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A Composition of Organic Hetero Compounds as an Antioxidant and Antiwear Additive for Mineral Lubricating Oils

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Abstract—As a multifunctional additive exhibiting antioxidant and antiwear activity for mineral lubricating oil, a composition of ammonium dialkyldithiophosphate (ADTP) with tetraalkyl thiuram disulfide (TDS) has been proposed, which provides lower sulfated ash, phosphorus, and sulfur contents compared with the traditional additive zinc dialkyldithiophosphate used for the same functions. Ammonium dialkyldithiophosphates bearing various alkyl radicals have been synthesized using structurally different amines. The antioxidant efficiency of ADTP samples has been shown by monitoring the formation and degradation of hydroperoxides in a hexadecane medium as a model of mineral oil. The tribological parameters of these compounds have been determined under boundary lubrication conditions.

Keywords: additives, antioxidants, organic hetero compounds, amines, tribological parameters

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Modern engine oils generally include quite a complex set of additives (the so-called additive package) for various applications, in particular, antioxidant and antiwear additives, such as zinc salts of dialkyldithiophosphoric acid. The phosphorus and sulfur atoms in their structure and the sulfated ash (zinc atoms) produced have a negative effect on the performance of exhaust control systems (catalytic converters, exhaust gas recirculation systems, particulate filters), with which internal combustion engines that meet the Euro-4 and Euro-5 standards are equipped. The negative effect of such additives on the operation of catalytic converters is associated with the deactivation of the additives by vitreous matter, the product formed on the surface as a result of decomposition of zinc dithiophosphates [1, 2]. As the sulfated ash and sulfur contents of oil increase, the amount of deposits in the exhaust gas recirculation system increases, the pores of particulate filters are intensively "clogged", and their performance declines. For these reasons, research-and-development works on next-generation motor oils, the so-called low- and zero-SAPS (Low Sulfated Ash, Phosphorus and Sulfur) oils, which are to contain low or no sulfated ash, phosphorus, and sulfur, have been launched and are in progress now abroad [3, 4].

To tackle these problems, we proposed an ash-free composition of organic hetero compounds, including ammonium dialkyldithiophosphate (ADTP) and tetraalkyl thiuram disulfide (TDS) [5]. It was shown that the composition introduced as an additive into mineral oil composition has an inhibitory effect during high-temperature (180°C) oxidation and exhibits tribological activity in friction and wear processes [6].

It was of interest to study the effect of the nature of the alkyl groups in the ammonium salt on the functional properties of the composition and to determine the optimal ratio of its components. Thus, the aim of this work was to synthesize TDS and various ADTP derivatives, to study the antioxidant action and behavior of the relevant compositions, and to determine their activity in the friction and wear processes.

EXPERIMENTAL

To synthesize ADTP samples containing various alkyl groups, the following primary and secondary amines were used: di(2-ethylhexyl)amine $(C_8H_{17})_2NH$ (**1**), dodecylamine $C_{12}H_{25}NH_2$ (**2**), octadecylamine $C_{18}H_{37}NH_2$, (**3**), didodecylamine $(C_{12}H_{25})_2NH$ (**4**), and dioctadecylamine $(C_{18}H_{37})_2NH$ (**5**).

Ammonium dialkyldithiophosphates were synthesized in two stages according to a published procedure [7]. In the first step, di-2-ethylhexyldithiophosphoric acid was prepared via the reaction of 2-ethylhexyl alcohol with phosphorus pentasulfide at 80°C. Then, alkylammonium salts of this acid were synthesized in an almost quantitative yield by reaction of the acid with the aforementioned structurally different amines at 100°C and a 1 : 1 molar ratio of the reactants in a toluene solution. The composition and structure of the

Table 1. Amount of sulfur and phosphorus atoms in components of the additive

Additive components	Ratio of components in mixture with oil, mass fraction	Amount, %		Atomic ratio	
		P	*S*	*S/P*	*P/S*
DF-11	1	0.094	0.194	2.07	0.48
TDS	1	none	0.202	–	–
ADTP-1	1	0.064	0.132	2.07	0.48
ADTP-1	0.75	0.048	0.099	3.13	0.32
TDS	0.25	none	0.051	–	–
ADTP-1	0.5	0.032	0.066	5.23	0.19
TDS	0.5	none	0.101	–	–
ADTP-1	0.25	0.016	0.033	11.55	0.09
TDS	0.75	none	0.152	–	–

compounds obtained were confirmed by elemental analysis and mass spectrometry.

Tetraalkyl thiuram disulfide was synthesized in two steps as well [8]. In the first step comprising the reaction of di(2-ethylhexyl)amine with a mixture of carbon disulfide and sodium hydroxide in toluene at 8–10°C, sodium di(2-ethylhexyl)dithiocarbamate was obtained, which was then oxidized with an aqueous iodine solution at 16–18°C to give tetra(2-ethylhexyl) thiuram disulfide.

The antioxidant activity of these ADTP samples was examined according to two procedures. In one of them, in accordance with the published method [9], the hydroperoxide buildup rate in a hexadecane medium as a model of mineral oil was determined in the kinetic regime of its auto-oxidation with oxygen at 170°C. The hydroperoxide concentration [ROOH] was measured iodometrically. To determine the character of hydroperoxide degradation, hexadecane was initially oxidized for a time corresponding to the maximum yield of hydroperoxides (0.25 mol/L) and their decomposition was then studied in an oxygen-free atmosphere by bubbling nitrogen through the solution of an ADTP sample in hexadecane. The concentration of the test compounds was 1×10^{-3} mol/L. Using the other procedure according to [10], high-temperature (180°C) oxidation of a model 1 : 1 (by volume) mixture of the industrial oils I-20 and I-40 was carried out in the presence of a catalyst (reduced copper) or pro-oxidant (copper naphthenate) with air bubbling (5×10^{-3} m^3/s) through the oil for 20 h with sample analysis every 5 h.

The tribological characteristics of the composition and its components in friction and wear processes were determined with a CETR (Center for Tribology Inc., USA) UMT-3 tribometer and a ChMT-1 four-ball tester with varying the additive concentration of 0.5–1.0 wt % in the 1 : 1 (by volume) mixture of I-20 and I-40 oils. In the case of UMT-3, the ball–disc friction pair reciprocating with an amplitude of 1 mm and a frequency of 50 Hz was used. The load on the ball (diameter, 12.7 mm; material, ShKh-15 steel) was applied in the stepwise manner by its increasing from 50 to 175 N with a step size of 25 N. The duration of each step was 20 min, and the total testing time was 2 h. The sample temperature was maintained at 80°C. The antiwear properties of the samples were evaluated at the end of testing on the UMT-3 machine with a MMI-2 toolmaker's microscope by measuring the ball and disc wear according to the DIN 51834 method [11] and the ball wear scar diameter on the ChMT-1 tester according to GOST (State Standard) 9490.

RESULTS AND DISCUSSION

Table 1 presents data on the amount of phosphorus and sulfur atoms in the synthesized additive components in both their individual state and various combinations in the lubricating oil in comparison with the conventional additive zinc dialkyldithiophosphate (DF-11).

From these data it follows that the minimal phosphorus and sulfur content in the composition is provided at an equal mass ratio of the components (0.5 : 0.5) in the additive formula.

Figure 1 shows the kinetics of buildup and consumption of hydroperoxides during autoxidation of hexadecane in the presence of ADTP, in which the amine moiety includes alkyl groups of various nature. Since the inhibitors are likely to be consumed at the beginning of the buildup of hydroperoxides, the reaction can occur in the system with the participation of reactant transformation products. As follows from the results presented above, the formation of hydroperoxides in the case of additive-free hexadecane occurs very quickly (they are present in a small fraction already in the starting hydrocarbon) to reach the maximal concentration of these reactive intermediates well

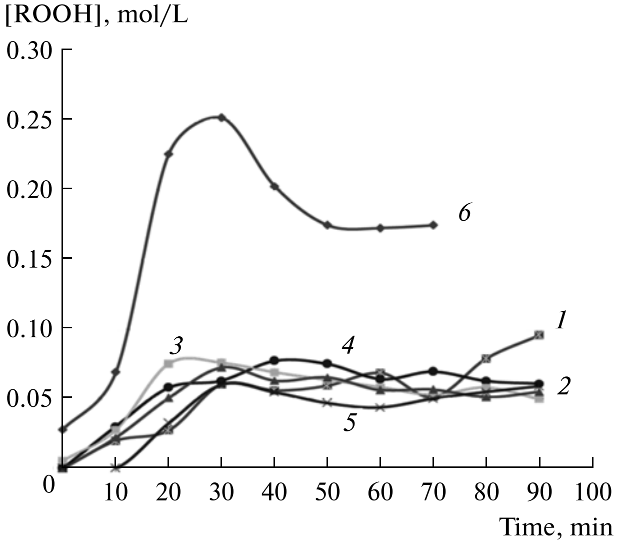

Fig. 1. Kinetics of buildup of hydroperoxide in ADTP solutions in hexadecane with [ADTP] = 1.0×10^{-3} mol/L: (*1*) ADTP-1, (*2*) ADTP-2, (*3*) ADTP-3, (*4*) ADTP-4, (*5*) ADTP-5, and (*6*) hexadecane.

above that for all ADTP samples, which have approximately the same effect. A small exception is ADTP that has dioctadecylamine making the amine component; there was a distinctly expressed induction period (~10 min) in the formation of hydroperoxides in this case.

It should be noted that the hydroperoxide buildup and consumption rate curves are self-oscillating in character in all cases. This pattern was reported by many investigators previously [12, 13], and it was explained in terms of the mechanism by which the high-temperature oxidation of hydrocarbons is accompanied by profound changes in the structure of the liquid phase, which changes are due to the formation and degradation of the micellar associates [14].

On the basis of the kinetic data (Fig. 1), the maximal concentration of hydroperoxides produced in hexadecane by the 30th min (time to reach $[ROOH]_{max}$ in pure hexadecane) were calculated for all ADTP samples. The maximal values of the hydroperoxide buildup rate according to the tangents drawn at the inflection points of the rate curves were also determined. These results are summarized in Table 2.

Table 2. Buildup of hydroperoxides in the presence of different ammonium dialkyldithiophosphates

System	$[ROOH]_{max}$, mol/L	$V_{max} \times 10^5$, mol/(L s)
Hexadecane (HD)	0.252	26.2
GD + ADTP-1	0.060	5.5
GD + ADTP-2	0.063	5.0
GD + ADTP-3	0.076	7.9
GD + ADTP-4	0.072	4.8
GD + ADTP-5	0.060	5.4

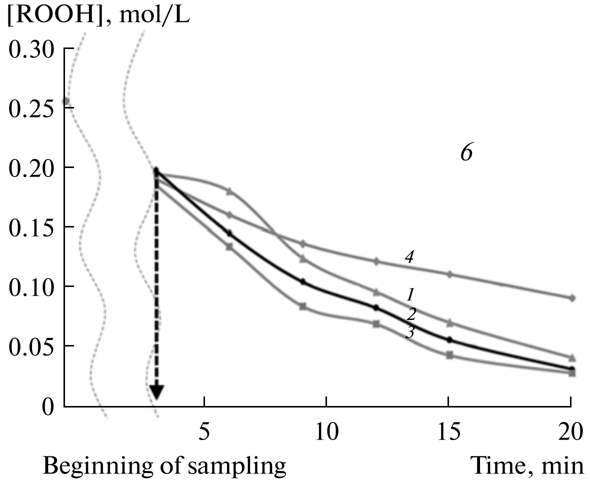

Fig. 2. Kinetics of degradation of hydroperoxides in the presence of ADTP with [ADTP] = 1.0×10^{-3} mol/L in hexadecane: (*1*) ADTP-1, (*2*) ADTP-4, (*3*) ADTP-5, and (*4*) hexadecane.

These data show that the minimal concentration of hydroperoxides is observed for solutions of ammonium dialkyldithiophosphate in which the alkyl radical comes from di-(2-ethylhexyl)amine or dioctadecylamine.

It is known that the effectiveness of oxidation inhibitors is determined not only by their ability to inhibit the formation of hydroperoxides in the system, but also the possibility to actively influence the rate of ROOH decomposition into molecular (nonradical) products. In accordance with this, we conducted experiments on the decomposition of hydroperoxides formed in hexadecane in the presence of various ammonium dialkyldithiophosphates (Fig. 2). On the basis of these data, the maximal rates of decomposition of hydroperoxides were calculated from the initial portions of the rate curves and the concentration of hydroperoxides remaining in the system by the 20th min were determined (Table 3).

As can be seen from the data in Table 3, the highest hydroperoxide degradation rate was in the case of ADTP containing the 2-ethylhexyl radical. The minimal concentration of undecomposed ROOH was approximately the same for all test ammonium dialkyldithiophosphates, although it was much lower than that in pure hexadecane.

During the catalytic high-temperature (180°C) oxidation of the model mixture of industrial oils and their solutions with additives, their viscosity increment

Table 3. Degradation of hydroperoxides in the presence of different ammonium dialkyldithiophosphates at 170°C

System	$V_{max} \times 10^4$, mol/(L s)	$[ROOH]_{min}$, mol/L
Hexadecane (HD)	1.67	0.0897
GD + ADTP-1	3.12	0.0397
GD + ADTP-4	2.94	0.0268
GD + ADTP-5	2.86	0.0301

as one of the characteristic indicators of oxidizability of lubricants was determined (Table 4).

The data in Table 4 show that the additive components and their composition exhibit inhibitory properties, which are particularly distinct in the presence of reduced copper wire, an oxidation catalyst. The best result was achieved in the case of the components mixed in equal proportions by mass, a fact that may suggest the synergistic effect.

Being introduced as additives into mineral oil, the synthesized compounds were also examined in friction and wear processes using the ChMT-1 tester. Table 5 presents the tribological characteristics obtained for different ammonium dialkyldithiophosphates in a white oil (WO) solution (0.5 wt %); the volumetric wear of the disc was determined on the UMT-3 tribometer.

As can be seen from these data, all the ADTP salts exhibit antiwear activity, lowering the wear scar diameter as compared with the additive-free oil. By this parameter, the most efficient additive among the samples is the salt containing the di(2-ethylhexyl)amine moiety. Note a high antiwear activity of the salts in comparison with the pure oil as determined by the volumetric disc wear; in this case, the best result was obtained for the salt containing the dioctadecylamine moiety.

Table 4. Results of high-temperature catalytic oxidation of a 1 : 1 (vol.) mixture of mineral oils (MO) I-20 and I-40 containing various components

Sample composition	Oxidation time, h	Viscosity $\nu_{+100°C}$ during oxidation		
		without catalyst	in the presence of	
			copper	copper naphthenate (0.1 wt %)
MO	0	12.29	12.29	12.29
	20	15.20	13.16	13.74
MO + 0.5% TDS	0	12.20	12.20	12.20
	20	15.37	13.20	13.15
MO + 0.5% ADTP-1	0	12.33	12.33	12.33
	20	15.30	12.86	13.15
MO + 0.5% TDS + 0.5%ADTP-1	0	12.33	12.33	12.33
	20	14.78	13.09	12.51

Table 5. Tribological characteristics of ammonium dialkyldithiophosphates

Formulation of system	Wear scar diameter (WSD), mm	Critical nonseizure load, P_{cr}, N	Weld load, P_w, N	Load wear index (LWI)	Volumetric disc wear, $V \times 10^3$, mm^3
White oil (WO)	0.77	80	135	36.90	1.7
WO + ADTP-1 (0.5%)	0.37	100	141	52.60	0.5
WO + ADTP-2 (0.5%)	0.65	106	150	46.39	0.6
WO + ADTP-3 (0.5%)	0.56	100	150	46.43	0.3
WO + ADTP-4 (0.5%)	0.66	84	150	38.02	0.7
WO + ADTP-5 (0.5%)	0.58	89	150	45.00	0.2

Table 6. Tribological properties of the composition of different formulas

Formulation	Wear scar diameter (WSD), mm	Critical nonseizure load, P_{cr}, N	Weld load, P_w, N	Load wear index (LWI)	Coefficient +of friction, f(60 min)
Mixture of I-20 + I-40 (base oil)	0.92	100	100	41.00	0.133
Base oil + TDS (1 wt %)	0.71	100	100	42.22	0.142
Base oil +ADTP-1 (1 wt %)	0.46	106	112	43.39	0.131
Base oil + ADTP (0.25 wt %) + TDS (0.75 wt %)	0.50	106	112	42.76	0.145
Base oil + ADTP (0.75 wt %) + TDS (0.25 wt %)	0.43	106	112	43.12	0.146
Base oil + ADTP (0.5 wt %) + TDS (0.5 wt %)	0.43	106	112	43.44	0.135
Base oil + DF-11 (1 wt %)	0.39	106	112	44.02	0.128

Chosen for further testing of the compositions with various formulas was the salt ADTP-1 as having the best antiwear performance in terms of linear wear of the metal surface (Table 6).

The results showed that the antifriction properties of the composition and its components are comparable with those of the initial mineral oil. The extreme-pressure activity also did not reveal the benefits of the composition. The antiwear effect is displayed to the greatest extent in the case of fifty–fifty ratio between the components of the additive, and is comparable with that of zinc dithiophosphate; however, unlike the latter, the composition is metal-free, i.e. is ashless, and the ratio of sulfur to phosphorus atoms is nearly three times below that of DF-11.

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