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SYNTHETIC LUBRICANTS

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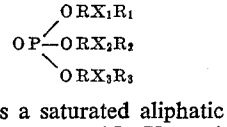
This invention relates to a new class of compounds which have been found to be particularly suitable for use as synthetic lubricants because of their low pour point, high viscosity index and unusually good load carrying properties. These compounds have also been found to be useful as addition agents for mineral lubricating oils, in which they serve as improvers of the load carrying properties of the same.

In the lubricant art, considerable progress has been realized in recent years in the production of lubricants characterized by one or more specific properties and adapted for particular uses. In the main, this progress can be contributed to two developments: the first, new refining procedures, and the second, addition agents capable of imparting particular properties to available lubricants. Thus, viscosity index improvers and pour depressants are added to automotive lubricants to render the lubricants more adaptable to wide changes in temperature conditions, while other agents are added to improve the load carrying properties of a lubricant which is to be employed, for example, under extreme pressure conditions.

Recently, in an effort to obtain superior lubricants endowed with specific and superior characteristics, a new field has been explored, namely, the synthesis of lubricants from various materials. Esters represent one class of materials which have attracted unusual interest as synthetic lubricants. In general, they are characterized by higher viscosity indices and lower pour points than mineral oils of corresponding viscosity. The esters described in the present specification have been found to exhibit very low pour point, high viscosity indices, and in addition unusually good load carrying properties. Lubricants possessing such properties are of special value in the lubrication of engines which are subjected to high temperatures such as combustion turbine engines, particularly those of the "prop-jet" type. Mineral oil lubricants containing added viscosity index improvers, thickeners or other highly non-volatile additives are undesirable for use in such engines because of the tendency to leave a residue which would accumulate and interfere with the operation of the engine. A synthetic lubricant of the type described in the present specification is especially adapted to use under such conditions, since the lubricant contains no additives and thus tends to leave no residue upon volatilization.

The new compounds of the present invention, adapted particularly for use as synthetic lubricants, comprise a new class of organo-substituted phosphoric acids, the class being defined by the general formula



in which R represents a saturated aliphatic hydrocarbon group of 2 to 3 carbon atoms; X_1, X_2, and X_3 each represent oxygen or sulfur; and R_1, R_2, and R_3 each represent an organic group which may be (1) an alkyl group, either straight chain or branched, containing 1 to 18 carbon atoms, or (2) a series of saturated aliphatic hydrocarbon groups, straight chain or branched, interlinked by oxygen or sulfur atoms, the total number of carbon, oxygen and sulfur atoms being from 4 to 18. The maximum number of oxygen or sulfur atoms or both in a given radical R_1, R_2 or R_3 is not greater than 5, and there is a chain of at least two carbon atoms between the atom X_1, X_2, or X_3 and the first oxygen or sulfur atom in such radical and a similar chain of at least two carbon atoms between each other pair of oxygen or sulfur atoms in the radical; and the total number of carbon, oxygen and/or sulfur atoms in all of the radicals joined to OP of the formula is about 24 to about 70. The more preferred compounds are those in which X_1, X_2, and X_3 represent the same oxygen or sulfur atom and R_1, R_2, and R_3 represent the same organic radical. In such cases, when R_1, R_2, and R_3 represent an alkyl group, such group should contain 4 to 18 carbon atoms.

The organo phosphates of the present invention may be conveniently prepared by contacting about three molecular proportions of a suitable ether alcohol or thioether alcohol, or mixtures of such alcohols in amounts totalling three molecular proportions of alcohol, with one molecular prportion of phosphorus oxychloride in the presence of a suitable medium such as benzene. When phosphorus oxychloride is employed it may be desirable to have present a basic substance such as pyridine to absorb the hydrogen chloride produced in the reaction. A typical method suitable for preparing any of the compounds of the present invention will be described in detail below. The ether alcohols and thioether alcohols may be prepared in great variety by the well known method of reacting alkylene oxides with alcohols or mercaptans. A class of ether alcohols which are particularly suitable for the preparation of the new compounds of the present invention are the "Carbitols," especially those which have the general formula

$$ROCH_2CH_2OCH_2CH_2OH$$

where R is an alkyl group of 4 to 12 carbon atoms.

Among the ether alcohols and thioether alcohols which have been found to be particularly suitable for use as starting materials in the formation of the organo phosphates of the present invention may be mentioned the following, although it is to be understood that these are illustrative only and the invention is not to be considered limited to the use of such compounds:

Ethylene glycol monomethyl ether
Ethylene glycol mono-n-butyl ether
Ethylene glycol mono-2-ethylbutyl ether
Ethylene glycol mono-2-ethylhexyl ether
Ethylene glycol mono-tert.-octyl ether
β-n-Butylmercaptoethanol
β-tert.-Octylmercaptoethanol
β-Dodecylmercaptoethanol
Diethylene glycol mono-n-butyl ether
Diethylene glycol mono-2-ethylbutyl ether
Diethylene glycol mono-2-ethylhexyl ether
Propylene glycol mono-n-butyl thioether
Propylene glycol mono-tert.-octyl thioether
Propylene glycol mono-n-dodecyl thioether
n-Butylmercaptoethoxyethanol
tert.-Octylmercaptoethoxyethanol
n-Dodecylmercaptoethoxyethanol
n-Butylmercaptopropoxypropanol
tert.-Octylmercaptopropoxypropanol
n-Dodecylmercaptopropoxypropanol
Propyleneglycol mono-n-butyl ether
Dipropylene glycol monomethyl ether

Dipropylene glycol monoethyl ether
Dipropylene glycol mono-n-butyl ether
Tripropylene glycol monomethyl ether
Tripropylene glycol monoethyl ether
Tripropylene glycol mono-n-butyl ether
Propylene glycol monoisopropyl ether
Dipropylene glycol monoisopropyl ether
Tripropylene glycol monoisopropyl ether

Many of the above listed ether alcohols, formed by the reaction of propylene oxide with aliphatic alcohols, are known in the industry as "Dowanols."

When the esters of the present invention are employed as lubricating oils, addition agents, such as thickeners, pour depressants, detergents, antioxidants, dyes, etc., may be present if desired.

Data will be given below showing properties of four typical examples of organo phosphates illustrating the present invention, these having been prepared by reacting phosphorus oxychloride with butyl Carbitol, 2-ethylhexyl Cellosolve, a mixture of two-thirds mol of butyl Carbitol and one-third mol of methyl Cellosolve, and β-tert.-octylmercaptoethanol, respectively. The properties listed show the particular suitability of the products for use as synthetic lubricants. The products were in each case formed by conducting the reaction in the following manner: A mixture of one mol of the alcohol, 1.1 mols of pyridine, and 92 ml. of benzene was colled to −5° C., and then 51.1 g. (⅓ mol) of $POCl_3$ was dropped in at such a rate that the temperature did not exceed 10° C. When the addition was complete, the mixture was refluxed for two hours, after which 150 ml. of water was added and the benzene layer separated. The latter was washed several times with water until it was neutral. After drying over a desiccant such as Drierite (an anhydrous $CaSO_4$), the solvent was distilled off at 5 mm. pressure and a bath temperature of 200–225° C.

The four products produced by the above typical reaction method were found to have the properties set forth in Table I.

they are of particular interest as synthetic lubricants. In addition to the use of these materials alone as synthetic lubricants, they are valuable for improving the film strength and oiliness properties of mineral oils with which they are blended. For this purpose, they are preferably blended in proportions ranging from 1% to 10% by weight of the mineral oil. The data in the last column of Table I show the usefulness of these compounds when blended with a mineral oil. The unblended mineral oil employed in these tests was capable of carrying only three weights on the Almen machine under similar conditions of test.

The mineral lubricating oil base stocks which may be improved in load-carrying capacity by the addition of the new compounds of the present invention may be derived from the various types of crude petroleum and may consist of distillates or blends of various kinds which have been refined by any of the conventional methods. Synthetic oils may also be used such as those obtained by the polymerization of olefins or by the hydrogenation of coal or its products. The base oils may vary considerably in viscosity and their properties depending upon the particular use for which they are desired.

If desired, other known addition agents, such as thickeners, pour depressants, antioxidants, dyes, etc., may be added to the mineral oil composition prepared in accordance with the present invention.

This case is a division of Serial Number 42,333 filed August 3, 1948, now abandoned.

What is claimed is:

1. As a new composition of matter the compound having the formula

$$OP(OCH_2CH_2SC_8H_{17})_3$$

where the group $—C_8H_{17}$ is a tert.-octyl group.

2. A mineral lubricating oil containing dissolved therein about 6% by weight of the compound

$$OP(OCH_2CH_2SC_8H_{17})_3$$

where the group $—C_8H_{17}$ is a tert.-octyl group.

Table I

Alcohol Reacted with $POCl_3$	ASTM Pour Point, °F.	Kinematic Viscosity		ASTM Slope	V. I.	Almen Machine Weights Carried (Gradual Loading)	
		100° F.	210° F.			Alone	6% in Mineral Oil[4]
Butyl Carbitol[1]	<−35	13.029	3.392	0.701	154	15	11
2-Ethylhexyl Cellosolve[2]	<−35	86.700	12.908	0.595	134	15	15
⅔ mol Butyl Carbitol, ⅓ mol Methyl Cellosolve[3]	−60	36.660	7.322	0.617	152	----------	----------
β-tert.-Octylmercaptoethanol	----------	3589.0	146.9	----------	----------	15	6

[1] Diethylene glycol monobutyl ether.
[2] Ethylene glycol mono-2-ethyl hexyl.
[3] Ethylene glycol monomethyl ether.
[4] Conventionally refined coastal naphthenic oil of 42 seconds Saybolt viscosity at 210° F. The unblended mineral oil carried only three weights on the Almen machine.

The above data indicate that the materials tested possess an uncommonly low pour point, high viscosity index, and high-load carrying characteristics, and since these materials have a viscosity within the lubricating oil range

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