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BIS-2-METHYL-2-NORCAMPHANEMETHANOL ALKANE-DIOATES AS SYNTHETIC ESTER LUBRICANTS

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This invention relates to a new group of compounds which have been found to be particularly suitable for use as synthetic lubricants.

Hydrocarbon or mineral lubricating oils are widely used as lubricants, but such materials suffer from certain disadvantages which limit their use in many applications. In particular, hydrocarbon oils undergo marked viscosity changes with changes in temperature and have relatively high pour points when they have a usable viscosity at high temperatures. Hydrocarbon lubricating oils having low pour points usually contain a considerable amount of volatile material which is lost at high temperatures. Hydrocarbon lubricating oils particularly suffer where extreme conditions of temperature are encountered, such as in turbo-jet aircraft engines. High engine temperatures in turbo-jet aircraft engines and the like are desirably employed to increase engine efficiency. In such a high temperature use, conventional hydrocarbon lubricating oils suffer thermal and oxidative breakdown to an undesirable degree.

In recent years a number of synthetic ester lubricants have been proposed to overcome some of the objections to hydrocarbon lubricating oils.

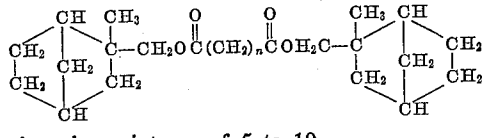
It is an object of this invention to provide a new group of synthetic ester materials that have particular utility as lubricants and which are not subject to many of the disadvantages inherent to hydrocarbon lubricating oils.

It is another object of this invention to provide a novel class of synthetic ester lubricants having improved resistance to thermal degradation.

It is likewise an object of this invention to provide new synthetic ester lubricants especially adapted to meet the high temperature requirements desired for lubricating turbo-jet engines and for related high temperature uses.

Other objects will be apparent from the description and claims which follow.

The class of compounds embodying the invention are esters of 2-methyl-2-norcamphanemethanol having the following formula:



wherein n is an integer of 5 to 10.

The esters of the present invention can be prepared by esterifying two molar proportions of 2-methyl-2-norcamphanemethanol with one molar proportion of a saturated dicarboxylic acid containing 7 to 12 carbon atoms including pimelic acid, suberic acid, azelaic acid, sebacic acid, nonanedicarboxylic acid and decanedicarboxylic acid. The 2-methyl-2-norcamphanemethanol used in the preparation of the present esters can be prepared by reacting cyclopentadiene with methyl methacrylate by the Diels Alder reaction, hydrogenating the resulting product to form methyl 2-methyl-2-norcamphanecarboxylate, and thereafter subjecting the resulting product to hydrogenolysis over copper chromite.

The present esters of 2-methyl-2-norcamphanemethanol have considerable utility as lubricants. By varying the choice of the dicarboxylic acid with which 2-methyl-2-norcamphanemethanol is esterified, lubricants having a diversity of viscosities and pour points can be obtained. The esters of the invention can be used directly as lubricants or they can be blended with other lubricants. If desired, minor proportionate amounts of such conventional additives as antioxidants, extreme pressure additives, viscosity index improvers, thickeners, anticorrosion agents and related materials can be incorporated into the present esters of 2-methyl-2-norcamphanemethanol.

The viscosity and pour point characteristics of typical ester lubricants of the invention are set out in Table 1 below. Also included in Table 1 for comparative purposes is a typical hydrocarbon oil of lower viscosity.

TABLE 1

Lubricant	Kinematic Viscosity in Centistokes		Pour Point, ° F.
	100° F.	210° F.	
Typical hydrocarbon oil	13	2.6	−30
Bis-(2-methyl 2-norcamphanemethanol) azelate.	106.6	11.96	−40
Bis-(2-methyl-2-norcamphanemethanol) sebacate.	106.5	12.18	−40

As can be seen from the data in Table 1, that while the hydrocarbon oil had a viscosity substantially less than the two representative ester lubricants of the invention, the hydrocarbon oil had a pour point that was higher than the ester lubricants of the invention. The viscosity data in Table 1 was determined by ASTM Method D–88–44. The pour point data in Table 1 was determined by ASTM Method D–97–47.

Table 2 below gives other physical properties of typical ester lubricants of the invention.

TABLE 2

Lubricant	ASTM Slope	Percent By Weight Evaporation Loss (6½ hours at 400° F.)
Bis-(2-methyl-2-norcamphanemethanol) azelate	0.67	5.7
Bis-(2-methyl-2-norcamphanemethanol) sebacate	0.66	4.2

The evaporation loss data in Table 2 was determined in accordance with methods described in Military Specification MIL–L–7808C.

The synthetic ester lubricants of the invention are particularly characterized as having good thermal stability. The improved thermal stability of the present esters is illustrated by the data in Table 3 below. For purposes of comparison, data concerning other known synthetic ester lubricants and closely related esters are included in Table 3.

TABLE 3

Ester	Percent Decomposition per Hour at 575° F.	Percent Change in 100° F. Viscosity After 8 Hour Heating at 575° F.
Bis-(2-methyl-2-norcamphanemethanol) azelate	0.06	−1.4
Bis-(2-methyl-2-norcamphanemethanol) sebacate	0.08	−1.8
Bis-(2-propyl-2-norcamphanemethanol) sebacate	0.11	−9.3
Bis-(2-ethylhexyl) sebacate	0.59	−17
2,2,4-Trimethyl-1,3-pentanediol dipelargonate	[1] 1.09	[1] −16
8 carbon oxo alcohol diester of 1,1-cyclohexanediacetic acid	[2] 1.6	[2] −19

[1] Determined at 550° F.
[2] Determined at 600° F.

As can be seen from the data in Table 3, the present esters of 2-methyl-2-norcamphanemethanol have substantially improved resistance to thermal degradation over other ester lubricants, and particularly noteworthy, over the closely related ester of 2-propyl-2-norcamphanemethanol. The data in Table 3 concerning the percent decomposition per hour of the various esters was based on the determination of the acid produced on heating samples of the various esters under nitrogen for eight hour periods. The viscosity determinations upon which the percent changes of 100° F. viscosity in Table 3 were based were determined by ASTM Method D-88-44.

The following examples illustrate the preparation of typical esters of 2-methyl-2-norcamphanemethanol.

Example 1

A mixture of 308 g. (2.2 moles) of 2-methyl-2-norcamphanemethanol and 202 g. (1 mole) of sebacic acid in 50 ml. of xylene was refluxed in a reactor fitted with a Dean-Stark separator for 14 hours. During the course of the reaction 36 ml. of water was evolved from the reaction mixture. The resulting reaction mixture was washed once with 100 ml. of 5% sodium hydroxide solution and once with 100 ml. of water. Excess 2-methyl-2-norcamphanemethanol was removed from the washed reaction product by distillation and the residue was distilled in a molecular still to give a substantially quantative yield of bis-(2-methyl-2-norcamphanemethanol) sebacate having a B.P. of 117°–126° C. at <1 micron of mercury and n_D^{20} 1.4883.

Example 2

By the method described in Example 1, 2.2 moles of 2-methyl-2-norcamphanemethanol and 1 mole of azelaic acid were reacted to give in a substantially quantative yield of bis(2-methyl-2-norcamphanemethanol) azelate having a B.P. of 130°–134° C. at 2–3 microns of mercury and n_D^{20} 1.4893.

Example 3

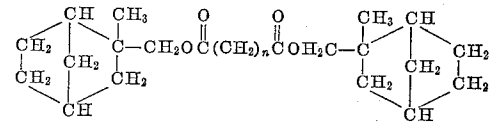
The 2-methyl-2-norcamphanemethanol esterified in accordance with the processes described in Examples 1 and 2 was prepared in the following manner. A mixture of 466 g. (7.06 moles) of cyclopentadiene, 820 g. (8.2 moles) of methyl methacrylate and 0.5 g. of hydroquinone were heated in an autoclave for 12 hours at 150° C. The resulting mixture was distilled to give 909 g. of methyl 2-methyl-bicyclo-[2.2.1]-5-heptene-2-carboxylate, B.P. 81°–89° C. at 20 mm. of mercury, n_D^{20} 1.4730. A 771 g. (4.65 moles) portion of the resulting distilled ester was hydrogenated over 39 g. of Raney nickel at 100° C. and at a pressure of 1500 p.s.i. Thereafter the Raney nickel catalyst was removed by filtration to yield methyl 2-methyl-2-norcamphanecarboxylate. Without further purification, the resulting methyl 2-methyl-2-norcamphanecarboxylate was subjected to hydrogenolysis over 80 g. of copper chromite at 250° C. and at a pressure of 4000 p.s.i. to give 577 g. of 2-methyl-2-norcamphanemethanol, B.P. 101°–105° C. at 17 mm. of mercury, and which crystallized on standing.

Thus, by means of this invention, a novel and highly useful group of synthetic ester lubricants is provided. The improved physical characteristics of the present esters make them eminently suitable for use as lubricants in applications where hydrocarbon lubricating oils are now used, as well as in high temperature applications where conventional hydrocarbon lubricating oils are unsuitable. Because of their improved thermal stability at high temperatures, the present ester lubricants have particular utility for use in turbo-jet aircraft engines and for related high temperature applications.

The invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A synthetic lubricant comprising an ester having the formula:



wherein n is an integer of 5 to 10.

2. A synthetic lubricant comprising bis-(2-methyl-2-norcamphanemethanol) azelate.

3. A synthetic lubricant comprising bis-(2-methyl-2-norcamphanemethanol) sebacate.

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