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LUBRICATING OIL COMPOSITION

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This invention relates to a new class of compounds which are useful as dispersants in hydrocarbon oils. More particularly, this invention relates to compounds of the polyester type formed by reacting a dibasic acid with an alkyl substituted diethanolamine, said polyesters finding particular utility as low temperature dispersants in mineral oils of lubricating viscosity.

The use of metallic detergents in internal combustion engine lubricating oil compositions is well known, particular utility for these detergents being found in lubricating oil compositions which are subjected to heavy duty service resulting in the oxidation of the oil with the resultant formation of sludges and varnishes. Although the metallic detergents such as metallic petroleum sulfonates have been very useful in maintaining these sludge and varnish formations suspended in the oil they have the disadvantage of being themselves subject to breakdown and deterioration resulting in the formation of a metallic ash which accumulates in the combustion chamber. Nor have these metallic detergents proven effective in dispersing the "blow-by" contamination of the lubricating oil when the engine is operated in light service and at low operating temperatures. When the engine is cold the cylinder walls act as a condenser for the fuel vapors and combustion products in the cylinder. These contaminants wash past or "blow-by" the piston rings into the crank case wherein they tend to emulsify and coagulate causing insoluble sludge deposits which the usual metallic detergents are unable to redisperse. To overcome these blow-by contaminants and to disperse the sludge deposits in the crank case, attempts have been made to provide ashless dispersants which will prove effective at the low operating temperatures found in light service internal combustion engines.

In accordance with the present invention, the dispersion of the low temperature sludge deposits can be attained by providing in the mineral lubricating oil base a small but effective amount of the liquid reaction product obtained by reacting approximately equal molar portions of a dibasic acid or an anhydride or ester thereof with an alkyl diethanolamine. The nitrogen-containing polyester thus formed can be added to the lubricating oil base in an amount sufficient to achieve the desired sludge dispersant properties. Generally, the polyester should be added to the base oil in amounts to give about 0.1 to 5 percent or more by weight on the base oil, and preferably, the polyester should be about .75 to 1.5 percent by weight of the base lubricating oil.

The dibasic acids which can be utilized in forming the polyesters of the present invention conform to the following general structural formula:

$$HOOC—R—COOH$$

wherein R is a divalent, non-aromatic hydrocarbon radical straight or branched, saturated or unsaturated, containing 12 to 38 carbon atoms. By the term "non-aromatic" in nature, I mean to include not only aliphatic hydrocarbon acids but also those acids which are nor-

mally monobasic in nature but have been converted to dibasic acids by the cyclization of their hydrocarbon group as well as cyclic naphthenic dibasic acids. Examples of suitable acids are dodecenylsuccinic, octadecylsuccinic, dimerized unsaturated fatty acids, such as linoleic, ricinoleic, etc. For the purposes of forming the superior low temperature dispersant, however, it is preferred that the dibasic acid be a branched one such as dimerized linoleic acid or dodecenylsuccinic acid. Not only are the dibasic acids useful but also their anhydrides and esters can be employed.

The alkyl substituted diethanolamines useful in preparing the polyesters of the present invention are those in which the alkyl substituent (R') contains from about 4 to 20 carbon atoms. Preferably the alkyl group is straight chained. Examples of useful alkyl diethanolamines can be enumerated as follows: butyldiethanolamine, octyldiethanolamine, dodecyldiethanolamine, octadecyldiethanolamine, etc.

The polyesters of this invention can be prepared by either of two general methods, i.e. they can be prepared by direct esterification of the dibasic acid or anhydride with the diethanolamine or a dibasic acid ester can be prepared by any of the recognized procedures and the desired polyester prepared by ester interchange between the acid ester and the diethanolamine. The preparations of polyesters found particularly advantageous for use as low temperature dispersants in mineral lubricating oils by each of these two methods are illustrated in the following examples which are not to be considered as limiting. In the example, the reaction providing the detergent additive was continued until the acid number was close to zero, e.g. less than about 1, which is the preferred procedure.

EXAMPLE I

Preparation of polyester by direct esterification.—A mixture of 79.8 grams of dodecenylsuccinic anhydride (0.30 mole) and 91.5 grams of dodecyldiethanolamine (0.30 mole) was placed in a 300 ml. 4-necked flask equipped with a Claisen head, condenser, thermometer and gas inlet tube through which nitrogen was bubbled during the reaction period. Approximately 0.2 gram of zinc stearate was added to the flask as a catalyst. The flask was heated under atmospheric pressure for about three hours at about 200–210° C. whereupon 4 mls. of water was collected. The reaction mixture was subsequently heated to 200° C. in vacuum under about 6–10 mm. of pressure for an additional 21 hours. The resultant product was a straw-colored, viscous polymer having the following properties:

Acid No. pH 11	.85
Base No. pH 4	68.00
Nitrogen ____percent__	2.63 (theory 2.6)

A similar polyester is obtained by replacing the dodecyldiethanol with octadecyldiethanol or butyldiethanol in an equal molar amount and the products have acid numbers of less than 1.

EXAMPLE II

Preparation of a polyester by ester interchange.—A mixture of 336 grams of the butyl ester of dimerized linoleic acid (about 2 double bonds per molecule) and 80.5 grams of butyldiethanolamine was placed in a 500 ml. 4-necked flask equipped as described in Example I. 4.16 grams of tetraisopropyl titanate (an ester interchange catalyst) was added to the flask. The mixture was heated under atmospheric pressure in a stream of nitrogen at about 200° C. until 65 grams of butyl alcohol was collected. The reaction product was subsequently heated in vacuum for 16 hours at 200° C. The resultant product was a very viscous, amber-colored polymer showing the following properties:

Acid no	0.0
Nitrogen (basic) percent	2.02

It is believed that the above reactions yield polyesters conforming to the following general formula:

$$HO\left(\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O-CH_2CH_2-\underset{}{\overset{R_1}{\overset{|}{N}}}-CH_2CH_2O\right)_yH$$

wherein R is as described above, R′ is the alkyl group of the diethanolamine described above and y is an integer or 1 up to the limit of compatibility of the polyester with the mineral lubricating oil, and preferably, y should be about 5 to 100. Compatibility is used to mean soluble, miscible or otherwise dispersible in the mineral oil without continued agitation and in the amounts required to impart the desired properties to the base oil. Also, in the polyesters R and R′ should have a total number of carbon atoms of about 22 to 44, preferably more than 30.

The following reactants were polymerized in accordance with the procedures outlined above to obtain polyesters.

Table I

Polyester Number	Preparation Example	Dibasic Acid	Alkyl Diethanolamine
1	I	Dodecenylsuccinic anhydride	Dodecyl.
2	I	do	Octadecyl.
3	I	do	Butyl.
4	II	Butyl ester of dimerized linoleic acid.	Do.
5		Sebacic Acid	Octadecyl.

The polyesters thus prepared were blended in a solvent-treated Mid-Continent neutral mineral oil having a viscosity of 160 SUS at 100° C. The dispersing ability of the oil-soluble polyesters was studied by diluting 50 mls. of the above mineral oil with 50 mls. of kerosene and adding to the blend about 1.0 percent by weight of the additive to be tested. To this blend was added 0.5 grams of carbon black (Benny & Smith carbon black, 24 micron size, pH 3.2). The resultant mixture was homogenized three times through a manually operated homogenizer. The mixture was then heated to about 150° C. and cooled to room temperature. One sample contained no additive and another sample contained 1.0 percent by weight of Du Pont LOA 564, a recognized ashless detergent. The ratings for the carbon black suspension test were made visually with the aid of an optical microscope. The suspension tests were conducted on both dry and wet carbon dispersions. For the wet carbon test, 1 percent by weight water was added by homogenization to the mixture. A summary of these tests is presented in Table II following. The additive numbers correspond to those of Table I.

As can be seen from an examination of this table, the better dispersants are formed from the compounds wherein the total carbon atoms in R+R′ is from 22 to 44 and R has at least 12 carbon atoms. For example, the additive prepared from sebacic acid and octadecyldiethanolamine was not as effective in dispersing and suspending the carbon black as additives 1, 2 and 4 of this invention. Similarly, additive 3 showed significantly poorer characteristics.

Additives Nos. 2 and 4 were further screened as detergents by conducting suspension tests on the sludge deposits which were collected from the oil pan of a Chevrolet engine which had been run under FL–2 conditions. The lubricating oil composition comprised a solvent-treated Mid-Continent neutral lubricating oil having a viscosity of 160 SUS at 100° F. and about 0.7 percent zinc dithiophosphate anti-oxidant. The deposits thus collected were washed several times with pentane by decantation and dried on a suction filter. The thus dried sludge was ground to a fine powder. A 10 percent benzene dispersion of the deposits was prepared by blending 50 gms. of the ground deposit in 50 gms. of benzene and homogenized several times. The sludge suspension tests were carried out by dissolving 1.0 percent by weight of the additives to be tested in 5 mls. of solvent-treated Mid-Continent neutral lubricating oil having a viscosity of 160 SUS at 100° F. and 5 mls. of kerosene. Two mls. of the above-formed sludge dispersion was then placed in the mixture. After boiling off the benzene, the samples were placed in test tubes and permitted to stand several weeks at room temperature. One of the thus prepared samples contained no additive and another contained Du Pont LOA 564 as a standard of comparison. The amount of agglomerated material was estimated visually with the assistance of an optical microscope and by an inspection of the settling rates.

In the test sample wherein no additive was used the sludge agglomerated and settled to the bottom almost immediately in the form of a hard cake which was impossible to redisperse by shaking the test tube. The polyesters Nos. 2 and 4 which were effective in the suspension of the carbon black were also found to be just as effective in suspending and dispersing the sludge deposits. Although the sludge settled to the bottom of the test tubes having these additives and Du Pont LOA 564, respectively, it could be readily redispersed by shaking the test tubes.

In order to evaluate the additives under actual operating condition several blends were and tested under FL–2 Chevrolet engine conditions. These blends were comprised of the following:

(*a*) Mid-Continent 95 VI neutral lubricating oil having a viscosity of 160 SUS at 100° F. plus about 0.7 percent zinc dithiophosphate.

(*b*) Composition (*a*) plus 1.0 percent additive No. 1.

(*c*) Composition (*a*) plus 1.5 percent additive No. 2.

Table II

Carbon Black Suspension Tests on Various Detergents

Detergent Additive No.	Results
None	Carbon black formed large agglomerates which settled out of oil-kerosene mixture almost immediately.
1% (active ingredient) du Pont LOA 564	Carbon black showed little tendency to agglomerate and remained suspended after several weeks. Presence of water did not promote excessive flocculation.
Additive No. 1	This additive appeared to be a good dispersant. The carbon black remained suspended for several weeks in either wet or dry state. Microscopic examination showed presence of more agglomerates than were present in test run with du Pont detergent LOA 564.
Additive No. 2	This additive was an excellent dispersant and appeared to disperse wet or dry carbon black equally as good as du Pont LOA 564.
Additive No. 3	This additive was a poor dispersant and maintained carbon black in suspension for only two days.
Additive No. 4	Tests showed this additive to be as good as du Pont LOA 564.
Additive No. 5	Both wet and dry carbon black dispersion containing this additive began to form agglomerates immediately. After one week no carbon black remained suspended.

(*d*) Composition (*a*) plus 1.2 percent additive similar to No. 4 except prepared from dimerized linoleic acid with about one double bond per molecule (Empol 3020R).

(*e*) An SAE 10W–30 oil containing basic barium mahogany sulfonate detergent, zinc dithiophosphate antioxidant, sulfurized sperm oil anti-wear agent, dimethyl silicone polymer anti-foaming agent, and Acryloid 763 (a 40 percent concentrate in mineral oil of methacrylate ester polymer in which ester groups are derived from a mixture of alcohols in the C_8 to C_{16} range).

(*f*) Composition (*d*) plus 1.2 percent additive No. 2.

A summary of the engine cleanliness ratings of the above blends is presented in Table III below.

Blend	Piston Skirt Average	Oil Control Ring	Oil Pan	Push Rod Chamber	Push Rod Cover	Timing Gear Cover	Rocker Arm Cover	Rocker Arms	Screen	Top Deck	Total Rating
(*a*)	4.4	9.5	3.0	6.0	6.0	6.0	6.0	9.5	10.0	6.0	66.4
(*b*)	3.3	8.6	7.0	7.0	8.0	7.0	9.0	9.5	9.0	9.0	77.4
(*c*)	4.4	9.3	3.0	7.0	7.0	6.0	9.0	9.5	9.0	8.0	72.2
(*d*)	4.3	9.1	5.0	7.0	7.0	6.0	9.0	9.0	9.0	9.0	74.4
(*e*)	3.6	9.5	8.0	7.0	7.0	8.0	8.0	9.5	10.0	8.0	78.6
(*f*)	4.8	9.8	8.0	9.0	8.0	8.0	9.0	9.5	10.0	9.0	85.1

The results of these tests indicate that the polyester additives which were effective in the carbon black and sludge suspension tests effectively promote engine cleanliness when the engine is operated under light service conditions. For example, comparing test (*a*) with (*b*), (*c*) and (*d*), it is seen that the additives promoted the overall engine cleanliness although it was also found that du Pont LOA 564 gave a better rating than additives Nos. 1 and 2. When a metallic detergent is present (test [*c*]), the addition of polyester No. 2 to the blend (test [*f*]) promoted the low temperature dispersing properties of the lubricating oil.

The lubricating oil base stock used as the major portion in the composition of this invention can be any mineral oil of lubricating viscosity. Frequently, the viscosity of such oils will be from about 50 SUS at 100° F. to 500 SUS at 100° F. If desired, the additives of this invention can be prepared in a small amount of the mineral oil base and stored as a concentrate which can later be blended in the desired portions with the final lubricating oil composition or the additive can be formed and added directly to the lubricating oil. In addition to the polyesters of the present invention other agents can be added to the final composition as desired, for example, pour depressors, VI improvers, other dispersants, anti-oxidants, foam preventers, anti-corrosive agents, etc. Not only do the polyesters of my invention improve the low temperature dispersant properties of mineral lubricating oils as pointed out above but they are also effective in improving the pour point of the base oil and in raising the viscosity index. Also, the polyester No. 2 of this invention acts as a stabilizer and sludge dispersant in petroleum fuel oils.

It is claimed:

1. A lubricating oil composition consisting essentially of a major portion of a mineral oil of lubricating viscosity and a polyester compatible with said mineral oil in an amount sufficient to impart sludge-dispersing properties to the lubricating oil composition, said polyester being characterized by the formula:

$$HO(\overset{\overset{O}{\|}}{C}-R-\overset{\overset{O}{\|}}{C}-O-CH_2CH_2-\overset{\overset{R_1}{|}}{N}-CH_2CH_2O)_yH$$

wherein R is a non-aromatic divalent hydrocarbon radical containing 12 to 38 carbon atoms, R′ is an alkyl radical containing 4 to 20 carbon atoms, R and R′ contain a total of 22 to 44 carbon atoms and y is from 1 to an integer providing the mineral lubricating oil-compatible polyester.

2. A lubricating oil composition consisting essentially of a major portion of a mineral oil of lubricating viscosity and a polyester compatible with said mineral oil in an amount of about 0.1 to 5.0 percent by weight, said polyester being characterized by the formula:

$$HO(\overset{\overset{O}{\|}}{C}-R-\overset{\overset{O}{\|}}{C}-O-CH_2CH_2-\overset{\overset{R_1}{|}}{N}-CH_2CH_2O)_yH$$

wherein R is a non-aromatic divalent hydrocarbon radical containing 12 to 38 carbon atoms, R′ is an alkyl radical containing 4 to 20 carbon atoms, R and R′ contain a total of 22 to 44 carbon atoms and y is from 1 to an integer providing the mineral lubricating oil-compatible polyester.

3. A lubricating oil composition consisting essentially of a major portion of a mineral oil of lubricating viscosity and a polyester compatible with said mineral oil in an amount of about 0.1 to 5.0 percent by weight, said polyester being characterized by the formula:

$$HO(\overset{\overset{O}{\|}}{C}-R-\overset{\overset{O}{\|}}{C}-O-CH_2CH_2-\overset{\overset{R_1}{|}}{N}-CH_2CH_2O)_yH$$

wherein R is the hydrocarbon portion of dodecylsuccinic acid, R′ is an octadecyl radical and y is from 1 to an integer providing the mineral lubricating oil-compatible polyester.

4. A lubricating oil composition consisting essentially of a major portion of a mineral oil of lubricating viscosity and a polyester compatible with mineral oil in an amount of about 0.1 to 5.0 percent by weight, said polyester being characterized by the formula:

$$HO(\overset{\overset{O}{\|}}{C}-R-\overset{\overset{O}{\|}}{C}-O-CH_2CH_2-\overset{\overset{R_1}{|}}{N}-CH_2CH_2O)_yH$$

wherein R is the hydrocarbon portion of dimerized linoleic acid, R′ is a butyl radical and y is from 1 to an integer providing the mineral lubricating oil-compatible polyester.

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