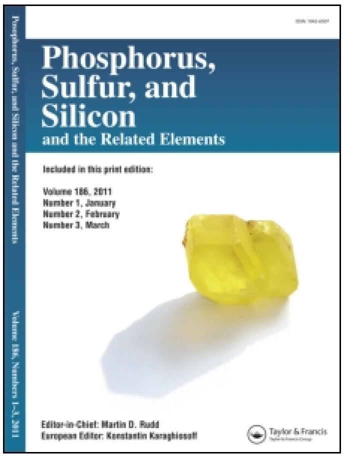

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Phosphorus Components in Lubricants: Structure-Activity Relationship

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PHOSPHORUS COMPONENTS IN LUBRICANTS: STRUCTURE–ACTIVITY RELATIONSHIP

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Phosphorus components are probably the earliest known and most important additives for lubricant applications. Phosphites, phosphates, thiophosphates, metal dithiophosphates, and amine phosphates are examples of common phosphorus additives being used in the lubricant industry. However, due to environmental concerns and to help conserve catalyst life of catalytic converters, there is a trend to reduce the phosphorus content in lubricant formulations. In order to achieve this goal, different types of phosphorus components have been studied for their tribological properties.

Keywords: Additive; antiwear; lubricant; phosphorus

Most lubricants nowadays incorporate one or more additives in order to enhance specific chemical or physical properties of the base oil employed. Some, such as antiwear, extreme pressure, and friction-reducing additives, make a direct contribution to lubricating effectiveness, whereas others, such as antioxidants, corrosion inhibitors, and detergents, protect the lubricant or the lubricated system against deleterious chemical changes during use. Phosphorus components in the lubricants reduce the rapid wear that can occur where a fluid film is lacking between the surfaces. Wear occurs when there is a loss of metal with the subsequent change in clearance between surfaces moving relative to each other. If continued, it will result in equipment malfunction. Metal-to-metal contact can be prevented by adding film-forming compounds such as phosphates, phosphites, dithiophosphates, and others that protect the surface by physical adsorption or chemical reaction. The action of phosphorus components as antiwear additives is generally based on the theory that the polar substances are first adsorbed on

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the metal surface, which then subsequently reacts with the metal in the friction zone under the influence of heat and mechanical energy, forming a phosphorus-rich layer. With the simultaneous formation and removal of reaction layer, metal–metal contacts are effectively suppressed.[1]

In this study, we have synthesized various ashless and metallic phosphorodithioates. The synthesized phosphorodithioates were evaluated in a solvent-refined, highly paraffinic, 150 neutral grade mineral base oil having a kinematic viscosity of 28.8 cSt at 40°C and 5.0 cSt at 100°C. The synthesized additives were evaluated for antiwear, antifriction, antioxidant, and extreme pressure properties. The antiwear properties of the blends are measured by Four Ball Test Apparatus, as per the ASTM D-4172 test method. The tester is operated with one steel ball under load rotating against three steel balls held stationary in the form of a cradle. Test lubricant covers the lower three balls. The rotating speed of the top ball is 1760 ± 40 rpm. The temperature of the lubricant is kept at 54°C for 60 min. Antiwear effectiveness of the lubricants is compared by measuring the average size of the scar diameters worn on the three lower clamped balls.

Extreme pressure properties were determined by measuring the weld load, in duplicate, on a four-ball machine according to the ASTM D-2783 test method while increasing load in stages. Antioxidant performance of the blends was determined by differential scanning calorimetry (DSC), adopting a temperature range of 100–350°C, a heating rate of 10°C/min, and an oxygen flow rate of 60–80 ml/min. The temperature at the onset of oxidation was taken as a criterion for the assessment of antioxidant performance. Antifriction properties were measured by an oscillating friction and wear test apparatus, under the point test conditions. The minimum stabilized value of the coefficient of friction, recorded during the continuous run, was taken as a criterion for friction.

RESULTS AND DISCUSSION

The tribological and oxidation performance ratings of various synthesized additives are given in Table I.

Antiwear Performance

As is evident from the data in Table I, amino diarylphosphorodithioates (ANPS) reduced the wear scar versus unformulated base oil by 60–65% at 0.5–1.0% dosage. This antiwear performance is better than octylamino diisoamylphosphorodithioate (NPS-1) and *S*-octyl diisoamylphosphorodithioate (ADP). Similarly, the antiwear behavior

TABLE I Performance Evaluation of Additives

Number	Additive code	Additive	Additive concentration (%w/w)	Coefficient of friction (μm)	Wear scar diameter (mm)	Weld load (kg)	On set of oxidation, temperature (°C)
1	ANPS-1	Octylamino diaryl phosphorodithioate	0.5	0.10	0.40	180	229.8
2	ANPS-1		1.0	0.90	0.35	180	235.7
3	ANPS-2	Dodecylamino diaryl phosphorodithioate	0.5	0.095	0.45	180	255.3
4	ANPS-2		1.0	0.08	0.40	180	265.2
5	NPS-1	Octylamino dipentylphosphorodithioate	0.5	0.09	0.55	180	261.1
6	NPS-1		1.0	0.09	0.65	180	264.3
7	NPS-2	Dodecylamino dipentylphosphorodithioate	0.5	0.115	0.40	180	273.2
8	NPS-2		1.0	0.11	0.45	180	265.2
9	DPDS	Bis(2-ethylhexyl)phosphorodithioic disulfide	0.5	0.105	0.45	160	219.1
10	DPDS		1.0	0.105	0.40	180	223.2
11	ADP	*S*-Octyl dipentylphosphorodithioate	0.5	0.11	0.65	160	189.3
12	ADP		1.0	0.105	0.6	160	196.7
13	MoDTP	Molybdenum bis(2-ethylhexyl)phosphorodithioate	0.5	0.075	0.40	160	259.6
14	MoDTP		1.0	0.075	0.35	200	253.8
15	ZDDP	Zinc bis(2-ethylhexyl)phosphorodithioate	0.5	0.105	0.40	200	264.0
16	ZDDP		1.0	0.10	0.35	200	264.0
17	TiDTP	Triisopropoxy titanium 2-ethylhexyl	0.5	0.105	0.5	200	221.2
18	TiDTP	phosphorodithioate	1.0	0.095	0.6	200	238.4
19	Base Oil		—	0.17	1.0	112	196.7

of ANPS-1 and -2 is equivalent to molybdenum bis(2-ethylhexyl)-phosphorodithioate and zinc bis(2-ethylhexyl)phosphorodithioate.

Extreme Pressure Performance

The comparative evaluation of extreme pressure (EP) properties of synthesized ANPS, NPS, DPDS, ADP, and metallic phosphorodithioates are given in Table I. All the synthesized phosphorus additives showed an increase in weld load from 43 to 79% with respect to base oil. Normally, a weld load push of 2–3 load increments was observed at the concentration range studied.

Antioxidant Performance

The antioxidant action of phosphorodithioate complexes is primarily attributed to their ability to decompose hydroperoxides. The performance of amino phosphorodithioates was found to be better than phosphorodithioic disulfide and *S*-alkyl phosphorodithioates. However, the antioxidant action of metallic phosphorodithioates is comparable to amino diarylphosphorodithioates (Table I).

Antifriction Performance

Table I shows the evaluation of synthesized additives on an oscillating friction test apparatus. The amino phosphorodithioates reduced the coefficient of friction by 50–60% as compared to the base oil, which is better than alkyl phosphorodithioates and alkylphosphorodithioic disulfide. However, when compared to metallic phosphorodithioates, molybdenum dithiophosphates showed the best antifriction performance.

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