United States Patent Office

2,764,551

Patented Sept. 25, 1956

2,764,551

ASHLESS DETERGENT ADDITIVE FOR LUBRICATING OILS

Paul V. Smith, Jr., Westfield, Samuel B. Lippincott, Springfield, and Clifford W. Muessig, Breton Woods, N. J., assignors to Esso Research and Engineering Company, a corporation of Delaware

No Drawing. Application May 17, 1954, Serial No. 430,418

6 Claims. (Cl. 252—51.5)

This invention relates to a new class of compounds which are particularly suitable for use as detergent additives in lubricating oil compositions. More particularly the present invention relates to a new class of compounds of the complex ester type which are formed by reacting a dibasic acid with a glycol and an amino alcohol. The invention also relates to lubricating oil compositions containing such new compounds as detergent additives.

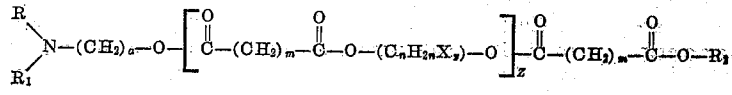
The art of metallic detergents for lubricating oil compositions adapted for use in internal combustion engines is well known to those versed in this field and has resulted in substantial improvements in lubricants. These detergents are particularly useful in lubricating oil compositions which are employed in internal combustion engines used in the operations of automobiles, aircraft, and similar vehicles, including diesel engines, to improve their operation by preventing or retarding corrosion, piston ring sticking, cylinder wear, and carbon and varnish formation. However, when metallic detergents are used in lubricating compositions where oil consumption is high and engine conditions are severe, such as in aircraft engines or where such concentrations of metallic detergents are used to maintain engine cleanliness under conditions where high deposit fuels of cracked or high sulfur nature are used such as in automobile and diesel operation, the ash content from the metallic detergent accumulates in the combustion chamber and is believed to cause pre-ignition, detonation, spark plug fouling, and valve burning.

Because these deficiencies of metallic detergents have been previously recognized, certain non-metallic or ashless detergents have been developed. However the performances of the ashless detergents of the prior art have not been entirely successful in regard to detergency. More specifically, the prior art ashless detergents have been inadequate in keeping deposit-forming materials suspended in the oil to thereby prevent coke, varnish, and other deposits from forming on critical engine parts. The present invention is designed to overcome this particular deficiency of the ashless detergents of the prior art. It is also an object of this invention to provide a detergent additive which is superior to the metallic detergents of the prior art in regard to detergency as well as to ash content.

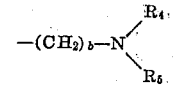
The new compounds of the present invention are of the complex ester type formed by reacting a dibasic acid with a glycol and an aliphatic monohydric alcohol as follows:

$$(\text{Monohydric Alcohol})-[(\text{Dibasic Acid})-(\text{Glycol})]_b-(\text{Dibasic Acid})-(\text{Monohydric Alcohol})$$

where b is an integer of value 1 to 5 and at least one of the two aliphatic monohydric alcohols is a tertiary amino alcohol. More particularly the new compounds of the present invention have the following general formula:



where R and R_1 are alkyl radicals each containing 1 to 10 carbon atoms; R_2 is a radical selected from the group consisting of (1) alkyl radicals containing 1 to 20 carbon atoms derived from primary alcohols, and (2) radicals of the formula



where b is an integer of value 2 to 4 and R_4 and R_5 are alkyl radicals containing 1 to 10 carbon atoms; X is a member selected from the group consisting of oxygen atoms and sulfur atoms; a is an integer of value 2 to 4; m is an integer of value 0 to 8; n is an integer of value 2 to 10; y is an integer of value 0 to 5; and Z is an integer of value 1 to 5. The molecular weight of the entire ester should be at least 300 and the various components of the ester should be selected so as to form an oil-soluble ester product.

The complex esters of this invention may be prepared by general esterification methods such as the method outlined in U. S. Patent 2,575,195, wherein the esters are prepared by a stepwise procedure. It will be understood however that the complex esters of this invention may also be prepared in a one-step procedure wherein the appropriate molecular proportions of all of the various reactants are esterified together in the same esterification reaction. The preparation of a particular complex ester of this invention utilizing this latter procedure will be set forth hereinafter in detail.

The dibasic acids which may be employed in the synthesis of the complex esters of the present invention have the general formula

$$HOOC(CH_2)_mCOOH$$

where m is an integer of value 0 to 8. These organic dibasic acids are the following:

Oxalic	Pimelic
Malonic	Suberic
Succinic	Azelaic
Glutaric	Sebacic
Adipic	

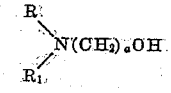
The glycols employed in preparing the esters of the present invention have the general formula

$$HO(C_nH_{2n}X_y)OH$$

where X represents an oxygen or sulfur atom, n is an integer of value 2 to 10 and y is an integer of value 0 to 5. Examples of these glycols are the following:

Diethylene glycol	1,3-propylene glycol
Triethylene glycol	1,2-propylene glycol
Tetraethylene glycol	1,4-butylene glycol
Pentaethylene glycol	1,3-butylene glycol
Dipropylene glycol	Hexamethylene glycol
Tripropylene glycol	Decamethylene glycol
Thiodiglycol	Neopentyl glycol
Ethylene	

The monohydric alcohols of this invention which contain a tertiary amino group have the general formula



where R and R_1 each represent alkyl radicals containing 1

to 10 carbon atoms and *a* is an integer of value 2 to 4. These alcohols are typified by the following:

Dimethylaminoethanol
Diethylaminoethanol
Dipropylaminoethanol
Dibutylaminoethanol
di-(2-ethylbutyl)aminoethanol
Di-n-hexylaminoethanol
Di-(2-ethylhexyl)aminoethanol
Di-C_8 oxoaminoethanol
Di-C_{10} oxoaminoethanol
Dimethylaminopropanol
Dimethylaminobutanol

The non-amino or regular alcohols of this invention have the general formula

ROH

where R is an alkyl radical derived from a primary alcohol containing 1 to 20 carbon atoms. Illustrative examples of these non-amino alcohols which may be employed in preparing the complex esters of the present invention are as follows:

Methyl	Heptyl
Ethyl	Octyl
Propyl	Nonyl
Butyl	Decyl
Isobutyl	Dodecyl
Amyl	Tetradecyl
Hexyl	Cetyl

A group of non-amino 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. 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 normally have a branched chain structure.

Among the various components of the complex esters of the present invention, certain preferences may be pointed out. The preferred dibasic acids are adipic, azaleic and sebacic; the preferred glycols are ethylene glycol and polyethylene glycols of the formula

$$HO(CH_2CH_2O)_dCH_2CH_2OH$$

where *d* is an integer of value 1 to 4; the preferred monohydric amino alcohols are diethylaminoethanol and dibutylaminoethanol; and the preferred monohydric non-amino alcohols are the C_8 to C_{13} Oxo alcohols. These components are preferred because they are readily available commercially and also because they produce an oil-soluble ester product on account of their chain lengths.

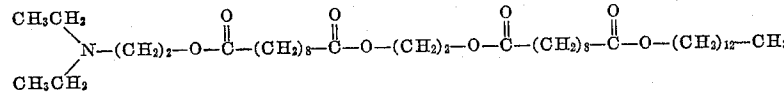
As an example of the present invention, a complex ester exhibiting unusually desirable detergent characteristics was prepared as follows: 50 grams of sebacic acid, 9 grams of ethylene glycol, 28 grams of C_{13} Oxo alcohol and 17 grams of diethylaminoethanol were added to 200 cc. of toluene in a 1 liter flask. The toluene was employed as an azeotroping or water-entraining medium for removing the water formed in the esterification reaction. The flask was equipped with a stirrer, thermometer, condenser and water take-off trap. The contents of the

flask were maintained at about 111° C. and atmospheric pressure for a period of 11 hours during which time 7.2 cc. of water were removed from the flask with the water-entraining toluene. Thereafter the contents of the flask were subjected to a distillation step which was carried out at 0.5 mm. of pressure and at a temperature of 180° C. to remove all materials boiling below 450° C. at atmospheric pressure. The residue in the flask amounted to about 71 grams and represented the complex ester made in accordance with the present invention. The complex ester had the following approximate analysis:

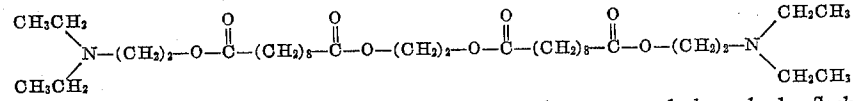
Constituent:	Weight percent
N	3.6
C	69.2
H	11.8

Based on the proportions of reactants employed and the above analysis, it is believed that the resultant product is a mixture of complex esters and that this mixture includes compounds having the following formulae:

(1)



and (2)



This complex ester product prepared above had a flash point of about 435° F., a pour point of less than —35° F., and had a kinematic viscosity of about 61.25 at 100° F. and a kinematic viscosity of about 8.55 at 210° F. In order to determine the suitability of the above complex ester as a detergent additive in lubricating oil compositions and also to determine its effectiveness in this regard as compared to the prior art detergent additives the following compositions were prepared:

Composition A

This particular composition consisted of 4% by weight of the complex ester of the present invention prepared by the aforedescribed procedure and 96% by weight of a phenol-treated, solvent dewaxed and filtered mineral lubricating oil base stock having a viscosity of 118 centistokes at 100° F. and 12.34 centistokes at 210° F.

Composition B

This particular composition consisted of 4% by weight of a commercially available ashless detergent additive of the prior art and 96% by weight of the lubricating oil base stock employed in Composition A.

Composition C

This particular composition consisted of 92% by weight of the lubricating oil base stock employed in Composition A and 8% by weight of an additive blend consisting of 62.5% of di-isobutyl phenol sulfide and 37.5% of calcium petroleum sulfonates.

Composition D

This particular composition consisted of 92% by weight of the lubricating oil base stock employed in Composition A and 8% by weight of an additive blend consisting of 62.5% of calcium di-isobutyl phenol sulfide and 37.5% of calcium petroleum sulfonates.

These four compositions and the lubricating oil base stock itself were then subjected to a Phorone-H_2SO_4 screening test in accordance with the procedure set forth in Serial Number 327,516 by Charles S. Lynch and Elmer B. Cyphers, now Patent No. 2,732,285, issued January 24, 1956. This particular test is based on the theory that the blow-by of fuel combustion products into an

engine crankcase, accompanied by oxidation and polymerization at high temperatures, is the major factor contributing to lubricant degradation. In this test phorone, which is an unsaturated ketone containing 9 carbon atoms, is employed to simulate the sludge-forming products of partial combustion and dilute H_2SO_4 is employed to simulate the SO_3 in the blow-by gases. The results of the Phorone tests have been demonstrated to accurately correlate with results of full-scale engine and road tests. The Phorone test is preferred over full-scale engine and road tests because it is economical since it requires considerably less time and equipment than do the full-scale tests.

In testing the above compositions, 100 grams of each composition was placed in a beaker together with 5 cc. of phorone. From 1 to 9 ml. of 10% H_2SO_4 were added to the compositions and the contents of each beaker were stirred for 40 minutes at a temperature of 275° F. Thereafter, the liquid content of each beaker was removed by pouring and the beakers were rinsed with heptane and wiped with a dry cheesecloth. The weight of hard beaker deposits (sludge) remaining was then determined after a second rinse and drying step.

The results of the Phorone-H_2SO_4 tests on the four compositions and the lubricating oil base stock itself were as follows:

Composition	10% H_2SO_4 (ml.)	Sludge (mg.)
Base Stock	1	10
A	9	0
B	5	6
B	8	105
C	8.5	8
D	8	12

These results show that the complex ester of the present invention is ideally suited for utilization as a detergent additive in lubricating compositions. Not only is it an ashless additive but it also demonstrates excellent detergent properties. It will be noted that all of the compositions which contain detergent additives (Compositions A, B, C and D) represented an improvement in regard to detergency as compared to the lubricating oil base stock itself. The compositions containing metallic detergents (Compositions C and D) showed better detergency properties than did the composition containing the commercially available ashless detergent additive (Composition B). However, it will of course be noted that Compositions C and D contained twice the additive concentration of Composition B (8% vs. 4%). Composition A containing the complex ester of the present invention was subjected to the most severe conditions in these experiments with 9 ml. of 10% H_2SO_4 being employed. Yet even at this severity Composition A showed no measurable amount of sludge. It will be noted that at lower testing severities the ashless detergents and metallic detergents of the prior art showed substantially more sludge formation than the composition made in accordance with the present invention. This was so even though the metallic detergents were employed in concentrations which were twice as much as that in the composition containing the additive of the present invention (8% vs. 4%).

When additives of the present invention are employed in lubricating oils, they are usually added in proportions of about 0.001 to about 10.0% by weight and preferably 1.0 to 6.0% by weight. The proportions giving the best results will vary somewhat according to the nature of the additive and the specific purpose which the lubricant is to serve in a given case. For commercial purposes, it is convenient to prepare concentrated oil solutions in which the amount of additive in the composition ranges from 25% to 50% by weight, and to transport and store them in such form. In preparing a lubricating oil composition for use as a crankcase lubricant the additive concentrate is merely blended with the base oil in the required amount.

The products of the present invention may be employed not only in ordinary hydrocarbon lubricating oils but also in the "heavy duty" type of lubricating oils which have been compounded with such detergent type additives as metal soaps, metal petroleum sulfonates, metal phenates, metal alcoholates, metal alkyl phenol sulfides, metal organo phosphates, thiophosphates, phosphites and thiophosphites, metal salicylates, metal xanthates and thioxanthates, metal thiocarbamates, amines and amine derivatives, reaction products of metal phenates and sulfur, reaction products of metal phenates and phosphorus sulfides, metal phenol sulfonates and the like. Thus the additives of the present invention may be used in lubricating oils containing such other addition agents as barium tert.-octylphenol sulfide, calcium tert.-amylphenol sulfide, nickel oleate, barium octadecylate, calcium phenyl stearate, zinc diisopropyl salicylate, aluminum naphthenate, calcium cetyl phosphate, barium di-tert.-amylphenol sulfide, calcium petroleum sulfonate, zinc methylcyclohexyl thiophosphate, calcium dichlorostearate, etc. Other types of additives such as phenols and phenol sulfides may be employed.

The lubricating oil base stocks used in the compositions of this invention may be straight mineral lubricating oils or distillates derived from paraffinic, naphthenic, asphaltic, or mixed base crudes, or, if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been carefully removed. The oils may be refined by conventional methods using acid, alkali and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents of the type of phenol, sulfur dioxide, furfural, dichlorodiethyl ether, nitrobenzene, crotonaldehyde, etc. Hydrogenated oils, white oils, or shale oil may be employed as well as synthetic oils, such as lubricating grade simple and complex esters of dibasic acids, carbonates and organic phenylates, polyethers, simple and complex formals, polyethyleneglycols, etc., as well as those prepared, for example, by the polymerization of olefins or by the reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products. Also, for special applications, animal, vegetable or fish oils or their hydrogenated or voltolized products may be employed in admixture with mineral oils.

For the best results the base stock chosen should normally be that oil which without the new additive present gives the optimum performance in the service contemplated. However, since one advantage of the additives is that their use also makes feasible the employment of less satisfactory mineral oils or other oils, no strict rule can be laid down for the choice of the base stock. Certain essentials must of course be observed. The oil must possess the viscosity and volatility characteristics known to be required for the service contemplated. The oil must be a satisfactory solvent for the additive, although in some cases auxiliary solvent agents may be used. The lubricating oils, however they may have been produced, may vary considerably in viscosity and other properties depending upon the particular use for which they are desired, but they usually range from about 40 to 150 seconds Saybolt viscosity at 210° F. For the lubricating of certain low and medium speed Diesel engines the general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity at 210° F. of 45 to 90 seconds and a viscosity index of 0 to 50. However, in certain types of Diesel engine and other gasoline engine service, oils of higher viscosity index are often preferred, for example, up to 75 to 100, or even higher, viscosity index.

In addition to the material to be added according to the present invention, other agents may also be used such as

dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organo-metallic compounds, metallic or other soaps, sludge dispersers, anti-oxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, voltolized fats, voltolized minerals oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. Solvents and assisting agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like may also be employed.

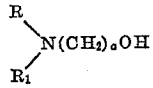
Assisting agents which are particularly desirable as plasticizers and defoamers are the higher alcohols having 8 or more carbon atoms and preferably 12 to 20 carbon atoms. The alcohols may be saturated straight and branched chain aliphatic alcohols such as octyl alcohol ($C_8H_{17}OH$), lauryl alcohol ($C_{12}H_{25}OH$), cetyl alcohol ($C_{16}H_{33}OH$), stearyl alcohol, sometimes referred to as octadecyl alcohol ($C_{18}H_{37}OH$), heptadecyl alcohol ($C_{17}H_{35}OH$), and the like; the corresponding olefinic alcohols such as oleyl alcohol; cyclic alcohols such as naphthenic alcohols; and aryl substituted alkyl alcohols, for instance phenyl octyl alcohol, or octadecyl benzyl alcohol; or mixtures of these various alcohols, which may be pure or substantially pure synthetic alcohols. One may also use mixed naturally occurring alcohols such as those found in wool fat (which is known to contain a substantial percentage of alcohols having about 16 to 18 carbon atoms) and in sperm oil (which contains a high percentage of cetyl alcohol); and although it is preferable to isolate the alcohols from those materials, for some purposes wool fat, sperm oil or other natural products rich in alcohols may be used per se. Products prepared synthetically by chemical processes may also be used, such as alcohols prepared by the oxidation of petroleum hydrocarbons, e. g. paraffin wax, petrolatum, etc.

In addition to being employed in lubricants the additives of the present invention may also be used in motor fuels, hydraulic fluids, torque converter fluids, cutting oils, flushing oils, turbine oils or transformer oils, industrial oils, process oils and generally as detergents in mineral oil products. They may also be used in gear lubricants and greases.

It is also contemplated that the complex esters of the present invention may be employed as lubricating oil base stocks because of their desirable flash point, pour point, viscosity, and viscosity index characteristics. When the complex esters of the present invention are so used, various addition agents may be incorporated therein for the purpose of improving their lubricating properties. For example, anti-oxidants, viscosity index improvers, thickeners, pour depressants, dyes, etc. may be added.

What is claimed is:

1. An oil-soluble esterification product obtained by esterfying about 2 moles of saturated dicarboxylic acid having 2 to 10 carbon atoms per molecule with about 1 mole of glycol having 2 to 10 carbon atoms per molecule, and about 2 moles of monohydric alcohol selected from the group consisting of (1) amino alcohols having the formula



where R and R_1 are alkyl radicals containing 1 to 10 carbon atoms and a is an integer of value 2 to 4, and (2) monohydric alcohols having the formula

$$R'OH$$

where R' is an alkyl radical containing 1 to 20 carbon atoms, at least 1 mole of the 2 moles of monohydric alcohol being amino alcohol, and then removing from the resultant esterification mixture by distillation all materials boiling below about 450° C. at atmosphere pressure, said esterification product being the residue remaining after the distillation.

2. A product according to claim 1 wherein said dicarboxylic acid contains 6 to 10 carbon atoms per molecule, said glycol has the formula

$$HO(CH_2CH_2O)_dCH_2CH_2OH$$

where d is an integer of value of 0 to 4, the radicals R and R_1 contain 2 to 4 carbon atoms, the integer a has a value of 2, and the radical R' contains 8 to 13 carbon atoms.

3. A lubricating oil composition comprising a major proportion of a mineral lubricating oil and about 0.001 to 10% by weight, based on the total composition, of a product as defined in claim 1.

4. A lubricating oil composition comprising a major proportion of a mineral lubricating oil and about 1 to 6% by weight, based on the total composition, of a product as defined by claim 2.

5. An oil-soluble esterification product obtained by esterfying about 2 moles of sebacic acid with about 1 mole of ethylene glycol, about 1 mole of a C_{13} alcohol and about 1 mole of diethylaminoethanol, and then removing from the resultant esterification mixture by distillation all materials boiling below about 450° C. at atmospheric pressure, said esterification product being the residue remaining after the distillation.

6. A lubricating oil composition comprising a major proportion of a mineral lubricating oil and about 1 to 6% by weight based on the total composition of a product prepared by esterifying about 2 moles of sebacic acid with about 1 mole of ethylene glycol, about 1 mole of a C_{13} alcohol and about 1 mole of diethylaminoethanol, and then removing from the resultant esterification mixture by distillation all materials boiling below about 450° C. at atmospheric pressure, said esterification product being the residue remaining after the distillation.

References Cited in the file of this patent

UNITED STATES PATENTS

2,094,608	Kritchevsky	Oct. 5, 1937
2,417,281	Wasson	Mar. 11, 1947
2,575,196	Smith	Nov. 13, 1951
2,628,974	Sanderson	Feb. 17, 1953