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A NEW DITHIOPHOSPHATE ADDITIVE FOR LUBRICATING OILS

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Technology was developed for production of TsD-7 dithiophosphate additive and its industrial production from a mixture of primary and secondary short-chain alcohols was organized. The lubricating, antioxidant, and scavenger properties of this additive in mineral oil were determined both combined with ash detergents and with no other additives in comparison to the properties of existing dithiophosphates. The results of bench engine tests of the new additive in group D motor oil are reported. The expediency of using the additive in oils for heavy-duty engines is demonstrated.

Most modern lube oils contain zinc dialkyl or diaryl dithiophosphates, which have antioxidant, anticorrosive, antiwear, and antiscuff properties. Despite the tendency toward a decrease in the phosphorus content in motor oils (for environmental reasons), preservation of or even a slight increase in the content of zinc dithiophosphates (0.13-0.17% zinc, 0.12-0.15% phosphorus) is predicted in promising class E 5-99 and SN-4 diesel oils [1].

The properties of zinc dialkyl dithiosphosphates are determined by selection of the feedstock – alcohols or alkylphenols – and by the production technology. It is believed that dialkyl dithiophosphates with longer alkyl chains are more thermostable and have better antioxidant properties than dialkyl dithiosphosphates with shorter chains but are inferior to the latter in lubricating properties [2].

Dialkyl dithiophosphates with secondary alkyl chains are less thermostable but have better antioxidant and lubricating properties than dithiophosphates with primary alkyl chains [3]. These concepts were confirmed by running tests (160,000 km) on 56 taxis with the same engines [4]. The oils contained both individual dithiophosphates and mixtures of dithiophosphates.

The greatest decrease in wear of the tappet cam was obtained with dialkyl dithiophosphates with primary alkyl radicals of short and medium length characterized by moderate thermal stability. The most thermostable zinc diaryl dithiophosphates were the least effective. Oils with dialkyl dithiophosphates produced from secondary alcohols were also best with respect to the oxidation induction period.

Oils with different dithiophosphates are similar with respect to the amounts of deposits left in the engine (on the piston skirt), low-temperature deposits and the degree of clogging of the oil filter.

It is believed that mixtures of dithiophosphates of different structure must be added to motor oils to obtain the optimum cumulative functional properties. For example, in group D diesel fuels, it is useful to combine the most thermostable diaryl dithiophosphates with dialkyl dithiophosphates whose other properties are better [5]. It is proposed that the latter be produced from a mixture of primary and secondary alcohols, which would simultaneously ensure sufficiently high thermostability and good lubricating properties [6].

Dialkyl dithiophosphates with a minimum of 50% secondary alkyl radicals are recommended for motor oils for modern heavy-duty diesel and carburetor engines [7]. The properties of zinc dialkyl dithiophosphates are also a function of the ratio of neutral and basic salts and consequently their production technology.

In Russia, DF-11, DFB, and A-22 dialkyl dithiophosphate additives are manufactured from a mixture of primary alcohols alone. In addition, the content of active elements in DF-11 and DFB additives is relatively low: 4.5-5% phosphorus, 4.7-5.5% zinc.

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TABLE 1

Indexes	Additive			
	VNIINP-354	DF-11	foreign dialkyl dithiophosphate	TsD-7
Active element content, %				
zinc	2.4	5.5	11.1	11.8
phosphorus	2.5	4.8	9.8	10.5
pH	3.8	6.1	6.1	5.8
Base number,* mg KOH/g	0	1.2	6	7.7
Concentration in oil in test, %	2.2	1.5	0.73	0.7
Lubricant properties in base oil				
SAE-10				
Δd_1	0.12	0.05	0.06	0.04
Δt_1	44	46	40	32
Δd_2	0.19	0.01	0.02	0.02
Δt_2	40	23	26	12
M-11 combined with 2% V-714 and 3% KND				
Δd_1	0.04	0.06	0.04	0.04
Δt_1	44	40	38	30
Δd_2	0.05	0.03	0.03	0.01
Δt_2	25	32	21	8

Note. *Determined by direct titration with 0.1 N HCl solution according to GOST 11362–76.

TABLE 2

Dithiophosphate	pH	Base number, mg KOH/g	Concentration in oil, %	Thermostability in I-40 base oil	
				with no other additives	with detergents
VNII NP-354	3.8	0	2.9	1.1	0.55
Foreign diaryl dithiophosphate	6.2	4.9	2.6	0.73	0.6
DF-11	6.1	1.2	1.5	0.42	0.4
A-22	5.9	4.4	0.9	0.41	0.39
TsD-7					
experimental	6.4	19	0.7	0.59	0.36
standard	5.8	7.7	0.7	0.46	0.4

Notes. 1. The selected concentrations of dithiophosphates in the tested oil ensured an equal content of active elements in it.

2. Thermostability of I-40 base oil with no additives: 0.21; with detergents: 0.36.

Additives of this type are manufactured abroad with no or with a small amount of oil diluents and consequently with a higher active element content. These additives differ in the structure of the alkyl radicals and correspondingly the level of the functional properties and consequently the area of application [9].

In developing the synthesis scheme and technology for manufacturing the new TsD-7 dithiophosphate additive, we began with both the dependences of the functional properties of the zinc dithiophosphates on the structure of the alcohols and attempted to use more readily available and less expensive alcohols as the stock.

The existing mechanisms of action of dithiophosphates were primarily established in studying them in base oils. However, the effectiveness of these additives can change significantly as a function of combination with other additives and the working conditions of the lube oil. For this reason, in selecting the alcohols, their molar ratio, and possible variants of the technology for producing the new additive, it was necessary to assess the functional properties of the samples of dithiophosphates obtained combined with other additives in motor oil (primarily alkaline detergents) in conditions close to the conditions of use of motor oils.

The antioxidant and scavenger properties were assessed by laboratory methods in conditions of thermocatalytic oxidation at 230°C based on the change in the optical density and increase in the viscosity of the oil and the corrosion of the lead in it [10, pp. 130-132].

The antiwear and antifriction properties were determined on a four-ball friction tester with the research method. Before the test, the balls were broken in in low-viscosity petroleum oil so that an impression 0.3±0.02 mm in diameter was rubbed on the lower balls.

The antiwear properties of the oil were judged by the average increase in the diameters Δd_1 of the impressions on the lower balls after 30 min of testing. Heating Δt_1 of the cup with the oil, characterizing its friction, was simultaneously recorded. Then in the second stage of the test, the oil with the additive was replaced by oil with no additive and the effect of the additive was evaluated with the values of Δd_2 and Dt_2 [11].

A mixture of short-chain primary and secondary alcohols was selected for synthesis of the new TsD-7 additive: the technology for producing this additive allowed avoiding addition of a large amount of diluent. A low-boiling solvent does not have to be used to treat the additive. The additive contains a minimum of 10% active elements – phosphorus and zinc.

The lubricating properties of the TsD-7 additive were compared with the properties of existing dithiophosphates. The tested additives were added to the base oil both individually and combined with detergents – VNII NP-714 (V-714) carbonated phenolate and KND sulfonate (Table 1). TsD-7 additive in SAE-10 base oil had better antifriction properties both individually and in combination with detergents than existing dialkyl dithiophosphates. The antifriction properties were markedly manifested in the second stage of the test.

These notions concerning the thermostability of dithiophosphates of different structure were obtained as a result of determining the temperature of the onset of decomposition of dithiophosphates by differential scanning calorimetry (DSC). However, for predicting possible fouling, it is important to estimate the amount of disperse phase formed at the working temperatures of the cylinder-piston group, which can exceed 250°C.

The amount of disperse phase can be judged with the method of determining the thermal stability of oils containing additives [10, pp. 135-136]. This method consists of the following. Products of oxidation, decomposition, and condensation forming a disperse phase accumulate in oil as a result of exposure to high temperatures in the presence of atmospheric air in contact with metal, i.e., in conditions close to the conditions of use, and this results

TABLE 3

Indexes	Oil						
	M-8G$_2$ with additive			M-8V with additive		M-6z/12G$_1$ with additive	
	V-354	DF-11	TsD-7	V-357	TsD-7	DF-11	TsD-7
Concentration of additive in oil, %	2.5	1.4	0.7	4	0.9	2.2	1.1
Antioxidant and scavenger properties (3 h, 230°C)							
increase in viscosity, %	68	65	49	51	32	43	39
optical density	0.33	0.32	0.26	0.48	0.29	0.23	0.21
corrosion of lead, %	8.4	7.2	7	11.2	6.4	3.6	5.2

TABLE 4

Indexes	M-10DM oil		Standard for group D oils
	experimental	commercial*	
Detergent properties, points			
piston ring mobility	0	0	max of 0
fouling of piston			
all grooves	4.3	3.6	–
including first	3.7	3	–
connectors	0.8	1.8	–
skirt	0.1	0.1	–
drainage holes	0	0	–
inner surface	0.8	0.3	–
total (inner and outer surfaces)	6	5.8	max of 7
Antiwear and anticorrosion properties			
weight loss, mg			
piston ring assembly	54	36	–
connecting rod inserts	43	135	max of 250
amount of deposits in centrifuge rotor, g	180	96	–

Note. * Manufactured at Slavneft'-Yaroslavneftorgsintez OJSC.

in fouling and sediment formation. The amount of disperse phase is judged by the change in the optical density of the oil as a result of stirring for 10 min at 240°C in contact with metals.

The results of estimating the thermal stability of different dithiophosphates added to I-40 base oil both individually and combined with detergents – carbonated calcium sulfonate and phenolate – are reported in Table 2. The tested dithiophosphates differed in the content of basic salts, which can be judged by the base number, determined by direct titration with 0.1 N HCl solution according to GOST 11362–76.

Despite the higher decomposition temperature determined by DSC, diaryl dithiophosphates formed a larger amount of disperse phase when exposed to high temperatures than dialkyl dithiophosphates. The large amount of basic salts in the dithiophosphate also causes the formation of a large amount of disperse phase in oil with no detergents (TsD-7 additive with a base number of 19 mg KOH/g in comparison to the same additive with a base number of 7.7 mg KOH/g).

In base oil with no detergents, the dithiophosphate with a low pH (VNIII NP-354) formed the largest amount of disperse phase. However, the difference in the oils in the tendency to form disperse phase at high temperatures in the presence of dithiophosphates with different pH is leveled after addition of basic detergents. This is seen from a comparison of the results of testing VNII NP-354 with pH 3.8 and foreign diaryl dithiophosphate with pH 6.2.

It follows from the results obtained that dialkyl dithiophosphates, which have a lower decomposition temperature than diaryl dithiophosphates, cause the formation of a smaller amount of disperse phase. On this basis, adding diaryl dithiophosphates to oils for heavy-duty engines is not totally justified.

The antioxidant and scavenger properties of oils containing TsD-7 additive were compared with the properties of a number of motor oils containing carbonated calcium sulfonate and phenolate in addition to existing dithiophosphates. As follows from Table 3, TsD-7 additive has the best antioxidant and scavenger properties.

Motor oil with TsD-7 additive and carbonated calcium phenolate and sulfonate satisfied the requirements for group D oils in testing in a D-245 engine (Table 4) and IM-1 unit (Table 5). This oil had a sulfate ash content of 1.4% and contained no calcium alkylsalicylate and high-temperature antioxidants.

The results obtained alter the core concept concerning the necessity of adding high-temperature antioxidants (calcium alkylsalicylate) and thermostable dithiophosphates (for example, zinc diaryl dithiophosphates, which are

TABLE 5

Indexes	M-10DM oil	
	standard according to GOST 20303	actual
Detergent properties, points		
piston ring mobility	max of 0	0
deposits on piston		
in grooves	max of 9	6.09
on skirt	max of 1.5	0
on inner surface	max of 4.5	2.24
including in the boss zone	max of 2.5	0
total	max of 17.5	8.33
Antiwear properties: weight loss of piston ring assembly, mg	max of 1200	607
Corrosion properties: weight loss of liner assembly, mg	max of 150	32.9

not very effective with respect to the basic functional properties) to heavy-duty diesel engines. High-quality oils for diesel engines can be produced using qualified calcium alkylphenolates and zinc dialkyl dithiophosphate with secondary alkyl radicals.

Production of TsD-7 additive has been organized at Naftan Industrial Association (Belorussia). It is approved for use in motor oils. M-10DM oil with a package of VDS-9902 additives containing TsD-7 additive has been approved for production and use based on the positive results of tests with a set of methods for qualified evaluation in automotive gasoline engines and automobile, tractor, and combine diesels.

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