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NITROGEN-CONTAINING OXYPROPYLATES OF PHENOL AND ITS DERIVATIVES AS OXIDATION AND CORROSION INHIBITING ADDITIVES TO ENGINE OILS

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Oxidation and corrosion inhibiting properties of nitrogen-containing phenol oligomers in base engine oil are investigated. It is shown that in the presence of benzoguanamine and benzoguanamine oxypropylates, the basic matrix containing products of oxypropylation of phenol and monoalkyl phenols (C_8-C_{12} alkyl radical) has a higher thermal stability and a lower corrosivity. The results obtained are substantiated.
Keywords: *phenol, monoalkyl phenols, oligomer, propylyene oxide, benzoguanamine, oil additives, base oil, oxidation and corrosion inhibiting properties.*

It is known that use of engine oils for heating in presence of air is accompanied by oxidation processes, which lead to formation of organic acids that are responsible for the corrosiveness of the oil [1, 2]. In order to prevent oxidation of the oil and corrosion of metallic parts, oxidation and corrosion inhibiting additives are used [3-5]. Among the latter, additives based on phenol and its derivatives are of high importance.

Commercial brands of similar additives are known: highly alkaline phenolates (V-7120, V-7130 D, etc.), products of alkylation of phenol with propylene trimers (technical specifications TU RV 300220696.016-2003, TU VU 390401182.018-2009) [6], barium and strontium salts of alkyl phenols and their conversion products (TsIATIM-339, TsIATIM-339s, VNIINP-360), salts of products of condensation of alkyl phenols with formaldehyde (BFK, IKhP-101, VNIINP-370), etc. These brands of additives, besides oxidation and corrosion inhibiting properties, exhibit other functional properties as well, such as deterging, wear-resisting, etc. [3]. In order to find new additives from among phenol oligomers, nitrogen-containing phenol oxypropylates were produced and the chemistry of the synthesis process, composition,

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structure, and physicochemical properties of these compounds were studied [7-9]. The synthesized oligomers were successfully tested earlier as additives of various kinds in base engine (trademark M-8) and industrial (I-40) oils [1-12].

In this paper, we report some data from studies of products of oxypropylation of phenol and monoalkyl phenols with C_8-C_{12} alkyl groups in the presence of such nitrogen-containing compound as benzoguanamine (1,3-diamine-5-phenyl-2,4,6-triazine) and oxypropylates of the latter as oxidation and corrosion inhibiting additives to engine oils. The composition of the tested oligomers is shown in Table 1.

The oxidation inhibiting properties of the oligomers were determined in accordance with GOST (Russian Federal Standard) 11063-77 in a DK-NAMI apparatus at 200°C over 10 h. To M-8 engine oil was added 1 wt. % of 50%-solution of oligomer in oil. The results of determination of oxidation inhibiting properties of oligomers of various compositions vis-a-vis known brands of additives, which were tested under identical conditions, are cited in Table 2. As can be seen, the phenol-based oligomer *3* is distinguished by high oxidation inhibiting properties; upon heat treatment the quantity of residue decreases by 96.36% compared to additive-free oil. Removal of impurities of the original reagents from the oligomer by vacuum distillation (specimen *10*) increases the effectiveness of the additive a little.

High effectiveness of specimens *3* and *10* can be attributed to the presence in the macromolecules of fragments capable of inhibiting radical formation in the oxidation process. Similar fragments are constituents of all original reagents and affect the oxidation inhibiting properties of the oligomers in different degrees. Possibly, such fragments are mobile hydrogen atoms of phenol and oxypropylene units, which, having been attached to the radicals formed upon oxidation, are capable of retarding the process, forming more stable radicals. Also, the unbound electron pair of nitrogen atoms in amine fragments probably overlaps with the unpaired electrons of the radicals and reduces the activity of the latter.

Table 1

Specimen No.	Content in oligomer, wt. %, of				
	alkyl phenols (C_8-C_{12} alkyl radical)	propylene oxide	polypropylene glycol	benzoguanamine	catalyst (potassium hydroxide)
	Oligomers produced without removal of impurities of original reagents				
1	40.07	29.79	29.79	-	0.35
2	34.93	43.28	14.45	7.04	0.30
3	20.31 (phenol)	63.53	-	16.16	-
4	-	33.45	50.21	16.34	-
5	39.08	48.43	-	12.49	-
6	-	78.82	-	21.18	-
7	-	30.47	45.93	23.60	-
	Oligomers rid of impurities of original reagents				
8	-	33.45	50.21	16.34	-
9	39.08	48.43	-	12.49	
10	20.31 (phenol)	63.53	-	16.16	-

Table 2

Specimen No. (Table 1)	Residue, wt. %	Decrease in residue quantity in comparison with oil without additive, wt. %	Kinematic viscosity at 100°C, mm^2/sec		Increase in viscosity in oxidation process, %
			before oxidation	after oxidation	
Without additives	1.87	-	8.07	9.12	13.01
1	1.93	3.21*	7.93	9.15	15.38
2	1.83	2.14	7.81	8.59	9.99
3	0.068	96.36	7.93	9.15	15.38
4	1.34	28.34	7.81	9.15	17.16
5	1.02	45.45	7.93	8.59	8.32
6	0.51	72.73	7.83	8.54	9.07
7	0.62	66.84	7.81	8.85	13.32
8	0.72	61.50	7.93	9.15	15.38
9	0.65	65.22	7.84	8.59	9.57
10	0.5	97.33	7.93	9.15	15.38
IKhP-21	1.49	20.32	8.01	9.31	16.23
DF-11	0.6	67.91	8.33	11.20	34.45

Note. *Quantity of residue increases.

The oligomers, which are oxypropylates of monoalkyl phenols, are ineffective (specimens *1* and *2*). Their effectiveness improves markedly with increasing amine content (specimen *5* relative to specimen *2*) and with removal of impurities of the original reagents from the oligomers (specimen *9*), mainly of propylene oxide and polypropylene glycol.

Oxypropylates of benzoguanamine, the main fragment in the oligomer macromolecules of which is amine, are distinguished by high oxidation inhibiting properties. As noted above, increase in amine content (specimen *7* relative to specimen *4*) and removal of original reagents (specimen *8* relative to specimen *4*) is amply manifest in the effectiveness of the additives. The increase in viscosity after oxidation in the presence of all of the synthesized specimens meets the requirements (not more than 25%).

Analyzing the data in Tables 1 and 2 it can be summed up that the oxidation inhibiting properties depend essentially on the component and quantitative composition of the oligomers and on the presence of impurities of the original reagents which have an adverse influence on the effectiveness of the additives. In terms of effectiveness of improving the thermal stability of the basic matrix, the oligomers can be put in the following order: oligomers of phenol and benzoguanamine with propylene oxide (specimens *3* and *10*) > oligomer of benzoguanamine with propylene oxide (specimen *6*) > oligomer of benzoguanamine with propylene oxide and polypropylene glycol (specimen *7*) > oligomers of monoalkyl phenols and benzoguanamine with propylene oxide (specimens *5* and *9*) > oligomer of monoalkyl phenols and benzoguanamine with propylene oxide in the presence of polypropylene glycol (specimen *2*) > oligomer of monoalkyl phenols with propylene oxide in the presence of polypropylene glycol (specimen *1*). From this series the influence of each of these components on the oxidation inhibiting properties becomes obvious.

Table 3

Specimen No. (Table 1)	Corrosion, g/m^2	Decrease in corrosion relative to oil with no additive	
		g/m^2	%
Without additive	70.2	-	-
1	78.6	8.4*	~12.0*
3	68.4	1.8	2.6
4	33.7	36.5	52.0
5	70.0	0.2	0.3
6	65.1	5.1	7.3
7	42.7	27.5	39.2
8	30.2	40.0	57.0
9	64.3	5.9	8.4
IKhP-21	32.4	37.8	53.8

Note. *Corrosion increased.

The oxidation inhibiting properties of the oligomers were determined in a DK-NAMI apparatus at 140°C over a period of 10 h following GOST 20502-75. We added 2.4 wt. % of 50%-solution of the oligomers in oil to M-8 engine oil and performed the tests. The test results for oxidation inhibiting properties of some specimens vis-a-vis the additive IKhP-21 tested under the same conditions are adduced in Table 3. As evident, oxypropylates of benzoguanamine (specimen *4*) are the most effective corrosion inhibitors. Removal of impurities of the original reagents from this specimen (specimen *8*) improves corrosion inhibiting properties; corrosion decreases more than twofold.

Thus, the proposed nitrogen-containing oligomers possess oxidation and corrosion inhibiting properties to different degrees. These oligomers were tested with positive results as additives for various functions, such as antimicrobial [10], thickening [11], deterging [8], and wear-resisting [12], etc., which prove them to be multifunctional.

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