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(54) Synthetic lubricant base stock formed from high content branched chain acid mixtures

Aus mit einem hohen Gehalt an verzweigt-kettigen Säuremischungen hergestellte synthetische Grundschnmieröle

Base lubrifiante synthétique formée à partir de mélanges d'acides dont une grande partie à chaînes ramifiées

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EP-A- 0 498 152 FR-A- 1 553 235
FR-A- 2 034 835 US-A- 4 826 633

• **PATENT ABSTRACTS OF JAPAN vol. 4, no. 159**
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The file contains technical information submitted after the application was filed and not included in this specification

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Description**BACKGROUND OF THE INVENTION**

5 [0001] This invention relates to a synthetic ester base stock and, in particular, to a synthetic ester base stock formed from an acid mixture having a high content of branched chain acid, and a lubricant from the base stock having increased viscosity at elevated temperatures and a decreased tendency to form deposits in high temperature uses.

[0002] Synthetic ester base stocks for use as chain oils and lubricants for gas turbine engines are well known. The base stocks are combined with standard lubricant additive packages to form the lubricant. In order for the lubricant to
10 have properties suitable for such high temperature use, the base stock must have certain physical properties. For example, it is a requirement that the lubricant for turbine oils meet the specifications set forth in military specification MIL-L-23699D. Chain oils should have low deposition properties at high temperatures, a viscosity of at least about 7.0 centistokes (cSt) and a reasonably low pour point below its ambient storage temperature.

[0003] In general, synthetic high temperature lubricants use esters as a base stock. The esters are formed by reacting a polyol, such as pentaerythritol, either monopentaerythritol (MPE) and/or dipentaerythritol (DPE) or trimethylolpropane (TMP) with various acids, both straight chain and branched. Japanese patent applications No. JP 55-105644 and No. 55-157537 disclose a neopentyl polyol ester of iso-C₉ acid and a straight chain saturated acid having from 4 to 18 and 2-24 carbon atoms, respectively, preferably 6 to 14 carbon atoms for air compressor oils. U.S. Patent No. 4,826,633, issued on May 2, 1989 and owned by the assignee herein, is directed to an ester base stock for a turbine oil
15 formed by reacting MPE and/or TMP with an acid mixture of straight chain C₅-C₁₀ acids and 5 to 40 weight percent branched chain C₇-C₁₀ acids. Lubricants formed from these esters have a decreased tendency to form deposits and have acceptably low pour points without use of DPE.

[0004] Several other United States patents disclose additional types of esters. For example, U.S. Patent No. 3,694,382, issued to Kleiman, et al. on September 26, 1972, discloses an ester blend for use as a synthetic lubricant.
20 The ester blend includes esters of trimethylolpropane and dipentaerythritol formed from a mixture of aliphatic monocarboxylic acids.

[0005] U.S. Patent No. 4,049,563, issued to Burrous on September 20, 1977, discloses a jet engine oil consisting of an ester of a C₄-C₁₂ monocarboxylic acid, a polyol selected from pentaerythritol, dipentaerythritol, tripentaerythritol, trimethylolpropane, trimethylolmethane, trimethylolbutane, neopentylglycol and mixtures thereof and a soluble methyl
25 phenyl polysiloxane.

[0006] U.S. Patent No. 4,064,058, issued to Walker on December 20, 1977, discloses a grease base stock including a blend of a normally liquid pentaerythritol ester product and a neopentyl glycol ester product.

[0007] U.S. Patent No. 3,360,465, issued to Warman on December 26, 1967, discloses synthetic ester lubricant compositions of pentaerythritol mixed esters. The pentaerythritol utilized includes at least 1.5 weight percent dipentaerythritol. The acid includes a mixture of from two to six monocarboxylic alkanolic acids having from five to nine carbon
30 atoms with some of the lower acids being branched chain.

[0008] Lubricant compositions containing pentaerythritol esters are also disclosed in EP-A-0 458 584 and EP-A-0 498 152.

[0009] Every lubricant has a characteristic tendency to form deposits when used in high temperature applications such as an engine or on industrial oven chains. If the deposits are excessive they will detract from the operating efficiency of the device and create other problems such as filter plugging in engines or track jumping of chains.

[0010] Accordingly, it is desirable to provide a synthetic lubricant base stock which provides lubricants having acceptable high temperature viscosity properties with improved resistance to formation of carbon deposits when used in high temperature applications.
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SUMMARY OF THE INVENTION

[0011] Generally speaking, in accordance with the invention, an improved synthetic ester base stock is prepared by reacting at least one neopentyl polyol of the type defined in claim 1 below, with a monocarboxylic acid mixture including
40 at least one C₅-C₁₀ normal alkanolic acid and between 60 and 90 weight percent of C₇-C₁₀ branched chain acid, based on the total weight of the acid charged. The polyol is a commercially available technical pentaerythritol. The straight chain monocarboxylic acids include those having between 5 and 10 carbon atoms, such as valeric acid (pentanoic acid), caproic acid (hexanoic acid), oenanthic acid (heptanoic acid), caprylic acid (octanoic acid), pelargonic acid (nonanoic acid), capric acid (decanoic acid) and mixtures thereof. The branched chain acid is preferably iso-C₉ acid, isononanoic acid. When mixed with a standard lubricant additive package the synthetic ester base stock prepared in accordance with the invention provides a lubricant having a viscosity at 98.9°C (210° F.) of at least 7.0 centistokes and remains cleaner at high chain oil operating temperatures than conventional chain oils.

[0012] Accordingly, it is an object of the invention to provide an improved synthetic ester base stock.
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[0013] Another object of the invention is to provide an improved synthetic ester base stock having a decreased tendency to form deposits when used in a high temperature environment.

[0014] A further object of the invention is to provide an improved synthetic ester base stock for high temperature applications and with a suitably higher viscosity.

[0015] Yet another is to provide a synthetic ester base stock with higher oxidative stability.

[0016] Still another object of the invention is to provide a synthetic ester base stock which when combined with a standard lubricant additive package provides a lubricant with a viscosity at 98.9°C (210° F.) of at least 7.0 centistokes and a pour point of less than -23°C (-10°F).

[0017] Still another object of the invention is to provide the use of a synthetic ester lubricant base stock as defined in claim 10 appended hereto as a high temperature chain oil lubricant base stock.

[0018] Still other objects and advantages of the invention will in part be obvious and will in part be apparent from the specification.

[0019] The invention accordingly comprises a composition of matter possessing the characteristics, properties and the relation of components which will be exemplified in the composition hereinafter described, and the scope of the invention will be indicated in the claims.

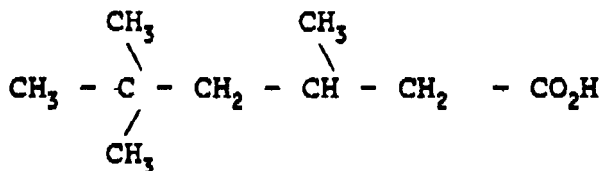
[0020] The synthetic lubricant base stock prepared in accordance with the invention is to be used with standard lubricant additive packages. The lubricant base stock is the reaction product of a neopentyl polyol as defined in the claims and a monocarboxylic acid mixture having a high branched chain acid content, preferably between about 60-90 weight percent of a branched chain acid, based on the total acid charge. When the base stock is mixed with a standard lubricant additive package, the lubricant has a viscosity at 98.9°C (210°F) of at least 7.0 centistokes and a pour point of less than -23°C (-10°F).

[0021] The neopentyl polyol comprises monopentaerythritol, C₅H₁₂O₄ (MPE, CAS #=115-77-5) which is a colorless solid with melting point of 255°-259°C; and dipentaerythritol, C₁₀H₂₂O₇ (DPE, CAS #=126-58-9) which is a colorless solid having a melting point of 215°-218°C; the commercially available technical grade pentaerythritol which is used in accordance with the invention including monopentaerythritol and typically between about 6 to 15 weight percent dipentaerythritol. In the preferred embodiments of the invention, the polyol is technical grade PE which includes about 12 weight percent DPE.

[0022] The acid component is monocarboxylic and includes at least one straight chain acid having 5 to 10 carbon atoms and a branched chain acid having from 7 to 10 carbon atoms. The branched chain acid preferably has nine carbon atoms, namely, iso-nonanoic acid. Suitable straight chain acids include, but are not limited to, valeric acid, oleanthic acid, caprylic acid, pelargonic acid and capric acid. Preferably, the straight chain acid component is valeric (C₅) or is a mixture of heptanoic (C₇) and caprylic-capric (C₈-C₁₀). The caprylic-capric acid is identified as having between 8 and 10 carbon atoms, but actually includes C₆ to C₁₂ acids and is substantially free of C₁₂ acid (less than 1%).

[0023] The amount of the preferred heptanoic and caprylic-capric mixture straight chain acid component suitable for use in preparing esters in accordance with the invention may vary widely. For example, the mixture may be from 30 to 70 weight percent heptanoic acid and the balance the caprylic-capric mixture. In a preferred embodiment, the normal acid mixture is 40-60 parts by weight of heptanoic acid and the balance caprylic-capric acids.

[0024] The branched chain acid may be iso-C₇ acid, iso-C₈ acid, iso-C₉ acid or iso-C₁₀ acid. Preferably, the branched chain acid used is the iso-C₉ acid or iso-nonanoic acid, specifically known as 3,5,5-trimethylhexanoic acid (3,5,5-trimethylhexanoic acid CAS # = [03302-10-1]). As used herein, iso-C₉ or iso-nonanoic acid is 3,5,5-trimethylhexanoic acid and has the formula:



Addition of the iso-nonanoic acid provides the necessary viscosity characteristics and improves the pour point characteristics of the base stock and improves the oxidative stability and deposition tendency.

[0025] The iso-acids other than iso-nonanoic can be used to provide base stocks which are suitable for turbine engine or chain lubricant applications. For example, iso-C₇, iso-C₈ and iso-C₁₀ acids are available, but these acids contain a complex mixture of isomers, unlike iso-C₉ acid which is mainly 3,5,5-trimethylhexanoic acid. The physical properties of an acid that is a complex mixture of isomers can change if the relative ratios of the isomeric components change and this affects the properties of an ester produced from the acid. Therefore, to produce a consistent ester product, it is preferable to use raw materials that consist of a single, high purity component, namely, iso-C₉ or iso-nonanoic acid.

[0026] The acid mixture is present in the reaction in an excess of about 5 to 10 weight percent for the amount of the polyol mixture used. The excess acid is used to force the reaction to completion. The excess acid is not critical to carrying out the reaction except that the smaller the excess, the longer the reaction time. After the reaction is complete, the excess acid is removed by stripping and refining. Generally, the esterification reaction is carried out in the presence of conventional catalysts. For example, a tin or titanium based catalyst of such a catalyst may be used. Tin oxalate is an example.

[0027] Lubricants including ester base stocks prepared in accordance with the invention are prepared by mixing a conventional additive package to the base stocks in conventional concentrations. Typical additive packages are described in U.S. Patent Nos. 4,124,513, 4,141,845 and 4,440,657. The two former patents describe additive packages based on an alkylphenyl or alkarylphenyl naphthylamine, a dialkyldiphenylamine, a polyhydroxy anthraquinone, a hydrocarbyl phosphate ester with an S-alkyl-2-mercaptobenzotriazole or an N-(alkyl)-benzothiazole-2-thione. The third patent describes additives of a selected tertiarybutylphenyl substitute phosphate and a selected alkyl amine.

[0028] The invention will be better understood with reference to the following examples. All percentages are set forth in percent by weight. These examples are presented for purposes of illustration only and are not intended to be construed in a limiting sense.

Examples 1-12

[0029] A variety of ester base stocks were prepared. In each of the following runs the raw materials identified in the Table and a tin oxalate catalyst were charged to a stirred reactor capable of attaining 238°-254°C (460°-490° F.) and a vacuum of at least 736.6 mm (29 inches) of mercury. The reactor was provided with a nitrogen sparge or blanket. The charge was heated to a reaction temperature between about 226.7° and 232.2° (440° and 450° F.) and the water of reaction was collected in a trap while the acids were returned to the reactor. As reflux slowed, vacuum was applied in order to maintain a reasonable reflux rate. When the hydroxyl value was reduced to a sufficiently low level (a maximum of 5.0 mg KOH/gm), the bulk of the excess acid was removed by distillation at the reaction temperature and maximum vacuum. The residual acidity was removed by treatment with lime and water. The resulting ester base stock was dried and filtered.

[0030] The viscosity at 98.9°C (210° F.) was determined in accordance with ASTM D-445 for each sample base stock together with the pour point in accordance with ASTM D-97.

TABLE I

Table Run					
RAW MATERIAL	1	2	3	4	5
Tech PE	17.1	17.8	14.8	--	15.3
Mono PE	--	--	--	14.4	--
Di PE	--	--	--	--	--
Valeric	--	12.2	--	--	--
Heptanoic	12.4	--	--	--	--
Caprylic-Capric	12.4	--	--	--	--
Isononanoic	58.1	70.0	42.6	42.8	59.3
Dodecanoic	--	--	42.6	42.8	25.4
PHYSICAL PROPERTIES					
Viscosity @ 98.9°C (210°F), cSt	8.91	9.9	10.1	9.51	10.6
Viscosity Index	114	97	129	128	110
Pour Point, °C (°F)	-42.8 (-45)	-34.4 (-30)			-37.2 (-35)
Freeze Point, °C (°F)			-1.1* (+30)	15.5* (+60)	

* Product Crystallizes at Room Temperature; Freeze point data are approximate since some liquid remains

[0031] Lubricants prepared in accordance with the invention have a decreased tendency to form deposits when used in high temperature applications. This reduced tendency was demonstrated by mixing base stock with an additive package as follows:

Additive Package For Panel Test Work

[0032]

Component	Parts by Weight
Base Stock	100
Tricresyl Phosphate	2.0
p,p'-Dioctyl-diphenylamine	1.0
Octylphenyl- α -naphthylamine	1.0
Benzotriazole	0.05

[0033] This additive package was selected as the standard package for comparing base stocks in the panel test.

[0034] In this bench panel test, a stainless steel panel is electrically heated by means of two heaters which are inserted into holes in the panel. The temperature is monitored by means of a thermocouple. The panel is placed on a slight incline and heated to 282.2°C (540° F.) The lubricant to be tested is dropped onto the heated panel and the characteristics are observed. The lubricant contacts the panel near the top of the incline and is observed as a central dark band. The lubricant then tends to thin out as it travels towards the lower end of the heated panel. It is along the oil-air-metal interface that the degradation of the lubricant is best observed.

[0035] The results of the panel test for compositions prepared in accordance with the composition of Run 1-2 of the Example showed little degradation along the oil-air-metal interface. These lubricants are an ester mixture formed by reacting technical grade pentaerythritol with an acid mixture including valeric or heptanoic and capric-caprylic as the normal acid and iso-nonanoic acids.

[0036] Runs 3-5 were lubricants formed from base stocks prepared by reacting technical grade PE or MPE and dodecanoic acid consistent with Runs 5 and 6 of Example 1 in JP 55-105644. The panel test results for a lubricant made from these esters formed from dodecanoic acid showed significantly increased carbonization along the oil-air-metal interface compared to Runs 1-2.

[0037] By preparing an ester from technical grade pentaerythritol and an acid mixture of a C₅-C₁₀ straight chain acid and a high iso- C₇ to C₁₀ acid content, synthetic ester lubricants having improved properties may be obtained. The lubricants have improved oxidation stability with lower depositing tendency at high temperatures, a viscosity at 98.9°C (210°F) of at least 7.0 cSt and improved pour points. Preferably, the iso-acid is iso-C₉ acid and is present from 60 to 90 weight percent of the total acid charge. Thus, the straight chain acid will be present from 10 to 40 weight percent of the acid charge which maintains good pour point characteristics and an improved viscosity index. When linear acids above C₁₀ are used, the resulting esters tend to crystallize at ambient temperatures. When linear acids having less than five carbon atoms are used, odor and corrosion problems arise.

Claims

1. A synthetic ester lubricant base stock, comprising the reaction product of:

a technical grade of pentaerythritol which is a mixture of monopentaerythritol and between about 6 and 15 weight percent dipentaerythritol; and

an acid mixture including (1) at least one straight-chain acid having between 5 and 10 carbon atoms and (2) an iso-acid selected from the group consisting of iso-C₇ acid, iso-C₈ acid, iso-C₉ acid, iso-C₁₀ acid and mixtures thereof;

the iso-acid being present in an amount of from 60 to 90 percent by weight of the acid mixture;

and

the resulting mixture of esters when admixed with a synthetic ester lubricant additive package having a viscosity at 98.9°C (210°F) of at least 7.0 centistokes.

2. The synthetic ester lubricant base stock of Claim 1, wherein the iso-acid is iso-nonanoic acid.
3. The synthetic ester lubricant base stock of Claim 1, wherein the iso-C₉ acid is 3,5,5-trimethylhexanoic acid.
- 5 4. The synthetic ester lubricant base stock of Claim 2 wherein the straight-chain acid(s) is/are a mixture of heptanoic acid (C₇) and caprylic-capric acid (C₈-C₁₀).
- 5 5. The synthetic ester lubricant base stock of Claim 4 wherein the C₇ and C₈-C₁₀ straight-chain acids are present in about equal amounts by weight.
- 10 6. The synthetic ester lubricant base stock of Claim 5 wherein the iso-nonanoic acid is present from 65 to 75% by weight of the acid mixture.
- 15 7. The synthetic ester lubricant base stock of Claim 2 wherein the normal acid is valeric acid.
8. The synthetic ester lubricant base stock of Claim 1, admixed with an effective amount of a synthetic ester lubricant additive package for improving the high temperature properties and the load factor of a lubricant.
- 20 9. A synthetic ester lubricant base stock according to anyone of the preceding claims wherein iso-nonanoic acid is present from 65% to 75% by weight of the acid mixture.
10. The use as a high temperature chain oil lubricant base of a synthetic ester lubricant base stock as defined in any one of the preceding claims.

25 Patentansprüche

1. Synthetisches Esterschmiermittel-Grundeinsatzmaterial, das das Reaktionsprodukt des folgenden umfaßt;

30 Pentaerythritol technischer Güte, das ein Gemisch von Monopentaerythritol und zwischen ungefähr 6 und 15 Gew.-% Dipentaerythritol ist; und

ein saures Gemisch, das (1) zumindest eine geradkettige Säure mit zwischen 5 und 10 Kohlenstoffatomen und (2) eine Iso-Säure einschließt, die aus der Gruppe ausgewählt ist, die aus Iso-C₇-Säure, Iso-C₈-Säure, Iso-C₉-Säure, Iso-C₁₀-Säure, und Mischungen hiervon ausgewählt ist;

35 wobei die Iso-Säure in einer Menge von 60 bis 90 Gew.-% des sauren Gemisches vorliegt; und

das sich ergebende Gemisch von Estern, wenn es mit einem synthetischen Esterschmiermittel-Additiv-Paket gemischt wird, eine Viskosität bei 98,9°C von zumindest 7,0 Centistoke aufweist.

40 2. Synthetisches Esterschmiermittel-Grundeinsatzmaterial nach Anspruch 1, bei dem die Iso-Säure Iso-Nonansäure ist.
3. Synthetisches Esterschmiermittel-Grundeinsatzmaterial nach Anspruch 1, bei dem die Iso-C₉-Säure 3,5,5-Trimethylhexansäure ist.
- 45 4. Synthetisches Esterschmiermittel-Grundeinsatzmaterial nach Anspruch 2, bei dem die geradkettige Säure(n) ein Gemisch aus Heptansäure (C₇) und Capryl-Caprin-Säure (C₈ - C₁₀) ist/sind.
- 50 5. Synthetisches Esterschmiermittel-Grundeinsatzmaterial nach Anspruch 4, bei dem die geradkettigen C₇ und C₈ - C₁₀-Säuren bezogen auf das Gewicht in ungefähr gleichen Mengen vorliegen.
6. Synthetisches Esterschmiermittel-Grundeinsatzmaterial nach Anspruch 5, bei dem die Iso-Nonansäure von 65 bis 75 Gew.-% des sauren Gemisches vorliegt.
- 55 7. Synthetisches Esterschmiermittel-Grundeinsatzmaterial nach Anspruch 2, bei dem die Normalsäure Valeriansäure ist.

8. Synthetisches Esterschmiermittel-Grundeinsatzmaterial nach Anspruch 1, das mit einer wirksamen Menge eines synthetischen Esterschmiermittel-Additiv-Paketes zur Verbesserung der Hochtemperatur-Eigenschaften und des Belastungsfaktors eines Schmiermittels vermischt wird.

5 9. Synthetisches Esterschmiermittel-Grundeinsatzmaterial nach einem der vorhergehenden Ansprüche, bei dem Iso-Nonansäure von 65 bis 75 Gew.-% des sauren Gemisches vorliegt.

10. Verwendung als Hochtemperatur-Kettenölschmiermittel-Grundlage eines synthetischen Esterschmiermittel-Grundeinsatzmaterials, wie in einem der vorhergehenden Ansprüche definiert.

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Revendications

1. Base lubrifiante d'ester synthétique comprenant le produit de la réaction de:

15 un pentaérythritol de qualité technique qui est un mélange de monopentaérythritol ayant entre 6 et 15 % en poids de dipentaérythritol; et
un mélange d'acides comprenant (1) au moins un acide à chaîne droite ayant entre 5 et 10 atomes de carbone et (2) un iso-acide choisi dans le groupe consistant en iso-C₇ acide, iso-C₈ acide, iso-C₉ acide, iso-C₁₀ acide et des mélanges de ceux-ci;
20 l'iso-acide étant présent en une quantité de 60 à 90% en poids du mélange d'acides; et
le mélange résultant d'esters lorsqu'il est mélangé avec un d'additif lubrifiant d'ester synthétique ayant une viscosité à 98,9°C (210°F) d'au moins 7.0 centistokes.

2. La base lubrifiante d'ester synthétique de la revendication 1 dans lequel l'iso-acide est l'acide isononanoïque.

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3. La base lubrifiante d'ester synthétique de la revendication 1 dans lequel l'iso-C₉ acide est l'acide 3,5,5-triméthylhexanoïque.

4. La base lubrifiante d'ester synthétique de la revendication 2 dans lequel les acides à chaîne droite est/sont un mélange d'acide heptanoïque (C₇) et d'acide caprylique-caprique (C₈-C₁₀).

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5. La base lubrifiante d'ester synthétique de la revendication 4 dans lequel le ou les acide(s) en C₇ et C₈-C₁₀ à chaîne droite est/sont présent(s) en quantités environ égales en poids.

35 6. La base lubrifiante d'ester synthétique de la revendication 5 dans lequel l'acide iso-nonanoïque est présent en 65 à 75% en poids du mélange d'acides.

7. La base lubrifiante d'ester synthétique de la revendication 2 dans lequel l'acide normal est l'acide valérique.

40 8. La base lubrifiante d'ester synthétique de la revendication 1 mélangé avec une quantité efficace d'additif de lubrifiant d'ester synthétique pour améliorer les propriétés à température élevée et le facteur de charge d'un lubrifiant.

9. La base lubrifiante d'ester synthétique selon l'une quelconque des revendications précédentes dans lequel l'acide iso-nonanoïque est présent en 65 à 75% en poids du mélange d'acides.

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10. L'utilisation d'une base lubrifiante d'huile de chaîne de haute température d'un base lubrifiante d'ester synthétique telle que définie selon l'une quelconque des revendications précédentes.

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