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COMPLEX ESTER SYNTHETIC LUBRICANT

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This invention relates to synthetic lubricating compositions. Particularly it relates to synthetic lubricants having utility at both high and low temperatures. More particularly the invention relates to new and improved synthetic lubricants of the ester type which exhibit outstanding characteristics as to pour point and low temperature viscosity.

In the lubricating art, considerable progress has been realized in recent years in the production of lubricants characterized by one or more specific properties and adapted for specific uses. In general, this progress is attributed to two developments, new and improved refining techniques, and addition agents capable of imparting particular properties to available lubricants. Thus, viscosity index improvers and pour point depressors are added to available automotive lubricants to render the lubricants more adaptable to change in temperature conditions. There are, of course, limits upon the range of effectiveness of these addition agents, and certain requirements cannot be met in every instance.

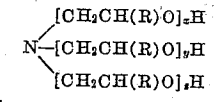
With the development of the "turbo-jet" and "turbo-prop" type aircraft engine, which operate at peak efficiency at extremely high altitudes, there has developed a corresponding need for a lubricant which is efficacious at the extremely low temperatures encountered at high altitudes or in frigid areas. Engine manufacturers and operations personnel dealing with these turbine engines must be supplied with a lubricant possessing exceptionally low viscosities at low temperatures and at the same time having satisfactory lubricating qualities at high temperatures.

The mineral lubricating oils which exhibit satisfactory low temperature viscosities have generally been found to have flash points that are dangerously low and high temperature viscosities that are below those required. In other words when the mineral oil is thin enough at low temperatures, it is too volatile at higher temperatures, where it is also too thin to possess satisfactory lubricity. It has been found that, generally speaking, additive agents do not satisfactorily furnish the required characteristics.

Recently, in an effort to obtain the superior lubricants needed for these turbine type engines, a new field has been explored, namely the synthesis of lubricants from various materials. Esters represent one class of materials which have attracted unusual interest as synthetic lubricants. Esters are generally characterized by high viscosity indices and flash points and lower pour points than mineral oils of a corresponding viscosity. It is with synthetic lubricants of the ester type having ASTM pour

points below about 35° F., preferably below about —15° F., flash points above about 300° F., preferably above about 375° F., and that have kinematic viscosities at 210° F. within the range of from 2 to 60 centistokes, preferably from 4 to 40 centistokes, that this invention is concerned.

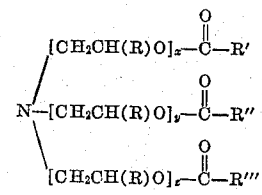
The new and improved synthetic lubricants of this invention are formed using as a nucleus a trialkanol amine having the following structural formula:



wherein R is hydrogen or an alkyl group and wherein x, y and z are integers of a value of from 1 to 5. Esters and complex esters of this trialkanol amine, as set out in detail below, have outstanding utility as synthetic lubricants.

TYPE I.—TRIESTERS OF MONOBASIC ACIDS

By reaction with a tri-molar proportion of a monobasic acid the following triesters are prepared:

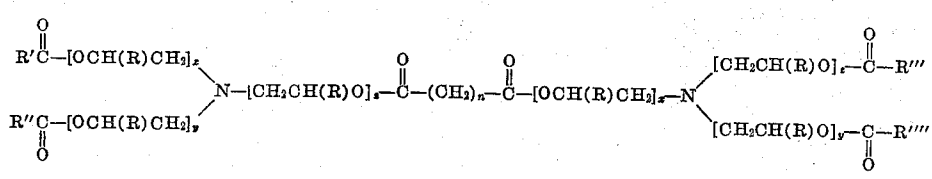


wherein R is hydrogen or a methyl group, wherein R', R'' and R''' are alkyl groups corresponding to the monobasic acid used and containing from 3 to 9 carbon atoms and wherein x, y and z are integers of a value of from 1 to 5.

The esterification of the trialkanol amines with monobasic acids is straightforward and is accomplished by methods known to the art. It may be carried out to the evolution of theoretical water in an inert atmosphere (nitrogen, carbon dioxide, etc.) with or without esterification catalyst such as p-toluene-sulfonic acid, $NaHSO_4$, sulfosalicylic acid, etc. To insure complete esterification of the amine compound, it is preferable to use an excess of the monobasic acid.

TYPE II.—DIBASIC ACID CENTERED COMPLEX ESTER

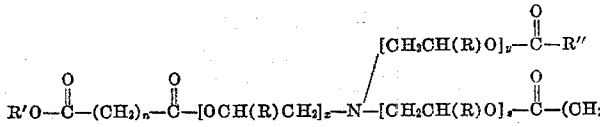
To form this complex ester, a two-thirds ester of the trialkanol amine is formed by heating to about 130° C. one mol of the trialkanol amine with two mols of a monobasic acid. This two-thirds ester, that is, a partial ester containing one unreacted hydroxyl group, is then esterified with a dibasic acid, two mols of the two-thirds ester reacting with each mol of the dibasic acid to result in a material having the following general formula:



In this formula R represents a hydrogen atom or alkyl group, R', R'', R''' and R'''' are alkyl groups corresponding to the monobasic acid employed and contain from 3 to 9 carbon atoms, x, y and z are integers having a value of from 1 to 5 and n is an integer of from 2 to 8 in the expression—$(CH_2)_n$— which corresponds to the "body" of the dibasic acid employed. The body of the dibasic acid may also contain oxygen or sulfur in ether or thioether linkages.

TYPE III.—A NITROGEN-CENTERED COMPLEX ESTER

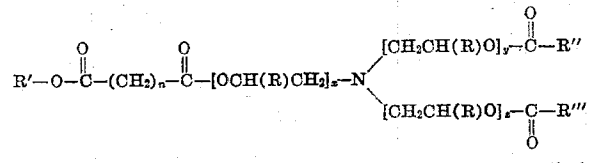
This compound is formed by reacting together two partial esters. First a one-third ester of the trialkanol amine is formed by reacting one mol of the trialkanol amine with one mol of a monobasic acid. The second partial ester is formed by reacting one mol of a dibasic acid with one mol of an alcohol. The two partial esters are then reacted together in proportion of two mols of the half ester of the dibasic acid per mol of the one-third partial ester of the trialkanol amine. The resulting nitrogen-centered complex ester has the structural formula as follows:



In this formula R represents hydrogen or an alkyl group, R′ represents the alkyl group of the alcohol used to form the partial ester (half ester) and $-(CH_2)_n-$ represents the body of the dibasic acid containing from 2 to 8 carbon atoms of either branched or straight chain configuration. Alcohols operable include ethyl, propyl, butyl, isobutyl, methyl, hexyl, octyl, capryl, decyl, isodecyl, C_8 Oxo, 2-ethylhexyl, 2-ethylbutyl, etc. R″ of the formula corresponds to the alkyl group and represents the body of the monobasic acid used to form a partial ester (one-third ester) of the trialkanol amine. This alkyl group contains from 3 to 9 carbon atoms. The letters *x*, *y* and *z* denote integers having a value of from 1 to 5 and *n* is an integer of from 2 to 8.

TYPE IV.—NITROGEN-CENTERED COMPLEX ESTER

The formation of this type of complex ester is brought about by reacting two molar proportions of a monobasic acid with a molar proportion of the trialkanol amine to give the partial (two-thirds) ester of the trialkanol amine. An equimolar proportion of this ester is then reacted with a molar proportion of a half ester of a dibasic acid which has been formed by reacting one mol of an alcohol with a molar proportion of a dibasic acid. This complex ester has the following general formula:



In this formula R represents hydrogen or an alkyl group; R′ represents an alkyl group having from 2 to 12 carbon atoms of either branched or straight chain configuration, and corresponds to the alcohol used in forming the partial ester of the dibasic acid; R″ and R‴ in the formula correspond to the alkyl groups of the monobasic acid used in forming the partial ester of the trialkanol amine and contain from 3 to 9 carbon atoms. The symbols *x*, *y* and *z* are small whole numbers of a value of from 1 to 5 and *n* is a number from 2 to 8.

Throughout the four types of esters R represents either hydrogen or an alkyl group. It is preferred that when R is an alkyl group it contains from 1 to 4 carbon atoms. When R is a hydrogen atom, for instance, derivatives of triethanol amine are contemplated. When R is a methyl group the formula covers derivatives of triisopropanol amine.

The monobasic acid throughout these three types of complex esters are restricted to those monobasic acids containing from 3 to 9 carbon atoms in the alkyl portion, that is to say, exclusive of the carboxyl group. Operable acids therefore contain from 4 to 10 carbon atoms per molecule, either of branched or straight chain configuration, and may be listed as including the following:

n-Butyric acid
Isobutyric acid
n-Valeric acid
Isovaleric acid
Caproic acid
2-ethylbutyric acid
n-Heptylic acid
Caprylic acid
2-ethyl hexanoic acid
Pelargonic acid
Oxo acids containing from 4 to 10 carbon atoms
Fischer-Tropsch synthesis acids containing from 4 to 10 carbon atoms
Capric acid

Whenever a dibasic acid has been used in the preparation of these complex esters the body of the acid is represented by $-(CH_2)_n-$ where *n* is described as being a number varying between 2 and 8. The body of the acid represented by this structure may also contain oxygen or sulfur in ether of thioether linkages. Since *n* may vary between 2 and 8, operable dibasic acids include succinic, glutaric, adipic, pimelic, suberic, azeleic, sebacic, diglycolic, β,β′-thiodipropionic acids.

The invention will be more clearly described by the following examples:

Example I

The following ingredients were heated in esterification apparatus consisting of a one-liter three-necked round bottomed flask equipped with a nitrogen inlet tube, a glass-seal stirrer, a water separator-condenser and a thermometer.

Triethanol amine	224 g. (1.50 mols).
2-ethylhexanoic acid	714 g. (4.95 mols).
Xylene	200 g.
Sodium acid sulfate	8 g.

After heating for 14 hours the esterification was completed giving 83 g. of water (81 g. theoretical). The ester-xylene mixture was filtered to remove the catalyst and then was distilled at a reduced pressure to give a main fraction consisting of 409 g. of a non-crystallizable material having the following properties:

Neutralization No. (ASTM–D–664).	0.53 mgm. KOH/gm.
Viscosity/210° F. cs	3.962.
Viscosity/100° F. cs	21.85.
Viscosity/0° F. cs	870.
Viscosity/—40° F. cs	13,834.
Viscosity index	73.
Actual pour, ° F	—70.
Flash point, ° F	445.
Fire point, ° F	500.

Example II.—Preparation of Type III triethanol amine complex ester, i. e.

C_7 Oxo alcohol-sebacic acid-$HOCH_2CH_2N(CH_2CH_2OH)$-sebacic acid-C_7 Oxo alcohol
$CH_2CH_2OOCC_8H_{17}$

FORMULATION

	G.
Triethanol amine, 1 m	149.2
Pelargonic acid, 1 m	151.0
Sebacic acid, 2 m	404.0
C_7 Oxo alcohol, 2 m	232.0
Excess alcohol, 30%	69.0
Heptane	100.0
Pure phenothiazine, 0.5%	4.2

PROCEDURE

The triethanol amine, pelargonic acid and heptane were heated to reflux temperature of 210° C. maximum over a 50 minute period during which time 20.3 cc. of aqueous distillate was obtained. The alcohol, sebacic acid and phenothiazine were then added and the heating continued for 5 additional hours during which time the maximum temperature obtained was 205° C. A total of 98 cc. of aqueous material was separated from the trap (90 cc. is theory). The ester product was washed with sodium carbonate solution-heptane-isopropanol mixture and finally twice with water-isopropanol before being stripped. The finished product was stripped to 152° C. overhead and 215° C. liquid temperature at 0.18 mm. pressure. This product weighed 750 g. giving a yield of about 90%. The color was dark red.

The properties of this lubricant are given below. Although the material has a high viscosity, its viscosity-temperature characteristics are outstandingly good. In fact they are superior to other complex ester materials of similar viscosity as can be seen by comparing the properties in the second column.

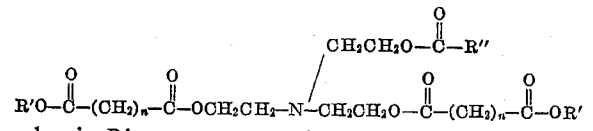
	Triethanol Amine-Pelargonic Acid-Sebacic Acid-C_7 Oxo Alcohol-Complex Ester	Polyethylene Glycol 200-Sebacic Acid-2-Ethylhexanol-Complex Ester
Kin. Vis.:		
210° F.	34.08	28.51
100° F.	192.4	197.2
0° F.	6,902	10,260
−40° F.	88,470	Too Viscous
Viscosity Index	141	137
Pour Point, ° F.	−45	−45
Flash Point, ° F.	495	535
Fire Point, ° F.	560	600
ASTM Slope:		
210/100° F.	0.435	0.496
210/0° F.	0.479	0.530
210/−40° F.	0.482	

The synthetic lubricating oils as described above may be used directly as lubricants or they may be blended with other lubricants such as mineral oils or other synthetic lubricants to obtain many combinations having special characteristics. It may also be desirable to add to the esters various improvers such as viscosity index improvers, e. g. a minor but viscosity index improving amount of a polymerized methacrylate ester, pour point depressors, oxidation inhibitors, detergents, corrosion and rust resisting agents and the like.

This application is a continuation in part of Serial No. 262,661, filed December 20, 1951, now abandoned, for the same inventors.

What is claimed is:

1. A synthetic lubricating oil having outstanding lubricating characteristics at both high and low temperatures which comprises a complex ester of the formula:

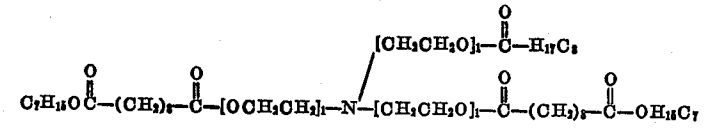


wherein R′ represents an alkyl group of from 2 to 10 carbon atoms, wherein R″ represents an alkyl group containing from 3 to 9 carbon atoms and wherein *n* is an integer of from 2 to 8.

2. A synthetic lubricating composition according to claim 1 wherein R′ is an alkyl group containing about 7 carbon atoms.

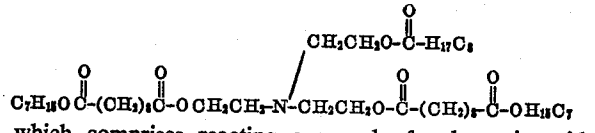
3. A synthetic lubricating composition according to claim 1 wherein *n* is 8.

4. A synthetic lubricating composition having outstanding lubricating characteristics at both high and low temperatures which comprises a complex ester of the formula



5. A synthetic lubricating composition according to claim 4 containing combined therein a minor but viscosity index improving amount of a polymerized methacrylate ester.

6. The process of preparing a complex ester synthetic lubricant having the formula



which comprises reacting one mol of pelargonic acid with one mol of triethanolamine at a reflux temperature of about 210° C. for about 50 minutes, separating an aqueous distillate from the reaction mixture, adding two mols of C_7 Oxo alcohol and two mols of sebacic acid to said reaction mixture, continuing heating for about five hours, separating an aqueous distillate from said reaction mixture and recovering said complex ester from the reaction products.

References Cited in the file of this patent

UNITED STATES PATENTS

1,918,222	Weisberg et al.	July 11, 1933
2,106,522	Ellis	Jan. 25, 1938
2,173,448	Katzman et al.	Sept. 19, 1939
2,547,188	Wayne	Apr. 3, 1951
2,563,609	Matuszak	Aug. 7, 1951
2,575,399	Seymour et al.	Nov. 20, 1951
2,637,698	Tutwiler	May 5, 1953
2,705,724	Cottle et al.	Apr. 5, 1955