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New Sulfur-, Nitrogen-, and Boron-Containing Multifunctional Alkylphenolate Additives for Motor Oils

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Abstract—Sulfur-, nitrogen-, and boron-modified alkylphenol additives for motor oils have been first produced by condensation of sulfurized alkylphenols with formaldehyde, alkanolamines, and boric acid followed by neutralization of the condensation products with calcium hydroxide. The structure of the resulting additives has been confirmed by IR spectroscopy. The functional properties of the additives in the composition of motor oils have been investigated. It has been found that they have high corrosion-preventing, antioxidant, and tribological properties and can be used as an additive for various motor oils. A lubricant composition M-14G_2 with high performance characteristics meeting the requirements of modern technology has been developed with the use of the additive IKhP-228.

Keywords: sulfurized alkylphenol, alkanolamines, formaldehyde, boric acid, multifunctional additives
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According to published data, boron atoms in boron-containing additives create a protective film by adsorption on the metal surface, thereby eliminate the catalytic effect of the metal in the oxidation of lubricating oils. Boron-containing compounds are effective antioxidants and metal corrosion inhibitors.

To improve the solubility in oils and improve the efficiency of boron–nitrogen-containing organic compounds, their complexes and borated ethers are mostly used. In addition, the presence of the O=B–O–B=O···HN< and $>^{+}N \rightarrow >\overline{B}-OH$ moieties in nitrogen-containing compounds, for example, in borated succinimides and amines, respectively, increases the thermal stability of the additives, extending the temperature range of their application, and the formation of protective B_2O_3, BN, Fe_3B_2 films promote the improvement of their antioxidant and tribological properties [1–6].

Based on the foregoing, one could assume that the introduction of sulfur, nitrogen, and boron atoms into the composition of alkylphenolate additives would significantly improve their performance characteristics.

EXPERIMENTAL

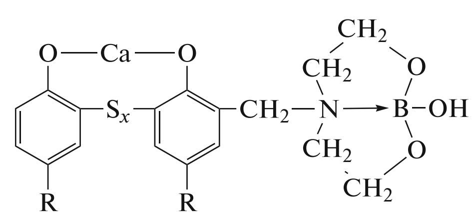
In searching for the routes of synthesis of new effective alkylphenolate additives, we synthesized sulfur-, nitrogen-, and boron-containing alkylphenolate additives IKhP-227 and IKhP-228, which had not been previously described in the literature. Sulfurized alkylphenol prepared according to the procedure described in [7] was used as the feedstock. The procedure for preparing the additives consists of the following steps:

—condensation of sulfurized dodecylphenol with formaldehyde and monoethanolamine (or diethanolamine) for 0.5–1.0 h at 80–90°C. The chemicals for the condensation were taken in the following ratio (parts by weight): sulfurized alkylphenol, 100; formaldehyde (in the form of 35% aqueous solution), 29.0 in the case of monoethanolamine (or 24.8 in the case of diethanolamine); monoethanolamine, 11.5; or diethanolamine, 10.6;

—treatment of the resulting products with boric acid, 6.6 (5.8) pph, at a temperature of 95–105°C for 1–1.5 h.

The suggested formulas of the synthesized additives are given below:

IKhP-227, the calcium salt of the condensation product of sulfurized dodecylphenol with diethanolamine, formaldehyde, and boric acid



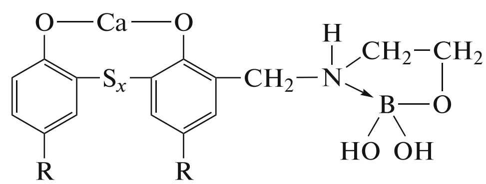
$R = C_{12}$; $x = 1, 2$

Table 1. Physicochemical and functional properties of boron-, nitrogen-, and sulfur-containing alkylphenolate additives

Heteroatomic additive sample	Base number, mgKOH/g	Sulfated ash, %	Kinematic viscosity, mm^2/s	*Composition, %			Oil M-8 + 5% additive			
				S	N	Ca	corrosion (in lead plates), g/m^2	stability by sludge induction period (30 h; sludge, %)	detergent properties (by PZV), points	wear scar diameter, mm
IKhP-227 (S,B,N)	123	11.7	85.3	1.8	0.66	2.8	3.4	0.09	0–0.5	0.32
IKhP-228 (S,B,N)	126	11.8	83.1	2.0	0.8	2.9	1.6	0.08	0.5	0.33
TsIATIM-339(S)	42	10.3	–	5.0	–	–	30.6	3.5	1.5	0.60
OLOA-218A (S)	147	17.5	–	4.9	–	5.0	10.8	0.41	0–0.5	0.40

*The boron content of the additives is 0.42–0.45%.

IKhP-228, the calcium salt of the condensation product of sulfurized dodecylphenol with monoethanolamine, formaldehyde, and boric acid



$x = 1, 2$; $R = C_{12}$

The structure of the additives synthesized from sulfurized alkylphenols, alkanolamines, and boric acid was confirmed by IR spectroscopy using a Nicolet-IS-10 Fourier transfrom IR spectrometer (spectral range 7800–400 cm^{-1}).

RESULTS AND DISCUSSION

The physicochemical and functional properties of the additives IKhP-227 and IKhP-228 were studied at a concentration of 5% in mineral oil M-8 using the following standard methods:

corrosion behavior according to GOST 20502; stability by the sludge induction period according to GOST 11063; detergent properties by the Papok–Zarubin–Vipper (PZV) method according to GOST 5726; and antiwear properties by the four-ball method according to GOST 9490.

Reference objects were the commercial additives OLOA-218A (superbasic calcium salt of alkylphenol sulfide) [10] and TsIAATIM-339, the neutral salt of sulfurized alkylphenol [11] tested under similar conditions.

The physicochemical and functional properties of the additives IKhP-227 and IKhP228 are given in Table 1. As can be seen, the test IKhP-227 and IKhP 228 samples are noticeably superior to the reference additives in antioxidant, corrosion-preventing, and extreme pressure properties under the testing conditions.

Thus, the additives IKhP-227 and IKhP-228 decrease the amount of oxidized oil sludge by a factor of 3.5–4, oil corrosiveness by a factor of 3–10, the wear scar diameter by a factor of 1.5, and the detergent properties by three times compared with the commercial additives. Simultaneously, the detergent properties of the mineral oil were improved to 0.5 in the presence of the experimental additives against 1.5 for TsIATIM-339 and remained at the same level in the of case of superbasic additive OLOA-218A.

In the IR spectra of the condensation products obtained by aminomethylation of sulfurized alkylphenol with alkanolamines, the phenolic OH group is observed as a broad, intense absorption band at 3346.50 cm^{-1} due to overlapping absorption bands of the alkanolamine NH and OH groups. The IR spectra of the condensed products after the treatment with boric acid exhibit a new band appears at 1116.38 cm^{-1}, which indicates the formation of –C–O– ether bonds.

In the spectra of the neutralized products—sulfurized alkylphenolate—there are no absorption bands of phenolic OH groups; the absorption bands due to –C–O– ether bonds are shifted somewhat toward high frequencies and manifest themselves in the absorption region of 1130.52 cm^{-1}, confirming the structure of the additives.

Note that the possibility of formation of N $\rightarrow$ B coordination bonds in the molecules of the additive is not ruled out, according to published data [8, 9].

With the use of the synthesized sulfur-, nitrogen-, and boron-containing additive IKhP-228 instead of the commercial additive MASK [12] and additives produced in industry, a lubricant composition of the

Table 2. Physicochemical and functional properties of the M-14G_2 oil composition with the additive IKhP-228

Parameter	Oil M-14G_2 GOST 12337 norm	Test oil with IKhP–228 additive	Commercial oil with MASK additive	Methods of determination	
				GOST	ASTM
Kinematic viscosity, mm^2/s	13.5–14.5	14.57	14.6	GOST 33	D 445
Viscosity index	No less than 90	90	90	GOST 25371	D 2270
Base number, mg KOH/g	No less than 7.0	8.2	7.1	GOST 11362	D 4739
Sulfated ash, %	No more than 1.3	0.96	1.29	GOST 12417	D 874
Mechanical impurities, wt %	No more than 0.01	0.015	0.015	GOST 6370	–
Open-cup flash point, °C	Not below 220	224	215	GOST 4333	D 92
Pour point, °C	Not below –12	–14	–12	GOST 20287	D 97
Tribological properties (20 ± 5)°C last nonseizure load, kg-f	No less than 34	36	34	GOST 9490	D 2266
critical load, N	No more than 823	875	823		
wear index at constant load of 196 N, mm	No more than 0.45	0.32	0.46		
Stability by sludge induction period (50 h, sludge), %	Withstands (0.5)	Withstands (0.19)	Withstands (0.5)	GOST 11063	–
Corrosivity (in lead plates), g/m^2	No more than 5.0	1.9	5.0	GOST 20502	D 665
Purity, mg, 100 g	No more than 600	500	500	GOST 12275	–
Color, ASTM units, (diluted 15 : 85)	No more than 4.0	4.0	4.0	GOST 20284	D 1500-04a
Density at 20°C, kg/m^3	No more than 905	905	905	GOST 3900	D 4052
Active elements, wt %					
calcium	No less than 0.23	0.27	0.24	GOST13538	–
zinc	No less than 0.045	0.046	0.047	GOST13538	
phosphorus	No less than 0.04	0.041	0.042	GOST 9827	

M-14G_2 oil type applied in industrial and train diesel engines was developed, as well as MASK—carbonated calcium alkylsalicylate [13].

As can be seen from the data in Table 2, the motor oil M-14G_2 developed in this work meets the GOST 12337 requirements in all the performance characteristics (antioxidant, corrosion-preventing, extreme pressure properties) and is superior to the commercial oil.

CONCLUSIONS

In searching for the routes of synthesis of new high-performance alkylphenolate additives, multifunctional sulfur-, nitrogen-, and boron-containing alkyl phenolate motor oil additives IKhP-227 and IKhP-228, which are not documented in the previous literature, have been obtained.

The additives are recommended for use both in the individual form and in compositions with other additives of the modern assortment of motor oils.

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