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COMPLEX PHOSPHATE ESTER SYNTHETIC LUBRICANT

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7 Claims. (Cl. 260—461)

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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 points, high viscosity indices, and exceptional load carrying capacities.

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 attributed 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 point 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 points and high viscosity indices. 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 nonvolatile additives are undesirable for use in such engines because of the tendency to leave a residue which accumulates and interferes 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,

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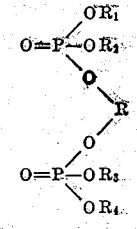
since the lubricant contains no additives and thus tends to leave no residue upon volatilization.

It is known that simple high molecular weight aliphatic esters of phosphoric acid possess properties which made them suitable for use as synthetic lubricating oils. It has been found, in accordance with the present invention, that complex phosphate esters, formed by esterifying a phosphate radical with both a glycol and a monohydric alcohol, have much higher viscosities than the simple phosphates and yet possess exceptional load carrying capacities, low pour points and high viscosity indices. Accordingly, the complex phosphate esters of the present invention are useful as lubricants where a higher viscosity oil is required.

The new compounds of the present invention may be more particularly defined by the formula



In this formula R represents a glycol radical and may consist of a saturated aliphatic hydrocarbon group, straight chain or branched, containing 2 to 18 carbon atoms, or it may be a series of saturated aliphatic hydrocarbon radicals linked by oxygen or sulfur atoms, or by both oxygen and sulfur atoms, provided there are at least 2 carbon atoms between each phosphate group and the nearest oxygen or sulfur atom and at least 2 carbon atoms between each pair of oxygen and/or sulfur atoms in the chain, and provided further that the total number of carbon, oxygen and sulfur atoms in the entire radical is from 5 to 80 and the number of sulfur atoms is not greater than 2. R_1, R_2, R_3, and R_4 of the formula each represent a monohydric alcohol residue which may be a saturated or unsaturated aliphatic hydrocarbon radical, either straight chain or

branched, containing 1 to 20 carbon atoms, or it may be a series of saturated aliphatic hydrocarbon radicals, straight chain or branched, interlinked by oxygen or sulfur atoms, or both oxygen and sulfur atoms, the total number of carbon, oxygen and sulfur atoms being from 4 to 20. The maximum number of oxygen and/or sulfur atoms in each of these radicals is not greater than 5, of which not more than 2 are sulfur atoms, and there is a chain of at least 2 carbon atoms between the phosphate group and the first oxygen or sulfur atoms in the chain and a similar chain of at least 2 carbon atoms between each pair of oxygen and/or sulfur atoms in the radical. The radicals R_1, R_2, R_3, and R_4 may be alike or different in the same molecule. In order to obtain a compound possessing desirable lubricating qualities it is desirable to choose organic radicals which will produce a compound having a molecular weight of at least 300.

Complex esters of the type described above may be conveniently prepared by reacting 2 molecular proportions of phosphorus oxychloride with 1 molecular proportion of a glycol and subsequently reacting the partial ester thus formed with 4 molecular proportions of a monohydric alcohol or of a mixture of such alcohols. The reactions with phosphorus oxychloride may be brought about by contacting the reactants in the presence of an inert liquid medium at a temperature which should be kept at least as low as about 10° C. to prevent the reaction from becoming violent, after which it is desirable to raise the temperature of the reaction mixture to at least 75° C. for a period of at least two hours to complete the reaction.

The glycols employed in preparing the esters of the present invention include ethylene glycol and any of the paraffinic homologues of the same containing up to 18 carbon atoms. These may include, for example, ethylene glycol, propylene glycol, butylene glycols, pinacone, trimethylene glycol, tetramethylene glycol, pentamethylene glycol, and the like. Since the glycols may also contain oxygen or sulfur atoms, compounds such as diethylene glycol, triethylene glycol, the polyethylene glycols of the formula

$$HO(CH_2CH_2O)_nCH_2CH_2OH$$

where n is 1 to 26, and the polypropylene glycols of the general formula

$$HO(\underset{R_1}{\underset{|}{CH}}-\underset{R_2}{\underset{|}{CH}}O)_n\underset{R_1}{\underset{|}{CH}}-\underset{R_2}{\underset{|}{CH}}OH$$

where either R_1 or R_2 is a methyl group and the other is hydrogen and where n is 1 to 20, may likewise be employed. Glycols containing sulfur atoms in thioether linkages may also be employed, and these include such compounds as thiodiglycol and 1,2-bis(2-hydroxyethylmercapto)ethane. There also may be used glycols containing both oxygen and sulfur in similar linkages; such a compound is bis-[2-(2-hydroxyethoxy)ethyl]sulfide.

The monohydric alcohols employed are typified by the following:

Methyl alcohol
Ethyl alcohol
n-Butyl alcohol
n-Hexyl alcohol
n-Octyl alcohol
2-ethylhexyl alcohol
Cetyl alcohol
Oleyl alcohol
Ethylene glycol mono-n-butyl ether
Ethylene glycol mono-2-ethylbutyl ether
Ethylene glycol mono-2-ethylhexyl ether
Ethylene glycol mono-iso-octyl ether
β-n-Butylmercaptoethanol
β-tert.-Octylmercaptoethanol
β-n-Dodecylmercaptoethanol
Diethylene glycol mono-n-butyl ether
Diethylene glycol mono-2-ethylbutyl ether
Diethylene glycol mono-2-ethylhexyl ether
Propylene glycol mono-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
Propylene glycol 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 ethylene oxide or propylene oxide with aliphatic alcohols, are known in the industry as "Dowanols," "Carbitols," or "Cellosolves."

A group of alcohols especially adapted for use in connection with the present invention are the so-called "oxo" alcohols, prepared by the reaction of carbon monoxide and hydrogen upon the olefins obtainable from petroleum products and hydrogenation of the resulting aldehydes. Materials such as diisobutylene and C_7 olefins are suitable for this purpose; also higher molecular weight olefinic materials are sometimes employed. The alcohols obtained in this manner are primary alcohols and they normally have a branched chain structure.

If desired, various addition agents may be incorporated in the esters of the present invention for the purpose of improving their properties with respect to their usefulness as lubricants. For example, antioxidants, viscosity index improvers, thickeners, pour depressants, dyes, etc., may be added.

Data will be given below showing the properties of six examples of complex phosphate esters within the scope of the present invention indicating the adaptability of these esters to lubricating service. All of these esters were prepared by a chain method which was carried out in detail as follows: In a 1-liter round bottomed reaction flask, fitted with a reflux condenser, was placed a charge consisting of 102 grams (0.66 mol) phosphorus oxychloride, 174 grams (2.2 mols) pyridiene and 180 ml. benzene. The mixture was cooled to −10° C. and 0.33 gram mols of the glycol was added dropwise at such a rate that the temperature never exceeded 10° C. After the addition was complete the mixture was stirred for a few minutes, cooled to −10° C., and 1.40 gram mols of the monohydric alcohol added dropwise, keeping the temperature below 10° C. The mixture was then refluxed for two hours, 300 ml. of water added, and the benzene layer separated. The latter was washed with water or dilute caustic solution until neutral, dried,

and stripped to a temperature of 200–225° C. at 5 mm. pressure.

The results of tests of various properties of esters prepared by the above general method are shown in the following table:

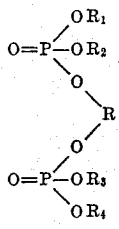
Reactants	Flash Point	Pour Point	Kinematic Viscosity		ASTM Slope	Viscosity Index	Almen Machine Wts. Carried (Gradual Loading)	
			100° F.	210° F.			Alone	6% in Mineral Oil [1]
2 mols $POCl_3$ 1 mol Ethylene glycol 4 mols 2-Ethylhexanol	350	−55	63.590	8.908	0.677	120	14	
2 mols $POCl_3$ 1 mol Ethylene glycol 4 mols Ethylene glycol monon-butyl ether	380	<−75	18.250	4.497	0.650	178	13	
2 mols $POCl_3$ 1 mol Triethylene glycol 4 mols 2-Ethylhexanol	350	−40	128.2	15.021	0.627	120	15	9
2 mols POCl 1 mol Triethylene glycol 4 mols C_8 Oxo alcohol	375	−15	702.7	56.780	0.527	121	15	11
2 mols $POCl_3$ 1 mol Triethylene glycol 4 mols Butyl Carbitol	360	−35	143.1	19.260	0.559	133	12	
2 mols $POCl_3$ 1 mol Thiodiglycol 4 mols C_8 Oxo alcohol	395	−30	284.9	30.790	0.545	127	13(?)	15

[1] Conventionally refined Coastal naphthenic oil of 40 seconds' Saybolt viscosity at 210° F. The unblended oil base carried only two weights on the Almen machine.

The above data indicate that the esters constituting the subject matter of the present invention possess characteristics, particularly with regard to viscosity index, pour point and load carrying capacity, which indicate their suitability for general use as lubricating oils and particularly for use where the presence of additives is not desirable. The esters of the present invention may also be blended with mineral lubricating oils to give lubricants of improved viscosity index and pour point. The esters may also be employed as grease bases and as plasticizers.

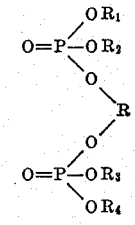
What is claimed is:

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



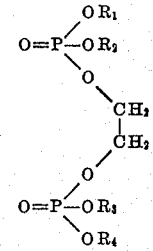
where R is an organic radical selected from the group consisting of (1) saturated aliphatic hydrocarbon radicals of 2 to 18 carbon atoms and (2) radicals consisting of a series of saturated aliphatic hydrocarbon groups linked through at least one non-carbon atom of the group consisting of oxygen and sulfur, each such hydrocarbon radical so linked containing at least 2 carbon atoms, the total number of carbon atoms and said non carbon atoms in the entire radical being from 5 to 80, and the number of sulfur atoms in the radical being not greater than 2; where R_1, R_2, R_3, and R_4 are organic radicals selected from the group consisting of (1) aliphatic hydrocarbon radicals containing 1 to 20 carbon atoms and (2) radicals consisting of a series of saturated aliphatic hydrocarbon radicals linked through 1 to 5 non-carbon atoms of the group consisting of oxygen and sulfur, there being at least 2 carbon atoms between each phosphate group and the nearest of said non-carbon atoms and between each pair of said non-carbon atoms, the total number of carbon atoms and said non-carbon atoms in each of the radicals R_1, R_2, R_3, and R_4 being from 4 to 20 and the total number of sulfur atoms in each radical being not greater than 2; and in which the components of the composition are so chosen that the molecular weight thereof is at least 300.

2. As a new composition of matter a compound of the formula



where R is a series of saturated aliphatic hydrocarbon groups linked through at least one oxygen atom, each hydrocarbon radical so linked by an oxygen atom containing at least 2 carbon atoms, the total number of carbon and oxygen atoms in the entire radical being from 5 to 80, where R_1, R_2, R_3, and R_4 each represent a radical consisting of a series of saturated aliphatic hydrocarbon radicals linked through 1 to 5 oxygen atoms, there being at least 2 carbon atoms between each phosphate group and the nearest of said oxygen atoms and between each pair of said oxygen atoms, the total number of carbon and oxygen atoms in each of the radicals R_1, R_2, R_3, and R_4, being from 4 to 20, and where the components of the composition are so chosen that the molecular weight thereof is at least 300.

3. As a new composition of matter a compound of the formula



in which R_1, R_2, R_3, and R_4 each represent a radical consisting of a series of saturated ali-

phatic hydrocarbon radicals linked through 1 to 5 oxygen atoms, there being at least 2 carbon atoms between each phosphate group and the nearest of said oxygen atoms and between each pair of said oxygen atoms, the total number of carbon and oxygen atoms in each of the radicals being from 4 to 20, and in which the components of the composition are so chosen that the molecular weight thereof is at least 300.

4. A composition according to claim 1 in which R_1, R_2, R_3, and R_4 each represent a 2-ethylhexyl radical.

5. A composition according to claim 3 in which R_1, R_2, R_3, and R_4 each represent the radical

$$—CH_2CH_2OC_4H_9$$

6. A composition according to claim 2 in which R of the formula represents the radical

$$—(CH_2CH_2O)_2CH_2CH_2—$$

7. A composition according to claim 2 in which R of the formula represents the radical

$$—(CH_2CH_2O)_2CH_2CH_2—$$

and in which R_1, R_2, R_3, and R_4 each represents the radical

$$—(CH_2)_2O(CH_2)_2OC_4H_9$$

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