PHOSPHO-SUBSTITUTED URETHANE LUBRICATING OIL ADDITIVES

Warren Lowe, Berkeley, Calif., assignor to Chevron Research Company, a corporation of Delaware

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This invention concerns novel polyfunctional compounds finding use as lubricating oil additives. More particularly, this invention concerns phosphoro-substituted diurethanes and their use as lubricating oil additives.

Numerous additives are incorporated in oils and greases to enhance their lubricating properties. A wide variety of materials have been employed to reduce friction and increase the load-carrying capacity of lubricants employed under boundary or extreme pressure (EP) conditions. When moving surfaces are separated by oil, as the load is increased and the clearance is reduced between the surfaces, the condition of boundary, or thin film, lubrication is reached. Metal-to-metal contact occurs, and wear or seizure results. Under these conditions, the effectiveness of lubricants in reducing wear or friction varies widely. At still higher loads, the condition commonly known as extreme pressure lubrication is reached. Scuffing, galling, and rapid wear or seizure may occur. The term "extreme pressure" is a misnomer since the damage results from the high temperature reached. Welding of asperities of two contacting surfaces occurs followed by metal transfer (galling) or cleavage in production of wear fragments.

In order to avoid the undesirable effects described above, EP agents are added. One class of EP agents contains heteroatoms such as chlorine, sulfur or phosphorus or combinations thereof which react with the metal surface. Included in this class are diithiophosphates and particularly popular are the zinc diithiophosphates. However, it has become increasingly more desirable to remove metal salts from lubricating media. The use of metal free EP agents is particularly desirable when one is using an anhydrous detergent, e.g., alkyl succinimide of polyalkylene polyamine, in order to avoid the presence of metals in the oil. Metals are undesirable since on decomposition and solubilizing portion of the molecule the metals may form deposits in the engine, interfering with the engine's efficient operation.

It has now been found that extreme pressure properties can be introduced into an oil or lubricating viscosity by combining with the oil a phosphorothioate-substituted urethane having from 1 to 2 phosphorothioate-substituted urethane groups per molecule and of from 16 to 50 carbon atoms per phosphorothioate-substituted urethane group.

For the most part, diurethanes will be used of the following formula:

$$\left{\begin{array}{c}
\text{R} \\
\text{H}_2\text{O}
\end{array}\right{\begin{array}{c}
\text{P}=\text{S} \\
\text{R}\text{H}_2\text{O} \text{NH}
\end{array}}$$

wherein R is hydrocarbylen of from 2 to 12 carbon atoms, more usually of from 6 to 10 carbon atoms, R2 is hydrocarbylen of from 2 to 14 carbon atoms, more usually of from 2 to 6 carbon atoms and desirably of from 2 to 4 carbon atoms, having from 2 to 3 saturated aliphatic carbon atoms as a bridge between the oxygen and the sulfur and R3 is hydrocarbylen of from 1 to 30 carbon atoms, more usually of from 2 to 25 carbon atoms and desirably of from 4 to 18 carbon atoms. (Hydrocarbylen is a divergent organic radical composed solely of carbon and hydrogen having its free valences on different carbon atoms and may be aliphatic, alicyclic, aromatic or combinations thereof, e.g., aralkyl and alkaryl, and may have aliphatic unsaturation, e.g., olefinic; hydrocarbylen is a monovalent organic radical composed solely of carbon and hydrogen which may be aliphatic, alicyclic, aromatic or combinations thereof, e.g., alkyl and aralkyl and may have aliphatic unsaturation, e.g., olefinic.)

A preferred group of compounds has the following formula:

$$\left{\begin{array}{c}
\text{S} \\
\text{R}\text{O}
\end{array}\right{\begin{array}{c}
\text{P}=\text{S} \text{R} \text{H}_2\text{O} \text{NH}
\end{array}}$$

wherein Ar is arylene of from 6 to 10 carbon atoms, Rα is arylene of from 2 to 6 carbon atoms, preferably of from 2 to 4 carbon atoms, and Rβ is hydrocarbylen of from 1 to 30 carbon atoms, desirably of from 4 to 25 carbon atoms and more desirably of from 4 to 18 carbon atoms.

A further preferred aspect of the invention is compounds of the following formula:

$$\left{\begin{array}{c}
\text{S} \\
\text{R}\text{O}
\end{array}\right{\begin{array}{c}
\text{P}=\text{S} \text{R} \text{H}_2\text{O} \text{NH}
\end{array}}$$

wherein the benzene ring is tri-substituted, two substituents being the phosphoroalkyl urethany radical (alternatively described as S- phosphoroalkylthiohexyloxy-carbonyl amino) which are preferably separated by at least 3 carbons on the benzene ring, i.e., meta or para, "alk" is arylene of from 2 to 6 carbon atoms, preferably of from 2 to 4 carbon atoms, Rα is hydrocarbylen of from 1 to 30 carbon atoms, more usually of from 4 to 25 carbon atoms, and desirably of from 4 to 18 carbon atoms, and Rβ is either hydrogen or lower alkyl of from 1 to 4 carbon atoms, preferably methyl.

As indicated, the hydrocarbylen bridging the two nitrogen of the carbamic acid is preferably aromatic, while the bridge between the carbamic acid and the phosphoroalkylthiohexyloxy-carbonyl amino is preferably aliphatic and free of aliphatic unsaturation. The hydrocarbylen groups indicated as Rα, Rβ and Rγ may be the same or different and are preferably aliphatic.

Illustrative of compounds which come within the scope of the above formulae are the following: ethanol-1,2-di-carboxylic acid di[2-(butoxyhexyloxyphosphonothioyloxy)ethyl] diester; toluene-2,4-di-carboxylic acid di[3-(dihexyloxyphosphonothioyloxy)propyl] diester; toluene-2,6-di-carboxylic acid di[2-(d-tetrapropenylphenoxy)phosphonothioyloxy] - 1 - butyl diester; cyclohexane - 1,4 - dicarboxylic acid di[2 - (butoxyhexyloxyphosphonothioyloxy) - 1 - phenyl] diester; benzene - 1,3 - dicarboxylic acid di[2 -(dihexyloxyphosphonothioyloxy) - 1 - hexyl] diester; cumene - 2,4 - dicarboxylic acid di[2 -(dicumylhexyloxyphosphonothioyloxy) - 1 - propyl] diester; hexane - 1,6 - dicarboxylic acid di[2 -(didecylhexyloxyphosphonothioyloxy)ethyl] diester; naphthalene - 1,4 - dicarboxylic acid di[2 -(butoxyhexyloxyphosphonothioyloxy)ethyl] diester; toluene - 2,4 - dicarboxylic acid di[2 -(dipentapropenylphenoxy)phosphonothioyloxy]ethyl] diester, etc. The nomenclature is based on the "Handbook for Chemical Society Authors," The Chemical Society, London, 1961 (pages 157-158).

The compounds used in this invention are readily prepared by reacting an alkylen oxide with O.O-dihydrocarbylen phosphorothiolothioic acid. The resulting alcohol is then reacted with the desired isocyanate compound. With disiocyanate, two molecules of the alcohol are used per disiocyanate.

The reaction between the phosphonothioyloxylic acid and the oxide is readily carried out by slowly adding the oxide to the phosphonothioyloxylic acid either next
or in a solvent while maintaining the temperature between about 100° to 200° F. Conveniently, the reaction can be carried out in the range of from about 100° to 175° F. Generally, about stoichiometric amounts of the reactants are used.

To the resulting alcohol is then added the desired isocyanate, either neat or in the presence of an inert solvent and the mixture heated from about 200° to 300° F. Approximately equivalent amounts of the materials are used.

Illustrative of O,O-dihydrocarlyl phosphorothionoic acids which find use are O,O-dibutyl phosphorothionoic acid, O,O-diethyl phosphorothionoic acid, O-buty1, O-phenyl phosphorothionoic acid, O-pentyl, O-hexyl phosphorothionoic acid, O,O-di-t-butyl phosphorothionoic acid, O,O-di-t-butyl phosphorothionoic acid, O,O-dipropylenephenyl phosphorothionoic acid, O,O-dihexylcarbonyl phosphorothionoic acid, O,O-pentapropylenephenyl phosphorothionoic acid, etc. The preferred phosphorothionoic acid will have a total number of carbon atoms of from 8 to 40, more usually from 8 to 16.

The alkylene oxides which find use are ethylene oxide, 1,2-propylene oxide, 1,3-propylene oxide, 1,2-butylene oxide, styrene oxide, 1,2-hexylene oxide, 2,3-buty1ene oxide, decene-1,2-oxide, etc.

The isocyanates which find use are phenyl isocyanate, toluene isocyanate, tolylene diisocyanate, phenylene diisocyanate, bis-phenyl isocyanate, hexane diisocyanate, etc.

The oils used with the compounds of this invention may be derived from natural or synthetic sources. Fluids of lubricating viscosity generally have viscosities of from about 35 to 50,000 Saybolt Universal seconds (SUS) at 100° F. Among natural hydrocarbonaceous oils are preferred those having a napthenic base, asphalitic base and mixed base oils. Illustrative of synthetic oils are hydrocarbon oils, such as polymers of various olefins, generally of from 2 to 6 carbon atoms, and alkylated aromatic hydrocarbons; and non-hydrocarbon oils, such as polyalkylene oxides, aromatic ethers, and silicones. The preferred media are the hydrocarbonaceous media, both natural and synthetic.

Usually included in the oils besides extreme pressure agents are various other additives. These additives include rust inhibitors, antioxidants, oiliness agents, detergents, foam inhibitors, viscosity index improvers, pour point depressants, etc. Usually, these will be present in the range of from about 0.1 to 10 weight percent, more usually from about 0.5 to 5 weight percent of the composition and generally each of the additives will be in the range from about 0.01 to 5 weight percent of the composition. It is of particular importance that the compounds of this invention are compatible with the various additives and do not interfere with their efficacy.

The amount added of the compounds of this invention will generally be in the range of about 1 to 5 weight percent of the oil composition. However, the compositions may be prepared as oil concentrates and the compounds of this invention may be present in amounts as high as 50 weight percent or even as high as 80 weight percent of the total composition.

The following example is offered by way of illustration and not by way of limitation.

**Example 1**

Into a reaction flask was introduced 1,581 g. of O-isobutyl, O-hexyl phosphorothionoic acid and 389 g. of butylene oxide, added drop-wise using a water bath to maintain the temperature under 150° F. At the end of the addition, the mixture was stirred at 140° F. for 4 hours and then stripped in vacuo while heating the solution to 275° F.

To a 148.6 g. aliquot of the above mixture was added 34.8 g. of tolyl disiocyanate (an 8:20 mixture of the 2,4- and 2,6-isomers) and the mixture stirred and heated at 250°-260° F. for 8 hours. The mixture was then stripped in vacuo at 250° F. leaving a residue of 183 g.

An oxidation test was carried out to determine the effectiveness of the compounds of this invention as inhibitors. Oils samples were prepared using 480 neutral oil containing 5 weight percent of a commercial ashless detergent (polyisobutylene) alkyl succinimide of tetraethylene pentamaine and 0.1 weight percent of terephthalic acid (corrosion inhibitor). Into one of the samples was added the exemplary composition of Example 1 in an amount providing a concentration of 40 m.M/kg. of phosphorous. To 23 g. aliquots of each of the above samples were added 0.2 cc. of a solution having 3,160 p.p.m. of copper, 2,670 p.p.m. of iron, 160 p.p.m. of manganese, 36,700 p.p.m. of lead and 1,631 p.p.m. of tin as their naphthenates, providing a mixture of metals which would be expected to be found in used crankcase oils after an L-4 Chevrolet Engine Test. The oil sample to be tested is then maintained at 340° F. and a 30 minute required to absorb 1000 ml. O₁₀₂ observed. Without the additive, the oxygen was absorbed in 0.42 hour, while the sample with the additive required 10.5 hours.

The results demonstrate the excellent protection from wear and the great enhancement in lubrication results resulting by the addition of the compounds of this invention to a compounded oil. Also, significant oxidation inhibition is also observed. It is evident that the compounds of this invention afford excellent protection under extreme lubricating conditions. Moreover, the compounds of this invention are compatible with a wide variety of additives which are included in compounded oils as demonstrated by its activity with a commercial ashless detergent, e.g., alkyl succinimides.

As will be evident to those skilled in the art, various modifications on this invention can be made or followed, in the light of the foregoing disclosure and discussion, without departing from the spirit or scope of the disclosure or from the scope of the following claims.

**Claim**

1. A lubricating oil composition comprising in a major amount an oil of lubricating viscosity and in an amount sufficient to impart extreme pressure properties to said lubricating oil, a composition of the formula:

   \[
   \left[ \frac{S}{O} \right]_\text{nP} \text{SR=CONH}_2\text{NR}
   \]
wherein R is hydrocarbylene of from 2 to 12 carbon atoms, R² is hydrocarbylene of from 2 to 14 carbon atoms and has from 2 to 3 saturated aliphatic carbon atoms as a bridge between the oxygen and the sulfur, and R³ is hydrocarbyl of from 1 to 30 carbon atoms.

2. A composition according to claim 1, wherein R is of from 6 to 10 carbon atoms, R² is of from 2 to 4 carbon atoms and R³ is of from 4 to 18 carbon atoms.

3. A lubricating oil composition comprising in a major amount an oil of lubricating viscosity and in an amount sufficient to impart extreme pressure properties to said lubricating oil, a composition of the formula:

\[
\left[ (R^4O)_nPSR^3O\rangle \right]_{Ar}
\]

wherein Ar is arylene of from 6 to 10 carbon atoms, R⁴ is alkylene of from 2 to 6 carbon atoms and R³ is hydrocarbyl of from 4 to 25 carbon atoms.

4. A lubricating oil composition according to claim 3, wherein said composition which imparts extreme pressure properties is of the formula:

\[
\begin{align*}
&\left( \overset{\text{CH}_3}{\text{H}_2\text{O}} - \overset{\text{S}}{\text{CH}_2} - \overset{\text{CH}_3}{\text{O} - \overset{\text{S}}{\text{O}}} \right), \\
&\left( \overset{\text{CH}_3}{\text{H}_2\text{O}} - \overset{\text{S}}{\text{CH}_2} - \overset{\text{CH}_3}{\text{O} - \overset{\text{S}}{\text{O}}} \right)
\end{align*}
\]

5. A lubricating oil composition according to claim 3, wherein said composition which imparts extreme pressure properties is of the formula:

\[
\left( \overset{\text{CH}_3}{\text{H}_2\text{O}} - \overset{\text{S}}{\text{CH}_2} - \overset{\text{CH}_3}{\text{O} - \overset{\text{S}}{\text{O}}} \right)
\]

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DANIEL E. WYMAN, Primary Examiner.

L. G. XIARHOS, Assistant Examiner.