United States Patent Office 3,702,824 Patented Nov. 14, 1972

3,702,824

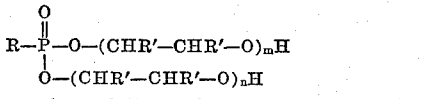
FRICTION REDUCING AGENT FOR LUBRICANTS

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No Drawing. Filed June 12, 1970, Ser. No. 45,931
Int. Cl. C10m 1/46
U.S. Cl. 252—49.8 7 Claims

ABSTRACT OF THE DISCLOSURE

Hydroxyalkyl esters of alkanephosphonates represented by the formula:



in which R is a substantially straight chain alkyl radical having from about 11 to 40 carbon atoms, R' is hydrogen or an alkyl radical having from 1 to 20 carbon atoms, *m* is an integer from 1 to 10 and *n* is 0 or an integer from 1 to 10, and a lubricating oil composition containing a hydroxyalkyl ester of alkanephosphonate.

BACKGROUND OF THE INVENTION

Field of the invention

The demands for improved performance of lubricating oil compositions spurs a constant search for new additives and lubricating oil formulations to achieve the desired goals. For example, an automatic transmission is a complex hydraulic mechanism which incorporates the functions of a torque converter, wet clutches and planetary gearing in a relatively compact sealed unit. This device requires a transmisison fluid which provides lubricity, extreme pressure properties and carefully selected frictional properties. The fluid must not be corrosive to copper alloys or in any way deleterious to the synthetic seals in the transmission. An important requirement for the fluid is that it maintain good lubricity and friction modifying properties under the prolonged high-shear, high temperature conditions encountered in this environment.

Carboxylic acids or their derivatives are widely employed as lubricity agents or friction modifiers in automatic transmission fluids. These lubricity agents provide commercial lubricants having a useful service life. The lubricants, however, are definitely limited in their stability which directly reduces their useful life. This is indicated by a rising coefficient friction in the fluid and by the early onset of erratic or harsh shifting in service and in automatic transmission tests. Automobile manufacturers and lubricating oil formulators have been particularly interested in trying to overcome the unsatisfactory properties of current automatic transmission fluids.

Description of the prior art

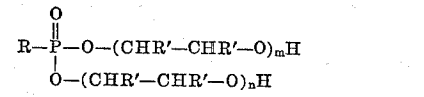
U.S. patent application, S.N. 778,335 filed on Nov. 22, 1968 now abandoned, discloses a lubricating oil composition containing an alkanephosphonic acid as a friction modifying agent.

U.S. patent application, S.N. 812,410 filed on Apr. 1, 1970, discloses a lubricating oil composition containing a zinc, calcium or alkyl-ammonium acid salt of alkanephosphonic acid as a friction modifying agent.

SUMMARY OF THE INVENTION

A novel class of hydroxyalkyl esters of alkanephosphonates has been discovered together with a mineral lubricating oil composition which exhibits a variety of valuable properties.

The hydroxyalkyl esters of alkanephosphonates are represented by the formula:



in which R is a substantially straight chain alkyl radical having from about 11 to 40 carbon atoms, R' is hydrogen or an alkyl radical having from 1 to 20 carbon atoms, *m* is an integer from 1 to 10 and *n* is 0 or an integer from 1 to 10.

A preferred hydroxyalkyl ester of alkanephosphonate is one conforming to the above formula in which R is a predominantly straight chain aliphatic radical, i.e. one in which at least 75 percent and preferably 80 percent or more of the aliphatic carbon atoms are in a single straight chain and R' is hydrogen or an alkyl radical having from 1 to 20 carbon atoms. A completely straight chain aliphatic radical for R is suitable. Particularly preferred are those compounds in which R is a straight chain alkyl radical having from 12 to 18 carbon atoms and R' is hydrogen.

Examples of suitable hydroxyalkyl esters of alkanephosphonate additives of this invention include:

hydroxyethyl n-tetradecanephosphonate,
bis-hydroxyethyl n-tetradecanephosphonate,
hydroxyethyl n-dodecanephosphonate,
hydroxyethyl n-octadecanephosphonate,
bis-hydroxyethyl n-octadecanephosphonate,
hydroxypropyl-n-octadecanephosphonate,
bis-hydroxypropyl-n-tetradecanephosphonate,
hydroxyethyl-hydroxypropyl-n-tetradecanephosphonate,
bis-(1-hydroxymethyl-propyl)-n-tetradecanephosphonate,
bis-(2-hydroxybutyl)-n-tetradecanephosphonate,
bis-(1-methyl-2-hydroxypropyl)-n-dodecanephosphonate,
bis-(2-hydroxy-pentyl)-n-dodecanephosphonate.

The following examples illustrate the method for preparing hydroxyalkyl esters of alkanephosphonates.

EXAMPLE I

Bis-hydroxyethyl-n-tetradecanephosphonate

50 grams (approximately 0.18 mole) of n-tetradecanephosphonic acid was placed in a reaction vessel fitted with a stirrer, temperature controller, gas inlet tube, and "Dry Ice"-cooled condenser. The flask was heated to a temperature in the range of about 110 to 120° C., liquefying the acid. Then ethylene oxide gas was bubbled over about 1½ hours into the mixture until adsorption ceased as evidenced by the sudden appearance of refluxing ethylene oxide. The reaction mixture was maintained under these conditions with a slow nitrogen stream passing through the mixture in the place of the ethylene oxide. After 1 hour, surplus ethylene oxide had been removed by nitrogen entrainment. The liquid product was recovered without further treatment.

Analysis of the product was as follows:

	Found	Calc.
Percent phosphorus	7.1	7.5
OH number	164	174
Total acid number	1.4	0

EXAMPLE II

Bis-hydroxypropyl-n-tetradecanephosphonate

79 grams (1.40 mole) of propylene oxide was added dropwise over about ½ hour to 210 grams (0.665 mole) of n-tetradecanephosphonic acid, the latter having been preheated to 120° C. The mixture was maintained at a temperature in the range from about 120 to 130° C. for

1 hour. On completion of the reaction, the bis-hydroxypropyl n-C_{14} alkanephosphonate was analyzed as follows:

	Found	Calc.
Percent phosphorus	7.3	7.2
Hydroxy number	219	260

EXAMPLE III

Mono/bis-hydroxyethyl n-octadecanephosphonate

75 grams (0.19 mole basis 7.8% phosphorus) n-octadecanephosphonic acid in a stirred reactor was dissolved in 200 ml. toluene, and 1 gram (.025 mole) sodium hydroxide in 5 ml. water was added. The mixture was heated to reflux at about 120° C., removing azeotroped water by use of a Dean-Stark trap. The substantially water-free solution was cooled to 100° C. and 22 grams (0.25 mole) ethylene carbonate was added. After refluxing the mixture 3 hours at about 118° C., the temperature was raised to 190° C. with removal of a major part of the toluene along with a separating distillate phase (presumably by-product ethylene glycol). After 6 hours total reflux at 190° C., 3.5 grams (0.04 mole) additional ethylene carbonate was added (an amount approximately equal to the glycol removed). After another 2 hours at 187–195° C., an IR spectrum of the solution indicated complete elimination of the carbonate material. The mixture was diluted with benzene, cooled to room temperature, and filtered free of sodium carbonate and other insolubles. The filtrate was distilled to 105° C./15 mm. to remove solvents and by-products. The 86 grams of product corresponds to 0.25 mole ethylene carbonate reacting.

Analysis of the product was as follows:

	Found	Calc. for 0.25 mole ethylene carbonate
Percent phosphorus	6.9	6.9
OH number	[1] 100	163
Total acid number	[1] 32.5	85

[1] These low values probably reflect the presence of the cyclic ester to be expected to form at high temperatures.

An important feature of this invention is the discovery of a mineral lubricating oil composition which exhibits friction modifying properties making the lubricant particularly suitable for use in automatic transmission service. The lubricating oil composition comprises at least 86 weight percent of a mineral lubricating oil and from about 0.01 to 5.0 weight percent of a hydroxyalkyl ester of an n-alkanephosphonate.

The automatic transmission fluid of the invention will generally be a fully formulated fluid containing minor amounts of conventional additives. For example, the automatic transmission fluid can contain from about 0.5 to 3.0 weight percent of a polymer of mixed alkyl esters of methacrylic acid having above 25,000 molecular weight, 0.25 to 5.0 weight percent of a reaction product of a polyalkylene polyamine and an alkenyl succinic acid, 0.1 to 5 weight percent of a zinc dialkylphenoxyalkyl dithiophosphate and from about 0.1 to 2.5 weight percent of an aryl-substituted alpha naphthylamine. The automatic transmission fluid of the invention is generally characterized by an SUS viscosity at 210° F. of 49 to 60, a viscosity index of at least 150 and a pour point below —40° F. and meets the essential Dexron specifications set by General Motors for automatic transmission fluids.

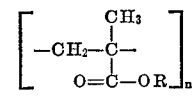
The mineral lubricating oil which constitutes at least 86 weight percent of the composition of the invention is a refined oil or a mixture of refined oils selected according to the viscosity requirements of the particular service. For automatic transmissions where the requirements include an SUS viscosity of the compounded oil at 210° F. of 49 minimum up to 60 and at 0° F. of 7,000 maximum (extrapolated), the base oil or the major component thereof is generally a distillate oil lighter than SAE–10 grade motor oil, such as one having an SUS viscosity at 100° F. less than 150 and generally between about 50 and 125. The distillate fraction can be a refined paraffinic distillate, a refined naphthenic distillate or a combination thereof. The flash point of the distillate component of the base oil will generally be substantially above 300° F.; if the distillate fraction constitutes the entire base oil, its flash point will usually be above 375° F.

A particularly preferred base oil comprises approximately 70 to 95 percent of a refined distillate oil and 5 to 30% of a refined residual fraction which imparts desired high flash point and lubricity to the base oil. A particularly preferred residual fraction comprises a paraffin base residuum which has been propane deasphalted and subjected to centrifuge dewaxing and which has an SUS at 210° F. below about 250. An effective base oil mixture comprises 68 percent of a furfural refined, acid treated, clay contacted, solvent-dewaxed, paraffin base distillate having an SUS at 100° F. of 100, a viscosity index about 100, a flash above 385° F. and a pour below about +10° F., 22% of an acid-treated naphthenic base distillate having an SUS at 100° F. of 60, a flash above 300° F., and a pour below —40° F., and 10% of a paraffin base residuum which has been propane deasphalted, centrifuged-dewaxed, and clay-contacted, and has an SUS viscosity at 210° F. of about 160, a flash above 530° F. and a pour of +5° F.

A surprising feature of the mineral lubricating oil composition of the invention is that it exhibits a marked reduction in friction between transmission clutch plates as the sliding speed approaches zero, a highly desirable feature for an automatic transmission fluid not possessed by lubricating oils containing carboxylic acids.

A relatively minor amount of a hydroxyalkyl ester of n-alkanephosphonate in a suitable lubricating oil is effective to provide an outstanding lubricating oil composition or an automatic transmission fluid. Generally, the ester is employed in the transmission fluid in an amount ranging from about 0.01 to 5.0 percent by weight with the preferred concentration of the ester being from 0.05 to 0.5 weight percent.

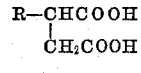
Viscosity index improvement of the fully formulated automatic transmission fluid of the invention is effected with a methacrylate ester polymer having the formula:



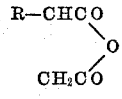
wherein R is an alkyl group, a dialkyl aminoalkyl group or a mixture of such groups containing from 1 to 20 carbon atoms and *n* is a member providing a molecular weight of the polymer in the range from 25,000 to 1,250,000 and preferably from 35,000 to 200,000. Various methacrylate ester polymers of this type are known which possess pour depressant and viscosity index improving properties. A very effective material of this type is a copolymer of the lower C_4–C_{14} alkyl methacrylate esters. A commercial methacrylate copolymer of this type which is primarily a viscosity index improver corresponds to the formula in which R represents about 32 percent lauryl, 28 percent butyl, 26 percent stearyl and 14 percent hexyl groups and having a molecular weight above 50,000. The methacrylate ester copolymer is employed in the base oil in a proportion ranging from about 0.5 to 10 percent by weight preferably from 1.0 to 5.0 weight percent based upon the oil composition in order to impart the desired viscosity, viscosity index and pour point. It is understood that other methacrylate ester polymers of the foregoing type can be employed.

A dispersant is generally present in the automatic transmission fluid. An effective dispersant comprises a composition resulting from mixing a substituted succinic com-

pound, selected from the class consisting of substituted succinic acids having the formula:



and substituted succinic anhydrides having the formula:

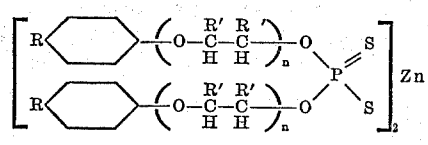


in which R is a large substantially aliphatic hydrocarbon radical having from about 50 to 200 carbon atoms with at least about one-half of a molar equivalent amount of a polyethylene polyamine and, in the case of the acid, heating the resultant mixture to effect acylation and remove the water formed thereby. The anhydride, however, may react without external heating and hence may be heated only if further reactions of the intermediate amic acid are desired. Suitable amines are diethylene triamine, triethylene tetramine, tetraethylene pentamine and amino-alkylated heterocyclic compounds. The reaction involves amidation of a dicarboxylic acid or anhydride thereof with a polymer to produce amino-substituted acyclic diamides, amic acids, polymeric amides, or a combination of these types of products. It will be noted that the amide groups may further react to form imide groups in the process.

Equivalents here means that a minimum of one-half mole of alkenylsuccinic anhydride or acid per mole of amine is required. This would be the least amount of acid which could react with all of the amine added (via amic acid or acyclic polyamide formation). The maximum amount of acid or anhydride possible to react is one-half mole per primary or secondary amino group. Generally, one or two moles of acid or anhydride per mole of amine, regardless of the total number of nitrogen atoms, is preferred. The reaction product is effective in amounts ranging from about 0.25 to 5.0 weight percent. Methods for preparing the polyethylene polyamine reaction products are well known and have been described in U.S. 3,131,-150 and 3,172,892.

An amine anti-oxidant is important in this fully formulated transmission fluid. Effective anti-oxidants are the aryl-substituted amine anti-oxidants exemplified by the phenyl naphthyl amines, phenylene diamine, phenothiazine and diphenylamine. A particularly preferred anti-oxidant is phenyl alpha naphthylamine. The antioxidants are effective in a concentration ranging from about 0.1 to 2.5 weight percent.

A zinc di(alkylphenoxypolyalkoxyalkyl) dithiophosphate is a valuable component of a fully formulated automatic transmission fluid. This compound is represented by the formula:



in which R represents an aliphatic radical having from 6 to 15 carbon atoms, R' is hydrogen or an alkyl radical having from 1 to 4 carbon atoms and *n* is an integer from 1 to 10. Particularly effective compounds in this class are the zinc di(nonylphenoxyethyl) dithiophosphate, zinc di (dodecylphenoxy-ethyl) dithiophosphate and zinc di (nonylphenoxy - ethoxyethyl) dithiophosphate. Zinc di (nonylphenoxyethyl) dithiophosphate is prepared by reacting a nonylphenolethylene oxide compound with phosphorus pentasulfide followed by neutralization of the acid formed with a basic zinc compound, such as zinc carbonate, zinc oxide or zinc hydroxide. The general preparation of the compounds in this class is disclosed in U.S. 2,344,-395 and 3,293,181. In use, it is convenient to prepare a mineral oil solution of the zinc di(C_{6-15} alkylphenoxy-polyalkoxyalkyl) dithiophosphate containing from 50 to 75 weight percent of the zinc salt. The salts are effective oxidation and corrosion inhibitors for automatic transmission fluids when employed in a concentration ranging from about 0.1 to 5.0 weight percent based on the hydraulic fluid.

Anti-foam agents are conventionally employed in hydraulic fluids because the fluids are rapidly circulated in operation and air can be entrapped. For this purpose, a silicone fluid of high viscosity, such as a dimethyl silicone polymer having a kinematic viscosity of 25° C. of about 1000 centistokes and above is preferably employed. A very satisfactory anti-foam agent for this purpose is prepared by diluting 10 grams of a dimethyl silicone polymer (1000 centistokes at 25° C.) with kerosene to provide a solution of 100 cubic centimeters. From 0.005 to 0.025 percent by weight of this concentrate is generally employed in the hydraulic fluid to provide from 50 to 200 parts per million of the silicone polymer based on the hydraulic fluid composition.

A fully formulated lubricating oil composition for automatic transmission service can be prepared from a base oil blend comprising 65 percent of a furfural-refined, acid-treated, clay-contacted, solvent-dewaxed, paraffin base distillate having an SUS at 100° F. of 100; a viscosity index about 100, a flash above 385° F. and a pour below +10° F., 22 percent of an acid-treated naphthenic base distillate having an SUS at 100° F. of 60, a flash above 300° F. and a pour below —40° F. and 13 percent of a paraffin base residuum which has been propane-deasphalted, solvent-dewaxed and clay-contacted and which had an SUS viscosity at 210° F. of 160, a flash of about 540° F. and a pour below 5° F. This base oil mixture had a flash above 375° F., a pour below 0° F. and a viscosity index of about 93.

A fully formulated automatic transmission fluid will comprise a base oil blend such as the foregoing and will contain from about 0.5 to 8 weight percent of an oil concentrate containing about 35% of a basic amino nitrogen-containing addition type copolymer comprising copolymers of butyl, lauryl, stearyl and dimethyl aminoethyl methacrylates in approximately 21:53:22:4 weight ratios (as described in U.S. 2,737,496); about 0.25 to 5.0 weight percent of an oil concentrate containing about 33% of the reaction product of approximately 1:1 mole ratio of tetraethylene pentamine and alkenyl succinic anhydride in which the alkenyl radical is polybutene of approximately 1200 average molecular weight (U.S. 3,172,-892); about 0.1 to 2.5 weight percent of phenyl alpha naphthylamine, about 0.1 to 5 weight percent of an oil concentrate containing about 50% of zinc di(nonylphenoxyethyl) dithiophosphate and from about 0.01 to 5 weight percent of the hydroxyalkyl n-alkanephosphonate of the invention.

The frictional effects of various hydroxyalkyl n-alkanephosphonate additive of the invention on a mineral lubricating oil was determined in a Low Velocity Friction Test. This test was conducted using a General Motors type friction surface, namely a test plate identical in composition to Borg Warner's SD–715 clutch plates, in sliding contact with steel. The coefficients of friction were determined at decreasing sliding speeds, i.e. from about 40 ft./min. down to about 1 ft./min. The test temperature was 250° F. and the applied load was 120 p.s.i.

The frictional effects of various hydroxyalkyl n-alkanephosphonates was determined in the Low Velocity Friction Test. The base oils employed were paraffin base mineral oils that had been solvent refined and solvent dewaxed. Base Oil A had an SUS viscosity at 100° F. of about 100 and Base Oil B had an SUS viscosity at 100° F. of about 340. The coefficients of friction for the various

blends at different sliding velocities are set forth in the table below:

TABLE I

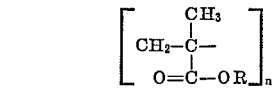
Run	Base oil plus wt. percent of hydroxyalkyl n-alkanephosphonate	Coefficient of friction sliding velocity, ft./min.	
		40 ft./min.	1.0 ft./min.[1]
1	Base Oil A	0.130	0.204
2	Base Oil A plus 0.2 wt. percent of bis-hydroxyethyl n-tetradecanephosphonate.	0.111	0.070
3	Base Oil A plus 0.16 wt. percent of dimethylester of n-tetradecanephosphonate.	0.130	0.197
4	Base Oil B	0.085	0.140
5	Base Oil B plus 0.275 wt. percent of bis-hydroxypropyl n-tetradecanephosphonate.	0.113	0.069
6	Base Oil B plus 0.275 wt. percent of bis-hydroxyethyl n-tetradecanephosphonate.	0.091	0.073

[1] Approximately.

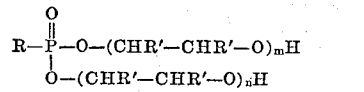
Runs 2, 5 and 6 show that the coefficient of friction of these blends was sharply reduced as the sliding velocity approached 1.0, a particularly valuable property for smooth shifting in automatic transmissions. In contrast, the coefficient friction of Base Oils A and B alone as well as Run 3 with dimethyl n-tetradecanephosphonate increased greatly as the sliding velocity decreased showing that these oils and fluid are unsatisfactory.

I claim:

1. A lubricating oil composition having an SUS viscosity at 210° F. of 49 minimum up to 60 effective for reducing the coefficient of friction between transmission clutch plates as the sliding speed approaches zero comprising at least 86 weight percent of a mineral lubricating oil, from about 0.5 to 10 weight percent of a methacrylate ester polymer having the formula:



wherein R is an alkyl group, a dialkyl aminoalkyl group or a mixture of such groups containing from 1 to 20 carbon atoms, n is a member providing a molecular weight of the polymer in the range from 25,000 to 1,250,000, from about 0.25 to 5.0 weight percent of a dispersant and from about 0.01 to 5.0 weight percent of a hydroxyalkyl alkanephosphonate represented by the formula:



in which R is a straight chain alkyl radical having from about 11 to 40 carbon atoms, R′ is hydrogen or an alkyl radical having from 1 to 20 carbon atoms, m is an integer from 1 to 10 and n is 0 or an integer from 1 to 10.

2. A composition according to claim 1 in which R is an alkyl radical having from 12 to 18 carbon atoms.

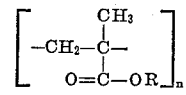
3. A composition according to claim 1 in which R′ is hydrogen or an alkyl radical having from 1 to 2 carbon atoms.

4. A composition according to claim 1 in which n is 0.

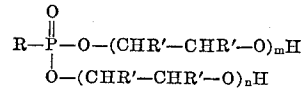
5. A composition according to claim 1 in which said hydroxyalkyl alkanephosphonate is bis-hydroxyethyl n-tetradecanephosphonate.

6. A composition according to claim 1 in which said hydroxyalkyl alkanephosphonate is bis-hydroxypropyl n-tetradecanephosphonate.

7. A method for operating an automatic transmission mechanism having friction means which comprises supplying to and driving said automatic transmission with a lubricating oil composition having an SUS viscosity at 210° F. of 49 minimum up to 60 effective for reducing the coefficient of friction between transmission clutch plates as the sliding speed approaches zero comprising at least 86 weight percent of a mineral lubricating oil, from about 0.5 to 10 weight percent of a methacrylate ester polymer having the formula:



wherein R is an alkyl group, a dialkyl aminoalkyl group or a mixture of such groups containing from 1 to 20 carbon atoms and n is a member providing a molecular weight of the polymer in the range from 25,000 to 1,250,000, from about 0.25 to 5.0 weight percent of a dispersant and from about 0.01 to 5.0 weight percent of a hydroxyalkyl alkanephosphonate represented by the formula:



in which R is a straight chain alkyl radical having from about 11 to 40 carbon atoms, R′ is hydrogen or an alkyl radical having from 1 to 20 carbon atoms, m is an integer from 1 to 10 and n is 0 or an integer from 1 to 10.

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U.S. Cl. X.R.

252—78; 260—953