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(54) **Lubricating oil compositions.**

(57) This invention relates to a lubricating oil composition which has a major proportion of a biodegradable base fluid which is a blend of (a) at least one ester of isotridecyl alcohol and a mono-, di or polycarboxylic acid, and (b) at least one hydrocarbon oil which has no more than 10%w/w of aromatic hydrocarbons, the rest being aliphatic. The proportion of (a) in the blend is from 25-55%w/w. The biodegradability of the base fluid renders the composition more environmentally friendly.

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The present invention relates to environmentally friendly lubricating oil compositions for automotive engines. Lubricating oil compositions for use in automotive engines are well known. These compositions usually contain a base fluid which may comprise mineral oils, hydrocarbon oils and/or synthetic fluids and conventional additives such as viscosity index (hereafter "VI") improvers, anti-oxidants, corrosion inhibitors, dispersants, anti-wear additives and sludge control agents. In recent years, automotive engine oil development has seen a steady trend towards lower viscosity multigrades, principally to improve fuel efficiency. The predominant viscosity grade has moved from a typically 20W/50 oil to a 10W/40 or a 5W/40 oil. The manufacturers of automotive engine equipment have also tightened the specifications for such oils in terms of oil consumption, bearing protection and shear stability. This has meant that the engine lubricant has had to become lower in volatility and more shear stable so that these thinner oils stay in the specified grade band longer. As a result, lubricating oils compositions based solely on conventional solvent refined mineral oils are no longer adequate to meet these stringent performance requirements. To meet these performance requirements, a growing demand has arisen for "special" base oils possessing superior qualities of volatility, VI and pour point. These special base oils have a VI above 120 and the requirement is primarily met by the use of paraffinic base oils which include inter alia oils based on hydrocracked wax distillates. It has also been suggested to use blends of such hydrocracked wax distillates with aliphatic esters in order to improve the performance of such base oils. These prior art compositions usually contain 80% w/w or more of a hydrocarbon or mineral oil and upto 20% w/w of an aliphatic carboxylic acid ester in the base fluid. Such compositions, whilst being very efficient and being to some extent biodegradable, still leave room for improvement.

It has now been found that base oil blends can be formulated which not only improve the biodegradability thereof but achieve the same without loss of performance at the same time exhibiting relatively lower emissions, lower fuel consumption and lower oil consumption.

Accordingly, the present invention is a lubricating oil composition which has a major proportion of a base fluid which fluid comprises a blend of:

a) at least one ester derivable from isotridecyl alcohol and at least one aliphatic mono-, di- or polycarboxylic acid, and

b) at least one hydrocarbon oil comprising upto 99.5% w/w of aliphatic hydrocarbons and no more than 10% w/w aromatic hydrocarbons such that the total of aliphatics and aromatics is 100% wherein the amount of component (a) in the blend is in the range from 25-55% w/w.

As described above, the base fluid comprises a blend of an ester and a hydrocarbon oil. The ester component (a) is derivable by the reaction of an aliphatic mono-, di- and/or poly-carboxylic acid with, isotridecyl alcohol under esterification conditions.

Specific examples of such esters include the isotridecyl esters of octane-1,8-dioic acid, 2-ethylhexane-1,6-dioic acid, nonane-1,9-dioic acid, decane-1,10-dioic acid and dodecane-1,12-dioic acid.

Similarly, the hydrocarbon oil component (b) in the blend suitably is a hydrocracked wax distillate. More specifically, such hydrocarbon oils can contain upto 99.5% w/w, preferably upto 97% w/w, of aliphatic hydrocarbons and no more than 10% w/w of aromatic hydrocarbons. The expression "aliphatic hydrocarbons" as used herein and throughout the specification is meant to include open chain aliphatic hydrocarbons as well as cycloaliphatic hydrocarbons such as e.g. naphthenic hydrocarbons. The total polycyclic aromatic hydrocarbons in the hydrocarbon oil is suitably less than 10 ppm, preferably less than 5 ppm and more preferably less than 1 ppm. Typically such hydrocarbon oil contains from 92-97% w/w of aliphatics and 3-8% w/w of aromatics.

The hydrocarbon oil component (b) in the blend is suitably prepared by feeding a waxy distillate through a hydrocracker at 70-95% conversion under elevated temperature and hydrogen pressure. In the first stage of this hydrocracker, sulphur and nitrogen compounds are removed and in the second stage the aromatics are hydrogenated to naphthenes; the hydrogenated products including the naphthenes are cleaved and rearranged to produce a controlled range of paraffins and isoparaffins. Fuels and lubricant products are separated by atmospheric distillation from the resultant hydrocracked products and the 5-35% heavy component is the hydrocarbon fraction used as the hydrocarbon oil component (b) in the blend. A product produced by this method is substantially free of any unsaturates. This feedstock can be further refined, if necessary, by conventional techniques such as additional fractionation, extraction or dewaxing to obtain the finished product. The resultant hydrocarbon oil has the following physical characteristics:

Colour (ASTM D 1500)	1.5 Max
Density (ASTM 1298)	0.83
KV(40 °)/cSt (ASTM D 445)	17.28
KV(100 °C)/cSt (ASTM D 445)	3.99 - 4.22
VI (ASTM D 2270)	123 - 128
Pour point/ °C (ASTM D 97)	-24 - -27
% S (XRF NFM 07053)	0.08 - 0.15
Total N/ppm	ca 12
Aromatics by HPLC/%	ca 7.7
Aliphatics By HPLC/%	ca 92.3
Polycyclic aromatics/ppm -	0.1

Of the aliphatic hydrocarbons in this hydrocarbon oil component (b), about 20% w/w comprises isoparaffins having an average carbon number of about 27.

The relative amounts of the ester component (a) and the hydrocarbon oil component (b) in the base fluid within the specified ranges above will depend upon the nature of the two components and their relative viscosities. For instance, if the hydrocarbon component (b) is within the physical characteristic specification defined above, and the ester component (a) is isotridecyldodecanedioate, the amount of ester (a) in the blend may suitably vary from 30-50% w/w, preferably from 40-50% w/w.

In addition to the above blended base fluid, the lubricating composition of the present invention comprises minor proportions of conventional additives which include inter alia the following: one or more sludge dispersants, one or more VI improvers, one or more anti-wear additives, and one or more anti-oxidants. Typically, the additive package used is known to comprise components which meet the stringent requirements of an API Performance Classification "SG". These requirements include successful testing in the following categories: rust test, dispersancy test, piston varnish test, low temperature sludge test and wear test. Such additives are commercially available as an additives package sold e.g. as an "SG Additive Package" under the names GBX 2900 and GBX 2905 (both ex Adibis Ltd, UK). Such an additive package suitably forms from 10-20% w/w, preferably from 11-16% w/w of the formulated lubricating composition. Examples of compounds that may be present in such a package include anti-rust agents such as the overbased calcium or magnesium sulphonates or phenates; anti-wear agents such as the zinc dithiophosphates, preferably the zinc dialkyl dithiophosphates containing 5-15% w/w phosphorus (normally prepared using a mixture of secondary alcohols and representing 0.05% -0.5% w/w of phosphorus, typically 0.1-0.14% phosphorus in the finished oil); ashless dispersancy agents such as derivatives of long chain hydrocarbon substituted succinimides, especially the polyisobutenyl succinimides; and sludge dispersants which are oil soluble salts such as amides, imides, oxazolines and esters of mono- or di-carboxylic acids or anhydrides.

The anti-oxidants typically contain phenolic compounds and a typical antioxidant is commercially available as ADX 545A (ex Adibis Ltd). The anti-oxidants are suitably present in an amount from 0.01-5% w/w, preferably from 0.1-2.0% w/w of the formulated lubricating composition.

The lubricating compositions also contain one or more VI improvers. Examples of such VI improvers include polymethacrylate type dispersants commercially sold as Plexol 1420 VX (Regd Trade Mark, ex Rohm GmbH) and hydrotreated polyisoprenes commercially sold as Shellvis 200 (Regd Trade Mark, ex Shell UK Ltd). In the case of the latter, it may used as a solution in the hydrocarbon oil component (b) above. The VI improvers are suitably present in an amount from 2 to 5% w/w of the formulated lubricating composition. Thus a typical formulated lubricating composition (A) can be represented by the following components in w/w %:

SG Additives Package (GBX 2905, ex Adibis Ltd)	15.4
ADX 545A (anti-oxidant, ex Adibis Ltd)	1.0
Plexol* 1420 (VI improver, ex Rohm GmbH)	3.1
Shellvis* 200 (VI improver, 10% soln, ex Shell UK Ltd)	6.0
Isotridecyldodecanedioate	22.59 and
Hydrocarbon oil**	52.71

* Registered Trade Mark

** The hydrocarbon oil is a hydrotreated wax distillate containing 92.3% w/w aliphatics and 7.7% w/w aromatics which is substantially free of any unsaturates and had a polycyclic aromatic content of about 0.1 ppm. An oil of this type is described above.

Variations of the formulated lubricating composition (A) shown above can also be formulated in which the relative amounts of ester and hydrocarbon oil are (B) 32.28% and 49.32% respectively or (C) 39.5% each.

It was found that the performance of the lubricating compositions formulated in this manner upon engine testing showed relatively lower emissions, lower fuel consumption, lower oil consumption and low nitrogen oxides emission. In addition, the formulated lubricating compositions according to the present invention were at least 80% biodegradable as measured by the CEC standard test procedure. The present invention is further illustrated with reference to the following Examples:

Examples - General

A base fluid was prepared using isotridecyldodecanedioate, and a hydrocracked wax distillate having the following physical characteristics:

Property	Typical Specification	Test Method
Colour	1.5 max	ASTM D 1500
Density	0.83	ASTM D 1298
KV 40/cSt	17.28	ASTM d 445
KV 100/cSt	3.99	ASTM d 445
VI	128	ASTM D 2270
PMC/°C	220	ASTM D 93
Pour Point	-27	ASTM D 97
Demulse/mins	<5	NFT* 60-125
Noack volatility/%	15.8	DIN 51581
Sulphur/%	0.08	XRF NFM 07053
CA/%	2	Brandes Method

*Correlates with ASTM D 1401

This hydrocarbon oil was used to prepare formulated lubricating oil compositions according to the formulation in (A) in the following Examples 1-3.

Example 1

SG Additive Package (GBX 2905, ex Adibis Ltd)	15.4% w/w
ADX 545A (Anti-oxidant, ex Adibis Ltd)	1.0% w/w
Plexol* 1420 (VI improver, ex Rohm GmbH)	3.1% w/w
Shellvis* 200 (VI improver, 10% solution, ex Shell UK Ltd)	6.0% w/w
Isotridecyl dodecanedioate	22.59% w/w
Hydrocarbon oil (as above)	52.71% w/w

*Registered Trade Mark

The formulation was prepared using standard lubricant blending techniques described e.g. in "Lubricants and Related Products" by D Klamann, published by Verlag Chemie, 1984.

The formulated composition had the following characteristics:

Property	Limits	Methods
Viscosity @ 100 ° C	13.6-14.5 cSt	ASTM D 445
Viscosity @ 40 ° C	75.0-83.0 cSt	ASTM D 445
Viscosity @ -25 ° C	<3500 cP	ASTM D 2602
Noack volatility	8.5-11.0%	DIN 51581
Biodegradability	>80%	CEC-L-33-T-82
Calcium	0.300-0.332	ICP
Phosphorus	0.102-0.114	ICP
Zinc	0.105-0.135	ICP

Example 2

SH Additive Package (eg OS 99099, ex Lubrizol Ltd)	15% w/w
Viscoplex* 2540 (VI Improver, ex Rohm GmbH)	3.0% w/w
Shellvis* 201 (VI Improver, ex Shell UK Ltd)	3.8% w/w
Isotridecyl dodecanedioate	38.1% w/w
Hydrocarbon oil (as above)	40.1% w/w

*Registered Trade Mark

The formulated composition had the following characteristics:

Property	Limits	Method
Viscosity @ 100 ° C	14.0 cSt	ASTM D445
Viscosity @ -25 ° C	3200 cP	ASTM D2602
Noack volatility	10.7%	DIN 51581
Biodegradability	87%	CEL-L-33-T-82
Calcium content	0.283	ICP
Phosphorus content	0.119	ICP
Zinc content	0.128	ICP

Example 3

SG Additive Package (eg GBX2905, ex Adibis Ltd)	16.4% w/w
Plexol* 1420 (VI Improver, ex Rohm GmbH)	3.1% w/w
GBX 2715 (VI Improver, ex Adibis Ltd)	5.0% w/w
Isotridecyl dodecanedioate	40.0% w/w
Hydrocarbon oil (as above)	35.5% w/w

*Registered Trade Mark

The formulated composition had the following properties:

Property	Limits	Method
Viscosity @ 100 ° C	14.5 cSt	ASTM D445
Viscosity @ -25 ° C	3300 cP	ASTM D2602
Noack volatility	10.4%	DIM 51581
Biodegradability	86%	CEC-L-33-T-82
Calcium content	0.310%	ICP
Phosphorus content	0.108%	ICP
Zinc content	0.125%	ICP

Upon standard engine testing each of the formulations described in Examples 1-3 above using the API-GS method, the following properties were observed:

Property	Performance
Volatility	Good
Low Temperature	Good
Oxidation Stability	
Industrial	Very Good
Automotive	
10W/40	Very Good
5W/40,50	Good
Detergency	
10W/40 (a)	Very Good
10W/40 (b)	Very Good
Dispersancy	
10W/40	Very Good
5W/40,50	Very Good
Seal Compatibility	
10W/40 (a)	Good
10W/40 (b)	Good
Wear/Friction	
10W/40 (a)	Very Good
10W/40 (b)	Very Good
5W/40,50	Very Good
Additive Solubility	Good

The biodegradability of the formulated lubricating composition according to the present invention was tested and compared with commercially available products using the test method shown in the table above. The results are tabulated below:

Present Invention	91%
Mobil 1	45%
Castrol GTX	63%
Shell Gemini	66%
Castrol Syntron	41%

From the above it is clear that the formulated compositions according to the present invention containing the blended base fluid according to the present invention show superior properties to those of prior art, especially in respect of their biodegradability.

Claims

1. A lubricating oil composition which has a major proportion of a base fluid which fluid comprises a blend of:

a) at least one ester derivable from isotridecyl alcohol and at least one aliphatic mono-, di- or poly-carboxylic acid, and

b) at least one hydrocarbon oil comprising up to 99.5% w/w of aliphatic hydrocarbons and no more than 10% w/w of aromatic hydrocarbons such that the total of aliphatics and aromatics is 100%, wherein the amount of component (a) in the blend is in the range from 25-55% w/w.

2. A lubricating oil composition according to claim 1 wherein the ester component (a) is selected from isotridecyl esters of
   i) octane-1,8-dioic acid,
   ii) 2-ethylhexane-1,6-dioic acid,
   iii) nonane-1,9-dioic acid,
   iv) decane-1,10-dioic acid, and
   v) dodecane-1,12-dioic acid.

3. A lubricating oil composition according to claim 1 or 2 wherein the hydrocarbon oil component (b) is a hydrocracked wax distillate.

4. A lubricating oil composition according to any one of the preceding claims wherein the hydrocarbon oil component (b) contains less than 10 ppm of polycyclic aromatic hydrocarbons, from 92-97% w/w of aliphatic hydrocarbons and 3-8% w/w of aromatic hydrocarbons.

5. A lubricating oil composition according to any one of the preceding claims wherein the aliphatic hydrocarbons in the hydrocarbon oil component (b) comprise about 20% w/w of isoparaffins having an average carbon number of about 27.

6. A lubricating oil composition according to any one of the preceding claims wherein the ester component (a) is isotridecyl dodecanedioate and the amount of ester in the blend is in the range from 30-50% w/w.

7. A lubricating oil composition according to any one of the preceding claims wherein said composition comprises, in addition, minor proportions of one or more additives selected from: sludge dispersants, ashless dispersancy agents, VI improvers, anti-wear additives, anti-rust agents and anti-oxidants.

8. A lubricating oil composition according to claim 7 wherein the anti-rust agent is an overbased calcium or magnesium sulphonate or phenate; the anti-wear agent is a zinc dithiophosphate; the ashless dispersancy agent is a long chain hydrocarbon substituted succinimide; the sludge dispersant is an oil soluble salt such as amides, imides, oxazolines and esters of mono- or di-carboxylic acids or anhydrides; the anti-oxidant is a phenolic compound; and the VI improver comprises a poly-methacrylate dispersant or a hydrotreated polyisoprene.

9. A lubricating oil composition according to any one of the preceding claims wherein said composition is at least 80% biodegradable as measured by the CEC standard test procedure.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 31 1497

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X A	EP-A-0 259 809 (IDEMITSU KOSAN COMPANY LIMITED) * page 4, line 12 - line 15 * * page 9; example 6; table 3 * ---	1,2,6-8 4	C10M105/00 C10M111/02 C10M169/04 //(C10M105/00, 105:04,105:34, 105:36) (C10M111/02, 101:02,105:34, 105:36)
A	FR-A-2 195 674 (SUN OIL COMPANY OF PENNSYLVANIA) * page 1, line 25 - line 37 * * page 2, line 7 - line 19 * * page 4, line 21 - page 5, line 2 * ---	1-4,7,8	
A	US-A-3 974 081 (A.J RUTKOWSKI) * column 1, line 61 - line 62 * * column 3, line 67 - column 4, line 7 * * column 4, line 25 - line 32 * * column 5, line 20 - line 26 * ---	1,2,9	
P,A	EP-A-0 468 109 (ETHYL PETROLEUM ADDITIVES) * column 6, line 47 - column 7, line 48 * * column 7, line 6 - line 7 * * column 7, line 27 - line 32 * * column 11, line 23 - line 39 * ---	1,7-9	
A	GB-A-1 131 926 (SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ) * page 2, line 4 - line 6 * * page 2, line 9 - line 10 * * claims 1,2,7,24,30 * ---	1,2,6-8	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C10M
A	DE-A-1 913 538 (TECHNOCHEMIE GMBH) ---		
A	DE-A-1 594 641 (TECHNOCHEMIE GMBH) -----		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	05 APRIL 1993	HILGENGA K.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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