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**ALUMINUM SALTS OF ALKYL  
ORTHOPHOSPHATES**

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2 Claims

**ABSTRACT OF THE DISCLOSURE**

This invention relates to certain novel aluminum salts of alkyl orthophosphates and to hydrocarbon fluid compositions containing such salts, which compositions have improved viscosity characteristics.

**BACKGROUND OF THE INVENTION**

Field of the invention

The viscosity-temperature relationship of a hydrocarbon fluid is one of its more important characteristics in that it is this relationship which is indicative of the relative change in viscosity with temperature. Thus, in motor oils of the type known as crankcase oils, it is desirable for the oil to have a viscosity that is sufficiently high at an elevated temperature to provide adequate lubrication and to prevent excessive oil consumption. On the other hand, the motor oil should have a viscosity sufficiently low at atmospheric temperature to provide ease of engine starting. Increasing the high temperature viscosity of an oil while decreasing its low temperature viscosity can be accomplished only by improving the viscosity-temperature relationship, or stated differently, by raising the viscosity index of the oil.

Description of the prior art

In order to reduce excessive change in viscosity with temperature, various viscosity index improvers have been developed. In the past, for example, polymerized esters of the acrylic series have been used to improve the viscosity-temperature relationship of mineral oils but these esters have not been entirely satisfactory inasmuch as their viscosity index improving characteristics is lost or substantially reduced when the oil in which they are incorporated is subjected to vigorous agitation and high shear rates and stresses. It is believed that the lowering of the viscosity index of an oil containing a long chain polymer as a viscosity index improving agent is a result of such polymer being split into polymers of shorter chain length by the shearing stress, the shorter chain polymers being less effective as viscosity index improvers.

In addition, aluminum soaps are presently being used as thickeners for gasoline, kerosene, and petroleum oils. The soaps have to be prepared in situ and the gelled gasoline, kerosene or petroleum oil is not stable to extended periods of storage or to heat.

**SUMMARY OF THE INVENTION**

We have found that certain aluminum salts of alkyl orthophosphates gel hydrocarbon fluids and impart excellent viscosity index characteristics to a mineral oil, and that the oil thus improved retains its high viscosity index

even when subjected to vigorous agitation and high shear rates and stresses. We have found further that a lubricating composition comprising a major amount of a lubricating oil and a minor amount of these aluminum salts of alkyl orthophosphates has a greatly improved pour point.

The lubricating oil to which the viscosity index improving agent is added according to the invention is preferably and advantageously a highly refined paraffinic oil. By the term "highly refined paraffinic oil" we mean a petroleum lubricating oil which has been refined by one of the more drastic refining methods known in the art, for example, by conventional aluminum chloride refining or by solvent extraction adapted to remove all or substantially all of the unsaturated and naphthenic constituents of the oil. Aluminum chloride refined or solvent extracted paraffinic base oil, such as a Pennsylvania oil, provides an excellent base oil for the composition of the invention. However, drastically refined Mid-Continent and Gulf Coastal oil may also be used. While the highly refined paraffinic oils are particularly desirable for use in forming crankcase lubricants, we do not wish to limit the invention to these oils alone, inasmuch as the aluminum alkyl orthophosphates are also useful in improving the viscosity index and/or pour point of oils derived from naphthenic and asphaltic crudes.

Organic phosphates that form suitable aluminum salts for the purposes of this invention are bis-hexadecyl, n-butyl, n-dodecyl, n-butyl, n-hexadecyl, isobutyl dodecyl, ethyl n-dodecyl and the C<sub>1</sub> to C<sub>8</sub> alkyl oleyl orthophosphates. Aluminum ethyl oleyl orthophosphate has been found to be particularly advantageous for improving the viscosity of the lubricating oils and for gelling gasoline.

The aluminum o-phosphate ester products can be employed per se or they can be added to the fluid in the form of a concentrate. In preparing a mineral oil concentrate, the aluminum product can be prepared in an organic solvent which can be flashed from the oil after formation of the concentrate. Organic solvents suitable for this purpose include hexane, isooctane, naphtha, benzene, toluene, and the like. When a mineral oil concentrate is prepared first, the concentrate can be added directly to the oil to be improved or it can be admixed with one or more other improving agents. Regardless of whether products are employed per se or in the form of a mineral oil concentrate, an amount is used sufficient to improve the viscosity index and/or pour point of the oil. For example, the products are useful when employed in amounts of about 0.1 to about 5 percent by weight. Amounts in excess of 5 percent are generally undesirable because the oil becomes too viscous for satisfactory use as crankcase lubricant. Excellent results have been obtained by the use in petroleum distillates, such as SAE 10 and SAE 25 lubricating oil, of amounts of the products between 0.1 and 0.5 percent by weight of the composition. It will be understood that the optimum amount will vary according to the particular mineral oil and according to the conditions to which the oil is subjected.

The lubricating oil composition of this invention can contain other addition agents normally added to lubricating oils for a specific purpose such as an oiliness and extreme pressure agent, an anti-oxidant, a corrosion inhibitor, a foam suppressant, a dye, a sludge inhibitor, and the like.

Aluminum alkyl orthophosphates when dissolved in gasoline, kerosene or other hydrocarbon fluid, in concentrations from 0.1–5% will cause them to gel. Gelled gasoline or kerosene can be stored for extended periods of time and is stable to heat. The degree of gelling can be controlled by the concentration of the orthophosphate salt in the fluid. For example, a one percent solution of aluminum ethyl oleyl orthophosphate in gasoline will flow like molasses and has good adhesion properties, whereas the present thickeners used for napalm bombs will not flow and have poor adhesion properties.

The gelled hydrocarbons can be thinned by the addition of more hydrocarbons. Also a mixture of hydrocarbons can be gelled i.e.—gasoline, kerosene and petroleum oil.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

##### Example I.—Preparation of aluminum ethyl oleyl orthophosphate

Into a two liter flask equipped with a mechanical stirrer, a dropping funnel and a thermometer are placed 178 gms. of ethyl oleyl orthophosphate, 400 ml. of water and 250 ml. of 95% ethanol. To this mixture is added 19 gms. of sodium hydroxide in 200 ml. of water. The temperature of the reaction mixture is maintained at 25° C. while 68 gms. of aluminum sulfate 18 H<sub>2</sub>O in 200 ml. of water is added slowly with rapid stirring. A finely dispersed precipitate is formed, which is filtered and left wet. The decomposition point of the solid was 237° C.

When one gram (dry weight) of wet aluminum ethyl oleyl orthophosphate is dissolved in 100 ml. of gasoline, a gel is formed. Heat and agitation greatly hastens the gelling of gasoline. The degree of thickening will be determined by the concentration of the additive in gasoline.

##### Example II.—Preparation of aluminum ethyl oleyl orthophosphate in situ in kerosene

The concentrate is prepared by adding 752 gms. (2 mols.) of ethyl oleyl phosphoric acid to 5248 gms. of

(cs.) at 210° F. of 5.5 and at 100° F. of 35.5. In each case the concentration of additive was 0.2%.

	Kinematic viscosity (cs.)	
	210° F.	100° F.
Aluminum ethyl oleyl orthophosphate.....	7.64	63.95
Lanthanum ethyl oleyl orthophosphate.....	5.72	37.50

##### Example IV.—Preparation of N-butyl dodecyl phosphoric acid

Into a 2-liter, 3-necked round bottom flask, equipped with a stirrer, reflux condenser, dropping funnel, thermometer, and means for cooling, there were charged 400 mls. of n-hexane. Then, 142 grams (1 mol.) of phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>) were gradually added to the hexane with stirring to form a slurry.

In the meantime, 372 grams (2 mols) of dodecyl alcohol and 148 gms. (2 mols) of n-butyl alcohol were mixed together to form an equimolecular admixture.

Then the above mixture of alcohols was added slowly to the hexane-phosphorus pentoxide slurry with stirring, keeping the temperature below 40° C. with cooling, the reaction being very exothermic.

After all the alcohol had been added, the reaction mixture was gradually heated to 66° C., the reflux temperature of hexane, and held there for one hour to complete the reaction.

The hexane solvent was removed by distillation under reduced pressure. The recovered dialkyl phosphoric acid is a white grease with a melting point of 30–33° C. and a refractive index at 25° C. of 1.4446.

The aluminum salt of the above product is readily formed by the methods shown in the above examples.

##### Example V

Following the procedure and using the test oil of Example III, the indicated aluminum orthophosphates, which were prepared by the same procedure illustrated in Example IV, were tested at the concentrations and with the results set out in the table.

TABLE

Aluminum orthophosphate	Decomposition point, ° C.	Physical appearance	Conc., wt. percent	Kinematic Viscosity (cs.)		V.I.
				210° F.	100° F.	
Bis hexadecyl.....	233	Light tan solid.....	.66	10.02	58.12	171
Ethyl dodecyl.....	255	White, waxy solid.....	.166	12.2	91.55	155
n-Butyl dodecyl.....	219	do.....	.5	23.09	153.74	190
n-Butyl hexadecyl.....	256	White solid.....	.66	28.58	166	141.5
iso-Butyl dodecyl.....	250	White, waxy solid.....	.66	6.7	42.32	121
Octyl oleyl.....	226	Cream colored rubbery solid.....	.1	6.25	47.24	84
Hexyl oleyl.....	192	do.....	.1	6.38	45.38	97
Methyl oleyl.....	245	Yellow grease.....	.1	6.02	40.18	103
n-Propyl oleyl.....	245	Cream colored rubbery solid.....	.1	6.51	45.3	103
iso-Propyl oleyl.....	238	Yellow grease.....	.1	5.89	38.82	103
n-Butyl oleyl.....	248	Cream colored rubbery solid.....	.1	6.86	46.19	114

kerosene and 52 gms. (.66 mol.) of aluminum hydroxide Al(OH)<sub>3</sub> with stirring. The mixture is heated to 125° C. with stirring until the reaction is complete which is evident by the disappearance of the Al(OH)<sub>3</sub> and also the thickening of the mixture. This kerosene solution was a clear, viscous amber liquid, which when added to lubricating oil will improve the viscosity of the oil.

##### Example III

To illustrate the results obtained when employing aluminum ethyl oleyl orthophosphate in comparison with the results obtained when employing a corresponding rare earth compound such as taught in U.S. Patent 2,983,679, the following experiments were run employing Amoco Test Oil SUS-165 (SAE) having a kinematic viscosity

The effect of the novel compounds of this invention in depressing the pour point of hydrocarbon fluids was determined by placing an 8 oz. round bottle, which was half-filled with the fluid containing a minor proportion of the desired additive, in a deep freeze at -5° F. for a specified time, removing the bottle, laying it horizontal and recording the time it takes the fluid to move one inch. Amoco Test Oil SUS-165 with no additive does not move in 60 seconds after 24 hours at -5° F. When containing 0.19 weight percent of aluminum ethyl oleyl orthophosphate the oil moved the one inch in 4.8 seconds after standing for 60 hours at -5° F. Similar results are obtained when employing other novel compounds of this invention.

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We claim:

1. Aluminum salt of (1) an alkyl oleyl orthophosphate wherein the alkyl group consists of the methyl, ethyl, n-propyl or iso-propyl radicals or (2) ethyl dodecyl orthophosphate.

2. Aluminum ethyl oleyl orthophosphate.

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