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SYNTHETIC LUBRICATING COMPOSITION

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This invention relates to synthetic lubricating compositions. Particularly the invention relates to synthetic lubricating compositions which have outstanding lubricating characteristics at both high and low temperatures which make them desirable for the lubrication of jet engines. More particularly the instant invention relates to branched chain alcohol esters of monobasic acids of a specific type.

In recent efforts to obtain superior lubricants for use in jet engines which operate at extremely high altitudes, there have been developed entirely new synthetic materials with lubricating properties. In general, these new synthetic lubricants have viscosity properties that are outstanding at both low and high temperatures, especially when compared to mineral lubricating oils.

For use in the lubricating of aircraft engines, particularly of the "turbo-jet" or "turbo-prop" type, a lubricant must meet very stringent viscosity properties. At low temperatures experienced at high altitudes, the lubricant must be sufficiently labile to flow through the circulatory system of the engine and allow movement of the lubricated surfaces without undue power requirement. A lubricant having an ASTM pour point below about +35° F. has been found generally satisfactory in this respect for general use. At high temperatures a lubricating oil must have sufficient "body" or "thickness" to furnish and maintain a lubricating film. It has been found that a lubricant that is satisfactory in this respect will have a viscosity at 210° F. of between about 2 and 60 centistokes. To prevent undue lubricant loss, due to volatility, and to insure against explosion hazards at the high temperatures sometimes encountered, a lubricating oil should have a flash point in excess of about 300° F. These requisites are inherent in the term "lubricating composition," as used in this application, and the materials of this invention are limited to those having properties within these ranges. In general, the preferred materials, as contemplated herein, and as the contemplated preferred embodiment hereof, will have ASTM pour points below about -25° F., ASTM flash points above about 375° F., and viscosities within a range of 2.6 to 13 centistokes at 210° F.

The materials of the instant invention cover only a limited number of the large class of esters of monobasic acids. They may be said to have the general formula



wherein R and R' are selected from the group consisting of alkyl groups having from about 8 to 18 carbon atoms in a straight chain configuration, and alkyl groups of a branched chain configuration containing from about 12 to about 28 carbon atoms and which contain one major side chain of from 4 to 14 carbon atoms. A further limitation exists in that R and R' may not be both branched or both straight.

It will be seen from the above that only a limited number of aliphatic monocarboxylic acids and alcohols may be used in the preparation of the esters of this invention.

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If R' is of straight chain configuration, that is if R' is derived from an aliphatic alcohol having from about 8 to 18 carbon atoms in a straight chain, then operable alcohols include the following: n-octanol, decanol, dodecanol, lauryl alcohol, Lorol alcohols, cetyl alcohol, etc.

When R' is of straight chain configuration, then R or the acid radical, must contain from 12 to 28 carbon atoms in branched chain configuration having one major side chain of from 4 to 14 carbon atoms. Operable acids include: 2-butyl octanoic acid, C₁₂-C₂₈ acids prepared by the oxidation of petroleum, C₁₂-C₂₈ acids prepared by alkali fusion of alcohols, C₁₂-C₂₈ acids prepared as a product from Guerbet alcohols.

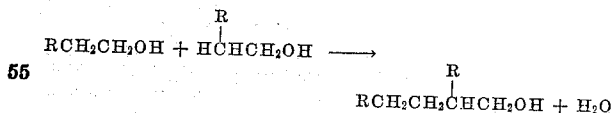
When R' is of branched chain configuration, then R is of straight chain structure containing from 8-18 carbon atoms and the acid used may be selected from the following: caprylic acid, capric acid, pelargonic acid, lauric acid, coconut fatty acids, myristic acid, palmitic acid, stearic acid, oleic acid.

Of the listed operable acids, particularly preferred are the mixture of acids described as "coconut fatty acids." This mixture of acids is prepared from coconut oil by a process comprising the saponification of coconut oil followed by acidification to recover the acids of the various mixtures obtainable, the mixture having an average chain length of about 12.5 is preferred.

When R' is of branched chain configuration and R is straight chain, then in order to be included in the limitations of the formula above, that is, to have from 12 to 28 carbon atoms with one major side chain of from 4 to 14 carbon atoms, the alcohols used to form the esters of this invention are prepared by one of two specific processes as follows:

1. *Dimerization of alcohols by Guerbet reaction.*—Higher molecular weight alcohols having but one major side chain are produced from primary or secondary alcohols by an alkaline condensation known as the "Guerbet" reaction. This reaction requires the presence of a methylene group adjacent to the carbinol (hydroxylated carbon) group. The sodium alcoholate of the reacting alcohol is generally used as a catalyst. However, metallic sodium has also been used since the sodium is converted to the alcoholate at the beginning of the reaction. Other alkaline agents such as sodium soaps, sodium borate, sodium alkyl borate, etc., may also be used, but are considered to be less satisfactory.

When relatively low concentrations of sodium alcoholate are used for the Guerbet reaction, that is, from 10 to 20 moles of alcohol per mole of alcoholate, water is eliminated according to the following equation:



The reaction is not so easily described when high concentrations of sodium alcoholate are used. Furthermore, the higher alcoholate concentrations produce higher yields of sodium salts of the acid. By the use of dehydrogenation catalyst such as copper, zinc, nickel, etc., however, there is a tendency to reduce the amount of salts produced while maintaining or improving the conversion to higher alcohols.

After condensation, the higher alcohols and unreacted alcohols may be distilled from the reaction mixture by distillation under reduced pressure or at atmospheric pressure for relatively low molecular weight alcohols. Steam distillation may also be used. In most cases, however, it is desirable to remove the salts of the fatty acids by extraction prior to distillation of the alcohols.

Satisfactory operation conditions for condensation of a primary alcohol by the Guerbet reaction are as follows:

1. Alcohol/caustic (NaOH) mol ratio of 10:1.
2. Dehydrogenation agent—1 gm. of copper powder per mol of alcohol charged.
3. Temperature—200° C. to 250° C.
4. Time—5 to 10 hours.

Although the above conditions are favorable for the Guerbetization of alcohols in the range of C₆ to C₁₄ it is possible for these conditions to be altered considerably. The alcohols may be condensed in the presence of an entraining agent for removal of water. Pressure may be desirable for alcohols boiling below the condensation temperatures. The temperature and time of reaction may be varied by use of different concentrations of caustic.

An example of the reaction described above is set out in detail below.

To a one gallon nickel reactor fitted with a large bore 30-inch condenser, there was charged

2340 g. (18 moles) C₈ alcohol
72 g. (1.8 mole) of flake NaOH
18 g. copper powder

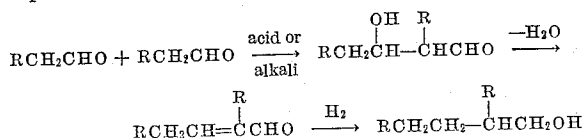
The mixture was heated with agitation and little or no cooling was applied to the condenser. Formation of the sodium alcoholate took place with the liberation of 1.8 moles of water during about one-half hour at a pot temperature of 170°–188° C. Heating and agitation were continued to 13 hours during which time the pot temperature rose to 206° C. The water from the condensation reaction was collected and the hydrogen which was liberated by the caustic fusion reaction was measured. The reaction product was removed from the reaction mixture while still hot by use of a vacuum.

The hot product was poured into approximately four liters of water, thus preventing the solidification of the alcoholate or of the sodium salts. After allowing to cool, the mixture was transferred to a 12 liter separatory funnel which was equipped with an agitator. Approximately two liters of water and two liters of petroleum ether were used in the transfer. After agitation, the aqueous layer was removed and the supernatant layer, alcohols and petroleum ether, was given a second wash with two liters of water.

The aqueous layers from the two washes were combined and extracted with one liter of petroleum ether. The total aqueous portion was acidified in the presence of one-half liter of petroleum ether and the acid extract was evaporated to obtain the yield of crude acids.

The two petroleum ether extracts of the alcohols were evaporated, leaving crude alcohol being a mixture of the unreacted alcohol and the dimerized alcohols. The unreacted alcohols were then distilled off in a short path still.

II. Dimerization of aldehyde by aldol condensation.—Aldehydes possessing a methylene group adjacent to the carbonyl group readily condense in the presence of an alkali or an acid to yield a beta-hydroxy aldehyde which is designated as an "aldol" product. This aldol product may be readily dehydrated to yield an unsaturated aldehyde which in turn may be hydrogenated to yield a saturated primary alcohol having twice as many carbon atoms as the aldehyde starting material. This reaction may be depicted as follows:



Such alcohols in general are the same as those prepared by the Guerbet reaction, when the alcohol of the same aldehyde is used. However, during the aldol condensation, small amounts of alcohols and acids may also be produced under some conditions, as shown by the follow-

ing typical 20 mm. distillation data on a product obtained by dehydrating and hydrogenating the aldol condensation product prepared from C₈ Oxo aldehyde in the presence of sodamide.

Fraction	Wt. Percent Yield
Initial, to 225° F. (Alcohol).....	16.4
225°–230° F. (Intermediate).....	0.9
Acids.....	17.8
330°–360° F. (C ₁₆ Alcohol).....	53.5
Bottoms.....	6.8
Trap—light hydrocarbons.....	4.6

If in the formula above, R is of branched chain configuration, having one major side chain of from 4 to 14 carbon atoms, then the acid used to formulate the ester is prepared from the alcohols as described above, i. e., by alkali fusion of C₁₂ to C₂₈ Guerbet dimerized or aldolized alcohols. In this case the esterifying alcohol may be any primary straight chain alcohol having from 8 to 18 carbon atoms, or mixtures thereof such as was described above.

In order to more explicitly describe the instant invention, the following detailed examples are given. It is understood, of course, that these examples are of an illustrative nature only, and are not to be considered as limiting the inventive concept.

EXAMPLE 1

A mixture of 121.2 g. (0.5 mole) of C₁₆ Guerbet alcohol (dimer of branched C₈ Oxo alcohol obtained by oxonation of propylene-butylene copolymer), 115.0 g. (0.525 mole) of coconut fatty acids, 1.2 g. NaHSO₄ catalyst and 75 g. of toluene was refluxed at 140° C. to 161° C. for 90 minutes during which time 9.0 cc. of water was collected. This material was diluted with 200 g. of hexane and washed twice with 150 cc. portions of 2% Na₂CO₃. Three 100 cc. portions of water were used to remove the alkali. The material was then distilled. The monoester boiling mainly at 185° C.–195° C. at 0.05 mm. weighed 188 g. (83% yield) and had the properties set out in Table I.

EXAMPLE 2

Following the procedure outlined in Example 1 above, a normal C₈ alcohol was dimerized by the Guerbet reaction and used to esterify the same coconut oil fatty acids of Example 1. Data on this ester are set out in Table I below.

EXAMPLE 3

C₂₆ Guerbet alcohol (95.5 g., 0.25 mole) prepared by dimerizing branched C₁₃ Oxo alcohol (obtained by oxonation of a C₁₂ olefin fraction containing mainly tetrapropylene) was refluxed with coconut fatty acids (57.3 g., 0.262 mole) and 75 g. of toluene in the presence of 0.8 g. NaHSO₄. The material was heated for 4 hours at 135° C. to 150° C. during which time 4.1 cc. of water was collected. The mixture was diluted with 300 g. Varsol-hexane mixture, washed thrice with 100 cc. of 2% Na₂CO₃ solution and twice with 100 cc. of water. The material was distilled. The monoester fraction boiling mainly at 235° C. at 0.1 mm. weighed 126 g. (86.5% yield) and had the properties set out in Table I below.

EXAMPLE 4

To illustrate the lubricating nature of the ester of Example 1, it was blended with 7.0 wt. percent of a polymeric methacrylate ester having about 9 carbon atoms in the side chains. This material is commercially available as a viscosity index improver. The standard inspections on the blend are set out in Table I below.

EXAMPLE 5

A synthetic ester lubricating oil comparable to that of Example 1 above was prepared by esterifying the coconut

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fatty acids with a C₁₆ Oxo alcohol. This alcohol was prepared by oxonating a C₁₅ polypropylene fraction in the Oxo process. The preparation was as follows:

A mixture of 440 g. (2.2 moles) of C₁₆ Oxo alcohol, 438 g. (2 moles) of coconut fatty acids, 4 g. of NaHSO₄ catalyst and 100 g. toluene was refluxed at 114° C. to 165° C. for a period of one hour during which time 37 cc. of water were collected (theory is 38 cc.). This mixture was diluted with 250 g. toluene and washed once with 100 cc. of 5% Na₂CO₃ and three 100 cc. portions of water. The material was then distilled. The monoester boiled over the range 187°–203° C. at 0.08 mm.

EXAMPLE 6

The C₁₆ Oxo alcohol as was used in Example 5 above was used in this example to esterify a C₁₃ Oxo acid prepared by oxidation of a C₁₃ Oxo alcohol via alkali fusion. The C₁₃ Oxo alcohol was prepared by the oxonation of a C₁₂ polypropylene fraction in the Oxo process. The ester was prepared as follows:

C₁₆ Oxo alcohol (121 g., 0.5 mole), C₁₃ Oxo acid (113 g., 0.53 mole), NaHSO₄ (1.2 g.) and toluene (75 g.) were heated to 162° C. for 4 hours. The water collected was 8.3 cc. After washing the ester with 2% Na₂CO₃ and water it was distilled. The fraction boiling at mainly 200°–210° C. at 0.1 mm. had the properties set out in Table I below.

EXAMPLE 7

In this example the C₁₆ Guerbet alcohol, prepared as described in Example 1 above, was used to esterify the C₁₃ Oxo acid of Example 6 above. This preparation was the same as described in Example 6. The product, distilling largely at 190°–200° C. at 0.05 mm., had the properties as set out in Table I below.

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To summarize briefly, the instant invention relates to synthetic lubricating compositions having outstanding lubricating characteristics at high and low temperatures which comprises ester materials of the formula



wherein R and R' are selected from the group of aliphatic monobasic acids having from about 8 to 18 carbon atoms in straight chain configuration, or substantially straight chained, and branched chain primary monohydric alcohols containing from about 12 to about 28 carbon atoms which contains one major side chain of from 4 to 14 carbon atoms. When R is branched, R' must be straight, and vice versa.

The synthetic lubricating compositions according to this invention may be used as such, or they may be blended with other lubricants, either natural mineral oils, or other synthetic lubricants. They are completely compatible with the various additive materials known to the lubrication art, and such materials as viscosity index improvers, pour point depressants, detergent inhibitors, oxidation inhibitors, extreme pressure agents, and the like, may be blended with these materials to enhance special characteristics. The synthetic lubricants of invention may be blended with any of the commonly used grease making soaps to form solid or semi-solid lubricants.

What is claimed is:

1. A lubricating composition having an ASTM pour point below about +35° F., an ASTM flash point above about 375° F., and a viscosity at 210° F. of about 2 to 13 centistokes which comprises an ester of the formula



wherein R and R' are alkyl groups selected from the class consisting of alkyl radicals having a straight chain con-

Table I
PROPERTIES OF SYNTHETIC LUBRICANTS
[Comparison of Oxo versus Guerbet alcohol derived monoesters]

Ex. No.	Ester	Viscosity, Cs. @ ° F.				V. I.	Pour Point, ° F.	Flash Point, ° F.	ASTM Slope 210°/			Hydrogen Combustion Test, ¹ mgs.	
		210	100	0	-40				100° F.	0° F.	-40° F.	Total Deposit	Varnish
1	C ₁₆ Guerbet Coconate	3.51	15.11	293	2,623	128	-60	425	0.736	0.732	0.727	5.5	1.8
2	n-C ₁₅ Guerbet Coconate ²	3.13	11.67	140	viscous	148	-10	420	0.711	0.696	0.700	6.7	1.9
3	C ₁₆ Guerbet Coconate	6.80	39.30	1,657	25,057	118	-70	+430	0.713	0.708	0.700	6.7	1.9
4	C ₁₆ Guerbet Coconate +7% Acryloid 747	7.25	31.84	593	viscous	164	-50	425	0.578	0.595	0.700	6.7	1.9
5	C ₁₆ Oxo Coconate	4.12	18.77	568	solid	142	-25	430	0.714	0.740	0.700	3.4	0.7
6	C ₁₆ Oxo C ₁₃ Oxoate	4.72	27.32	1,630	37,100	93	-65	425	0.767	0.782	0.778	1.7	0.9
7	C ₁₆ Guerbet C ₁₃ Oxoate	3.98	22.07	1,028	19,611	74	-75	395	0.792	0.787	0.792	5.6	1.4

¹ 5 gm. sample placed in a tared beaker and ignited. Total incombustible material reported varnish and carbon. Carbon removed mechanically and beaker re-weighed to obtain varnish.

² Made from n-C₈ alcohol.

Examination of the data of Table I above points out the superiority of the esters of the invention over similar esters having an equal number of carbon atoms. It is shown by the data above that the Guerbet esters are superior to the Oxo esters by virtue of the lower pour points, better low temperature viscosities, and a downward curvature when viscosity is plotted on the ASTM chart against temperature. All of the Guerbet esters have decreasing ASTM slopes whereas the Oxo esters show increasing slopes in the lower temperature regions. This downward curvature of the slope indicates much better properties at temperatures where viscosity increase is very material.

With 7.0% of a commercially available polymethacrylate viscosity index improver, the C₁₆ Guerbet ester is thickened to the point at which its low temperature viscosity nears the low temperature viscosity of the C₁₆ Oxo ester. The former ester is then far superior in high temperature characteristics, as well as in pour point, viscosity index, and ASTM slope.

figuration and containing from about 8 to about 18 carbon atoms and alkyl radicals containing from about 12 to about 28 carbon atoms in a configuration such that there is present one major side chain containing from about 4 to about 14 carbon atoms, and wherein one of said alkyl groups has a branched chain configuration and the other alkyl group has a straight chain configuration.

2. A lubricating composition having an ASTM pour point below about +35° F., an ASTM flash point above about 375° F., and a viscosity at 210° F. of about 2 to 13 centistokes which comprises an ester of the formula



wherein R is the alkyl radical of an aliphatic monobasic acid having from about 8 to about 18 carbon atoms in straight chain configuration and wherein R' is the alkyl radical of a branched chain primary monohydric alcohol containing from about 12 to about 28 carbon atoms and which contains one major side chain of from 4 to 14 carbon atoms.

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3. A synthetic lubricating composition according to claim 2 wherein R contains an average of 12.5 carbon atoms.

4. A lubricating composition having an ASTM pour point below about +35° F., an ASTM flash point above about 375° F., and a viscosity at 210° F. of about 2 to 13 centistokes which comprises an ester of the formula



wherein R is the alkyl radical of a branched chain aliphatic monobasic acid containing from about 12 to about 28 carbon atoms and containing one major side chain of

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from 4 to 14 carbon atoms and wherein R' is the alkyl radical of a primary aliphatic monohydric alcohol containing about 8 to 18 carbon atoms in straight chain configuration.

References Cited in the file of this patent

- "Structural Guides for Synthetic Lubricant Developments," I. & E. Chem., vol. 42, No. 12, December 1950, page 2417 pertinent.
- "Aliphatic Esters," I. & E. Chem., vol. 45, No. 8, August 1953, page 1768 pertinent.