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LUBRICANTS CONTAINING GROUP IVB
METAL PHOSPHATES

George M. Hain, New Brunswick, and Anthony J. Revukas, Cranford, N.J., assignors to Cities Service Oil Company, a corporation of Delaware
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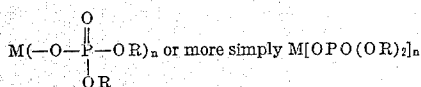
This invention relates to lubricating compositions. More particularly this invention relates to lubricating compositions containing a minor quantity of certain metal [di(hydrocarbyl) orthophosphates].

At slow sliding speeds, heavily loaded surfaces lubricated with petroleum oils or other lubricants have a tendency to exhibit stick-slip phenomena. In an automatic transmission for a limited slip differential application, this tendency manifests itself as a "squawk." On machine tool table carriages stick-slip is evidenced by violet chatter in the table travel and in inaccuracy in positioning the machine elements.

The cause of stick-slip motion is due to the sharp changes in the coefficient of friction with speed of the adjacent lubricated surfaces. When the static coefficient of friction for the lubricated surfaces is lower than the kinetic coefficient of friction, no stick-slip occurs. To inhibit or eliminate stick-slip tendencies the prior art has employed various sulfurized materials such as that of sulfurized sperm oil as additives to petroleum oil in order to reduce the static coefficient of friction sufficiently to prevent stick-slip tendencies. However, the sulfurized sperm oil and similar materials fail to eliminate stick-slip tendencies at high operating temperatures.

It has now been found that a lubricating composition containing a major quantity of a lubricant base and a minor quantity of a [di(hydrocarbyl) orthophosphate] of a Group IVB metal of the Periodic Table inhibits stick-slip tendencies over a wide range of loads, speeds and temperatures.

The [di(hydrocarbyl) orthophosphates] employed in the lubricating compositions of this invention can be represented by the generic formula



wherein M is a metal of Group IVB of the Periodic Table, each R is a hydrocarbon group and n is equal to the valence of the metal M. Since the metal can be trivalent or tetravalent M can be 3 or 4. Preferably the metal is tetravalent and n is then 4. The metal can be titanium, zirconium or hafnium and preferably titanium. A suitable Periodic Table can be found on page 314 of the Handbook of Chemistry and Physics, Twenty-ninth Edition (1945).

The hydrocarbon group, simply referred to as hydrocarbyl herein, as represented each by R in the above generic formulae can be one having from about 2 to about 30 carbon atoms. Preferably each hydrocarbyl has from about 6 to about 20 carbon atoms. The hydrocarbon group can be aliphatic, cycloaliphatic or aromatic, e.g. alkyl, alkenyl, phenyl, phenylalkyl, alkphenyl, cycloalkyl and the like. Illustrative of suitable hydrocarbon groups there can be mentioned those of isopropyl, butyl, isobutyl, tertiary butyl, 2-ethylhexyl, 3,4-diethyldodecyl, eicosyl, phenyl, 4-octylphenyl, n-butylphenyl, cyclohexyl, 4-isopropylcyclohexyl, oleyl, and the like.

Illustrative of the orthophosphate additives employed in this invention there can be mentioned; titanium tetra[di(isopropyl) orthophosphate]; zirconium tetra[di(3-butyl-octyl) orthophosphate]; titanium tetra[di(2-ethyl-5-butyl

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tridecyl) orthophosphate]; zirconium tetra[di(2-propyl-ethyl) orthophosphate]; titanium tetra[di(2,4-diethyloctyl) orthophosphate]; titanium tetra[di(2-methyloctyl) orthophosphate]; titanium tetra[bis(2-methylpropyl-methylethyl) orthophosphate]; titanium IV[di(2-ethylhexyl) orthophosphate-di(isobutyl) orthophosphate-di(2-methylnonyl) orthophosphate-di(3-butyl-octyl) orthophosphate]; titanium tri[di(2-ethylhexyl) orthophosphate]; zirconium tetra[di(2-ethylhexyl) orthophosphate]; zirconium tri[(2-ethylhexyl-2-methylpropyl) orthophosphate]; titanium tetra[di(octylphenyl) orthophosphate]; zirconium tetra[di(methylphenyl) orthophosphate]; titanium tetra[di(tricosylphenyl) orthophosphate]; zirconium tetra[di(pentylphenyl) orthophosphate]; titanium tetra[di(octylphenyl pentylphenyl) orthophosphate]; zirconium tetra[(2-ethylhexyl) methylphenyl orthophosphate]; zirconium tetra[di(octyl) orthophosphate]; and the like.

The metal [di(hydrocarbyl) orthophosphate] should be soluble in the lubricant base at the concentrations employed. For this purpose it is preferred that each of the hydrocarbon groups of the orthophosphate be branched chain alkyl, alkphenyl or phenalkyl, for example 2-ethylhexyl, 4-octylphenyl, or 8 phenyloctyl.

The quantity of metal di(hydrocarbyl) orthophosphate in the lubricant compositions of this invention is in minor amounts such as that of from about 0.1% to about 5% by weight based on the weight of the lubricating composition and preferably from about 0.5% to about 3% by weight based on the weight of the lubricating composition.

The orthophosphate additives of this invention may be prepared in any suitable manner. According to one method of preparation, a suitable organic hydrogen orthophosphate, e.g. di(oleyl) hydrogen orthophosphate, or a mixture of such phosphates is placed in a reaction flask together with about half its volume of a suitable solvent such as dry toluene. The reaction flask is preferably equipped with a mechanical stirrer, thermometer, gas inlet tube, reflux condenser and a pressure equalizing funnel with a long stem dipping into the solvent. The temperature of the reaction flask is raised to between about 110° C. to about 130° C. while stirring vigorously and titanium or zirconium tetrachloride with an equal volume of an organic solvent is added in spurts by means of the pressure equalizing delivery funnel. The tetrachloride is preferably introduced in amounts of about 1.1 moles of tetrachloride for each 4 moles of the organic hydrogen orthophosphate. Hydrogen chloride is evolved copiously by the reaction. Stirring and heating under reflux to 130° C. is continued until evolution of hydrogen chloride stops. Removal of byproduct hydrogen chloride is promoted by flushing the reaction flask with dry nitrogen by means of the gas inlet tube. The solvent is removed by distillation and reduced pressure such as 10–80 millimeters, the final temperature being about 130° C. The yield of product can be between about 85% to about 95% of theory based on hydrogen orthophosphate reactant.

In the orthophosphate additives prepared as described hereinabove, the titanium or zirconium has a valence of 4. Similar compounds in which these metals have a valence of 3 may be prepared in a similar manner, e.g. by using titanium or zirconium trichloride rather than tetrachloride as a starting material and reacting the trichloride with about 3 moles of the organic hydrogen orthophosphate.

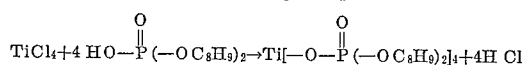
A typical lubricating composition of this invention comprises a major portion of a mineral or synthetic base lubricant and a minor portion of a metal[di(hydrocarbyl) orthophosphate], sufficient to inhibit stick-slip tendencies, dissolved in the lubricant base. The lubricating composi-

tions containing a lubricant base and the orthophosphate additive can be further improved to meet any desired lubricating requirement by incorporating therewith various other additives such as anti-oxidants, pour point depressants, viscosity index improvers, thickeners, soaps, and dyes. Typical anti-oxidants include 2,6-ditertiarybutyl-p-cresol, and the like. Pour point depressants include the polymeric acrylic esters and polyolefins. Typical thickeners include alkali metal soaps, aliphatic acids, bentonite clays and silica gels. Illustrative of lubricant bases which can be employed in this invention there can be mentioned: various silicone oils, polyesters and mineral oil. The preferred lubricant base is mineral oil.

The following examples are illustrative of the invention.

EXAMPLE 1

Preparation of titanium tetra[di(2-ethylhexyl) orthophosphate]



Two-thousand grams of di(2-ethylhexyl) hydrogen orthophosphate (6 moles) was placed in a reaction flask together with about 1 liter of dry toluene. The reaction flask was equipped with a mechanical stirrer, thermometer, gas inlet tube, reflux condenser and a pressure equalizing funnel with its long stem dipping into the solution. The temperature in the reaction flask was raised to about 120° C. while stirring vigorously and 330 grams (1.7 moles) of titanium tetrachloride dissolved in about 300 grams of toluene were added in spurts by means of the pressure equalizing delivery funnel to the orthophosphate. Hydrogen chloride was evolved copiously by the reaction. Stirring and heating under reflux to 130° C. was continued until evolution of hydrogen chlorides stopped. The solvent was removed by distillation at reduced pressure. The resulting solvent free crude product of titanium tetra[di(ethylhexyl) orthophosphate] was washed with water, taken up in half its volume of normal pentane, and then dried over anhydrous sodium sulphate. After filtering, the pentane was removed by distillation with the final temperature being 130° C. and 20 millimeters pressure. The yield of dark amber colored product was 1,900 grams or 95% of theory based on orthophosphate. The product has a viscosity at 100° F. of 1337 SUS and at 210° F. a viscosity of 180 SUS. The density of the product at 20° C. was 1.055. The titanium content of the compound was 3.59% and phosphorous content was 9.29%.

EXAMPLE 2

Following the procedure of Example 1, but by substituting equal molecular quantities of di(4-octylphenyl) hydrogen orthophosphate for the di(2-ethylhexyl) hydrogen orthophosphate there was produced titanium tetra[di(4-octylphenyl) orthophosphate]. Similarly there can be substituted equal molar quantities of zirconium tetrachloride or hafnium tetrachloride to prepare the corresponding zirconium or hafnium derivatives of the organic hydrogen orthophosphates.

EXAMPLE 3

A suitable lubricating oil composition is prepared by dissolving one part, by weight, of titanium tetra[di(2-ethylhexyl) orthophosphate] into 99 parts by weight of 100 neutral mineral oil.

EXAMPLE 4

A suitable grease composition is prepared by intimately admixing 10 parts of lithium 12-hydroxystearate and 1 part of titanium tetra[di(2-ethylhexyl) orthophosphate] dissolved in 89 parts of 300 SUS at 100° F., of mineral oil. All "parts" given herein are on a weight basis.

All percentage values given herein are on a weight basis unless otherwise indicated.

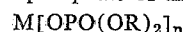
What is claimed is:

1. A lubricating composition comprising a major quantity of a lubricant base and minor quantity sufficient to inhibit squawk of a metal [di(hydrocarbyl) orthophosphate] wherein the metal is a Group IVB metal of the periodic table and each hydrocarbyl group contains from about 2 to about 30 carbon atoms.

2. A lubricating composition comprising a major quantity of a hydrocarbon lubricating oil and a minor quantity sufficient to inhibit squawk of a metal [di(hydrocarbyl) orthophosphate] wherein the metal is a Group IVB metal of the periodic table and each hydrocarbyl group contains from about 2 to about 30 carbon atoms.

3. A composition of claim 2 where the metal has a valence of 4 and each hydrocarbyl group is branched chain alkyl of from about 6 to about 20 carbon atoms.

4. A lubricating composition comprising a major quantity of a hydrocarbon lubricating oil and from about 0.1% to about 5.0% by weight of the hydrocarbon lubricating oil of an orthophosphate of the formula



dissolved in said oil wherein M is a Group IVB metal of the periodic table, R is a hydrocarbon group of from 2 to about 30 carbon atoms and n is equal to the valence of the metal M.

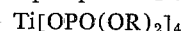
5. A composition of claim 4 wherein n is 4 and each R has from about 6 to about 20 carbon atoms.

6. The composition of claim 5 wherein each R is branched chain alkyl.

7. A composition of claim 5 wherein each R is phen-alkyl.

8. A composition of claim 4 wherein each R is alk-phenyl.

9. A lubricating composition comprising a major quantity of a hydrocarbon lubricating oil and from about 0.1% to about 5.0% by weight of the hydrocarbon lubricating oil of an orthophosphate of the formula



dissolved in said oil, wherein each R is hydrocarbyl having from about 6 to about 20 carbon atoms.

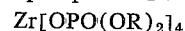
10. A composition of claim 9 wherein R is branched chain alkyl and the quantity of the orthophosphate is from about 0.5% to about 3%, based on the weight of the hydrocarbon lubricating oil.

11. A composition of claim 9 wherein R is alkphenyl and the quantity of orthophosphate is from about 0.5% to about 3%, based on the weight of the hydrocarbon lubricating oil.

12. A composition of claim 9 wherein each R is 2-ethylhexyl.

13. A composition of claim 9 wherein each R is 4-octylphenyl.

14. A lubricating composition comprising a major quantity of a hydrocarbon lubricating oil and from about 0.1% to about 5.0% by weight of the hydrocarbon lubricating oil of an orthophosphate of the formula



dissolved in said oil, wherein each R is a hydrocarbon group having from about 6 to about 20 carbon atoms.

15. A composition of claim 14 wherein each R is branched chain alkyl and the quantity of orthophosphate is from about 0.5% to about 3%, based on the weight of the hydrocarbon lubricating oil.

16. A composition of claim 15 wherein each R is 2-ethylhexyl.

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DANIEL E. WYMAN, *Primary Examiner.*

75 P. P. GARVIN, *Assistant Examiner.*