² (5)		(6) Термоокислит. стабильность T_{250}, мин.	(7) Стабильность по методу НАМИ-ВНИИ НП (9)		(10) Моющий потенциал, %	Моющие свойства по методу ПЗВ (ухудш. балл) (11)
			140°С	160°С		Осадок, % (8)	Прирост вязк. при 100°С		
(12) Д-11+5% магниевой соли	0,49	14,14	0,15	2,7	51	9,5	8,59	95	0,5
(13) Д-11+5% кальциевой соли	0,56	14,40	0,15	2,1	51	12,8	8,58	95	0,5
(14) Д-11+5% бариевой соли	1,56	20,52	0,55	92		15,7	8,41	83	0,5

KEY: (1) Index; (2) Oil and additives; (3) Ash content, %; (4) Viscosity at 100°C, cSt; (5) Corrosion of a lead plate, g/m^2; (6) Thermooxid. stability T_{250}, min; (7) Stability according to the method of NAMI-VNII NP; (8) Residue, %; (9) Viscosity increase at 100°C, cSt; (10) Detergent potential, %; (11) Detergent properties according to the PZV method (rugged.) marks; (12) magnesium salt; (13) calcium salt; (14) barium salt.

[Д-11 = D-11]

Alkylphenol, naphthenic sulfonic acid and the condensation product of alkyphenol with formaldehyde were used as the other compounds.

Additives synthesized by neutralizing the polymer compound-phosphorus pentasulfide reaction product by magnesium oxide together with commercial alkylphenol (additive IKhP-388), sulfonated diesel oil (additive IKhP-433), with alkylphenol and formaldehyde (additive IKhP-451) and with the condensation product of alkylphenol with formaldehyde (additive IKhP-435) contained 2-3% sulfur, 2-2.5% phosphorus and had an ash content of 8-10%.

Table 3 indicates that all the obtained additives effectively improve the detergent, dispersive and anticorrosive properties of oil D-11. In terms of antioxidant properties the additives obtained using sulfonated diesel oil are inferior to the other additives.

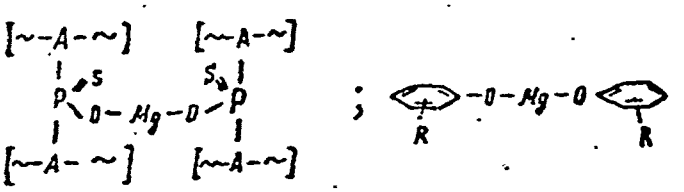
Table 3. Oil qualities of D-11 with polymer multifunctional additives.

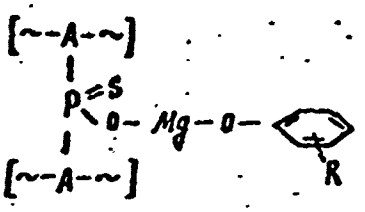
Наименование показателей (1)	Коррозия свинцовой пластинки, г/м² (2)		Термоокислительная стабильн. T_{250}, мин. (3)	Моющий потенциал, % (4)	Моющие свойства по методу ПЗВ (ужест.), баллы (5)
	140°С	160°С			
Д-11 +5% ИХП-388	отсут.	отсут.	41	90	0-0,5
Д-11 +5% ИХП-433	отсут.	34,3	30	87	0-0,5
Д-11 +5% ИХП-435	отсут.	19,1	55	90	0-0,5
Д-11 +5% ИХП-451	отсут.	отсут.	39	86	0-0,5
Д-11 +5% ИХП-361	отсут.	-	73	90	0,5-1
Д-11 +5% ИХП-395	отсут.	-	46	80	1-1,5

KEY: (1) Index; (2) Corrosion of lead plate, g/m^2; (3) Thermo-oxidant stability T_{250}, min; (4) Detergent potential, %; (5) Detergent properties according to PZV method (rugged.), marks.
[Д-11 = D-11; ИХП = IKhP; отсут. = none]

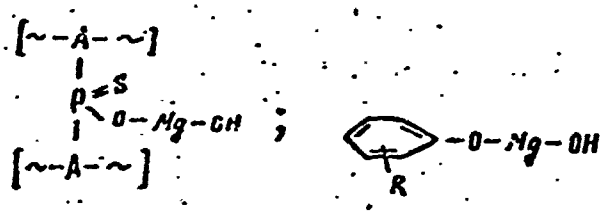
The results of engine tests of the oils with synthesized additives showed that of the sulfur-, phosphorus- and metal-containing additives the most effective is additive IKhP-388 [10].

It may be assumed that the composition of additive IKhP-388 (product of using magnesium oxide to neutralize a mixture consisting of alkylphenol and the reaction product of phosphorus pentasulfide and a copolymer of isobutylene with styrol) contains simple and compound salts of derivative thiophosphinic acid and alkylphenol compositions as follows:





main salts:



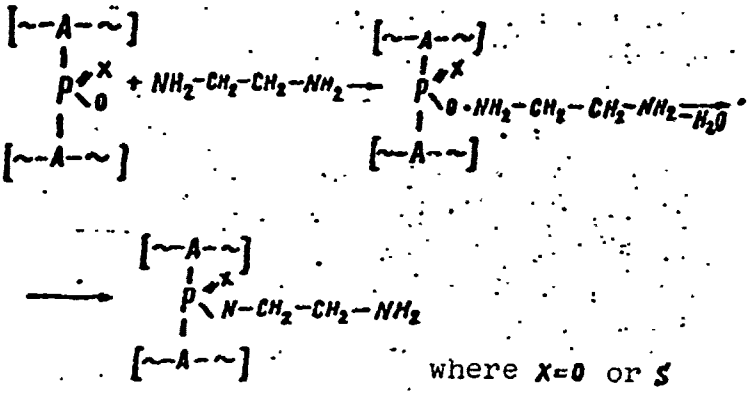
and also salts of a more complex structure.

Engine tests of oils with additive IKhP-388 on different carburetor (GAZ-51, ZIL-130, et al.) and diesel (OD-9, YaAZ-204, YaMZ-238 NB, et al.) engines showed high operational qualities for this additive. On the basis of additive IKhP-388 an effective composition of additives (5% IKhP-388 + 1.2% INKhP-21 + 0.003% PMS-200 A) to oils was developed for modern supercharged diesel and carburetor engines.

The highly positive results of laboratory studies and engine tests recommend additive IKhP-388 for broad bench and operational testing on different engines. At the present an experimental installation has been designed for obtaining this additive.

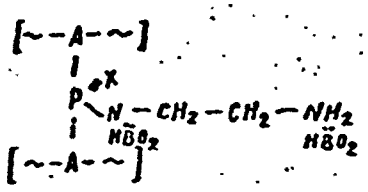
Effective sulfur-, phosphorus-, nitrogen- and boron-containing polymer multifunctional additives have been synthesized by successive treatment of the hydrolyzed reaction product of phosphorus pentasulfide with a copolymer of isobutylene with styrol by ethylenediamine (synthesis of additive IKhP-361) or ethanolamine (synthesis of additive IKhP-395) and boric acid [11]. The data of Table 3 show that the additive IKhP-361 possesses high detergent, dispersive, anticorrosive and antioxidant properties and with respect to these properties it surpasses additive IKhP-395.

Obviously, when the hydrolyzed reaction product of phosphorus pentasulfide with the polymer compound is neutralized, at first ammonium salts of disubstituted phosphinic acid replace an atom of nitrogen, and then subsequently lose a molecule of water and become acid amides:



where X=O or S

When boric acid is treated, an atom of boron is obviously bound with an atom of nitrogen by a coordinate bond because of unshared P-electrons of the nitrogen atom:



The results of laboratory studies of additive IKhP-361 confirmed the results of numerous engine tests using different engines, which also showed the high operational qualities of oils containing this additive.

Thus, as a result of studies on the synthesis and application of sulfur- and phosphorus-containing polymer additives a number of polymer multifunctional additives has been obtained, of which the most effective are the sulfur-, phosphorus-, and metal-containing additive IKhP-388 and the sulfur-, phosphorus-, nitrogen- and boron-containing additive IKhP-361.

BIBLIOGRAPHY

1. Пат.США № 3100749, 1963.
2. Пат.США № 3108964, 1963.
3. Бельг.пат. № 626428, 1963.
4. Брит. пат. № 936650, 1963.
5. Пат.США № 3202606, 1965.
6. Франц.пат., № 1468953, 1967.
7. Равикович А.М., Падихенская М.В. Присадки к маслам и топливам. Гостоптехиздат, 1961.
8. Фуфаев А.А. и друг. Присадки к маслам (труды второго Всесоюзного научно-технического совещания). Изд."Химия". М., 1966.
9. Кулиев А.М. и др. Присадки к смазочным маслам. Труды ИХП АН Азерб.ССР, вып.П, 1970.
10. Кулиев А.М. и др. Присадки к смазочным маслам. Труды ИХП АН Азерб.ССР, вып. П, 1969.