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(54) Title: ANTIWEAR AUTOMOTIVE FORMULATIONS

(57) Abstract: An automotive engine oil comprising a base oil and an antiwear additive system comprising a complex ester. The antiwear additive system preferably further comprises a phosphorus-containing and/or sulphur-containing antiwear additive. The antiwear additive system of the invention has superior antiwear properties and also reduced metal, phosphorus and sulphur levels compared to current commercial antiwear agents such as ZDDP.



WO 2005/111179 A1

ANTIWEAR AUTOMOTIVE FORMULATIONS

The present invention relates to automotive engine oils comprising a base oil and an antiwear additive system comprising an ester and the antiwear additive system preferably further comprising a phosphorus-containing and/or sulphur-containing antiwear additive and the use of automotive engine oils comprising the antiwear additive system.

The automotive industry is under pressure to meet higher engine oil performance requirements whilst at the same time lowering emissions. The International Lubricant Standardisation and Approval Committee (ILSAC) GF-4 requirements for automotive engine oil have recently been published. One key area where the specification has been tightened is the level of phosphorus. This is because phosphorus has been identified as a catalyst poison for the catalysts that are used in emission control systems. The allowed phosphorus level will now be a maximum of 0.08%, for GF-4, by weight in the automotive engine oil, which is a 20% reduction from the level set in the GF-3 requirements. However ILSAC's original aim was a maximum allowed phosphorus level of 0.05%, which is indicative of future legislation reducing the proposed 0.08% level further. In fact the proposed level for GF-5 is 0.05%.

It is expected that focus will now move to other elements in the engine oil, as well as phosphorus, that could impact emission control systems. For example sulphur is known to poison deNO_x catalysts and ash residues from metals are known to plug after-treatment particulate traps.

Antiwear protection in modern automotive engine oils is mainly provided by the additive zinc dialkyl dithiophosphate (ZDDP), which contains phosphorus, sulphur and zinc. It is believed that the ZDDP degrades at potential wear points in the engine to form a polyphosphate glassy film which protects the potential wear points. The ZDDP is typically supplied as a concentrated solution (typically 80-99% ZDDP) in mineral oil. At current use levels (typically 0.5-1.5% of ZDDP solution) it is believed that ZDDP accounts for more than two thirds of the sulphur and all of the zinc and phosphorus present in most engine oils. It is clear that this additive has a major effect on the emission control systems and as such the use of alternative antiwear additives needs to be explored.

Investigations undertaken by the inventors have led to the identification of an ester which is suitable to be used in an antiwear additive system, either by itself or to be used in conjunction with a reduced level of a phosphorus and/or sulphur containing antiwear additive in automotive engine oils. The antiwear additive system of the invention not only has reduced metal, phosphorus and sulphur levels but surprisingly also can provide antiwear properties that are similar to those of commercial antiwear additives in automotive engine oils.

According to the present invention, an automotive engine oil comprising a base oil and an antiwear additive system comprising a complex ester which is obtained by an esterification reaction between at least one polyfunctional alcohol and at least one polyfunctional carboxylic acid and a chain-stopping agent, wherein:

- (a) said polyfunctional alcohol is an aliphatic polyol;
- (b) said at least one polyfunctional carboxylic acid is selected from an aliphatic dicarboxylic acid having from 5 to 18 carbon atoms and a dimer fatty acid or mixtures thereof;
- (c) said chain-stopping agent is selected from an aliphatic monocarboxylic acid having from 5 to 24 carbon atoms and an aliphatic monofunctional alcohol having from 5 to 24 carbon atoms

with the resultant complex ester having a kinematic viscosity at 100 °C ranging from 10 to 300 mm²/s and a non-polarity index (NPI)

$$\text{NPI} = \frac{\text{total number of carbon atoms} * \text{molecul. weight}}{\text{number of carboxylate groups} * 100}$$

ranging from 20 to 500.

the automotive engine oil

The term automotive engine oil includes both gasoline and diesel (including heavy duty diesel) engine oils.

the base oil

The base oil of the automotive engine oil may be chosen from any of the Group I to Group VI base oils as defined by the American Petroleum Institute (API). The base oil may be a mixture of Group I to Group VI base oils.

at least one polyfunctional alcohol

The aliphatic polyol preferably is of formula $R(OH)_n$ where n is an integer, which ranges from 1-10 and R is a hydrocarbon chain, either branched or linear, more preferably branched, of 2 to 15 carbon atoms. The polyol is suitably of low molecular weight, preferably in the range from 50 to 650, more preferably 60 to 150, and particularly 60 to 100. Examples of suitable polyols include ethylene glycol, propylene glycol, trimethylene glycol, diols of butane, neopentyl glycol, trimethylol propane and its dimer, pentaerythritol and its dimer, glycerol, inositol and sorbitol. Preferably the polyol is a neopentyl polyol. Preferred examples of neopentyl polyols are neopentyl glycol, trimethylol propane and pentaerythritol. Preferably the neopentyl polyol comprises at least 50% by weight of trimethylol propane, more preferably at least 70%, even more preferably at least 90%.

polyfunctional carboxylic acid

The term dimer fatty acid is well known in the art and refers to the dimerisation product of mono- or polyunsaturated fatty acids and/or esters thereof. Preferred dimer fatty acids are dimers of C10 to C30, more preferably C12 to C24, particularly C14 to C22, and especially C18 alkyl chains. Suitable dimer fatty acids include the dimerisation products of oleic acid, linoleic acid, linolenic acid, palmitoleic acid, and elaidic acid with oleic acid being particularly preferred. The dimerisation products of the unsaturated fatty acid mixtures obtained in the hydrolysis of natural fats and oils, e.g. sunflower oil, soybean oil, olive oil, rapeseed oil, cottonseed oil and tall oil, may also be used. Hydrogenated, for example by using a nickel catalyst, dimer fatty acids may also be employed.

In addition to the dimer fatty acids, dimerisation usually results in varying amounts of oligomeric fatty acids (so-called "trimer") and residues of monomeric fatty acids (so-called "monomer"), or esters thereof, being present. The amount of monomer can, for example, be reduced by distillation. Particularly preferred dimer fatty acids used in the present invention, have a dimer content of greater than 50%, more preferably greater than 60%, particularly greater than 65%, and especially greater than 70% by weight. The trimer content is preferably less than 50%, more preferably in the range from 1 to 35%, particularly 10 to 30%, and especially 15 to 25% by weight. The monomer content is preferably less than 5%, more preferably in the range from 0.1 to 4% by weight.

Examples of suitable aliphatic dicarboxylic acids include glutaric, adipic, pimelic, suberic, azelaic, sebacic, undecanedioic, dodecanedioic, tridecanedioic, tetradecanedioic, pentadecanedioic, hexadecanedioic acids and mixtures thereof. The aliphatic dicarboxylic acid preferably has from 7 to 16 carbon atoms, more preferably from 8 to 14 carbon atoms. The aliphatic dicarboxylic acid is preferably linear. Azelaic acid, sebacic acid and dodecanedioic acid are particularly preferred.

chain stopping agent

The aliphatic monocarboxylic acid or monofunctional alcohol, may be used to react with any OH or COOH groups respectively which remain unreacted after reaction between the polyfunctional alcohol and the polyfunctional carboxylic acid. Examples of the aliphatic monocarboxylic acid include the saturated straight chained acids of pentanoic, hexanoic, heptanoic, octanoic, nonanoic, decanoic, undecanoic, dodecanoic, tridecanoic, tetradecanoic, pentadecanoic, hexadecanoic, heptadecanoic, octadecanoic, arachidic, behenic and lignoceric acids and mixtures thereof. Examples also include unsaturated and/or branched variants of the disclosed saturated, straight-chained acids. The aliphatic monocarboxylic acid preferably has 7 to 20 carbon atoms, more preferably 8 to 18 carbon atoms. It may be branched or straight chained and preferably is saturated. Particularly preferred monocarboxylic acids are a mixture of octanoic and decanoic acids, and isostearic acid.

Examples of the aliphatic monofunctional alcohol include pentanol, hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol and mixtures thereof.

- ; Examples also include unsaturated and/or branched variants of the disclosed saturated, straight chained acids The aliphatic monofunctional alcohol preferably has 7 to 16 carbon atoms, more preferably 8 to 14 carbon atoms. It may be branched or straight chained and preferably is saturated. 2-Ethylhexanol is particularly preferred.
-) The resultant ester has a kinematic viscosity at 100°C of 10 to 300, preferably 15 to 250, more preferably 20-200 and especially 25-100 mm²/s.

The resultant ester has a NPI value in the range 20 to 500, preferably 30 to 480, more preferably 40 to 300 and especially 40 to 150.

The resultant ester has an average molecular weight in the range 400 to 2700, preferably 500 to 2500, more preferably 550 to 2000, especially 800 to 1500.

Preferred resultant esters include an ester which is the reaction product of a neopentyl polyol, preferably at least one of neopentyl glycol, trimethylol propane and pentaerythritol more preferably trimethylol propane with a dimer acid and a monocarboxylic acid or monofunctional alcohol having 5 to 24 carbon atoms, preferably a monocarboxylic acid having 7 to 16 carbon atoms, more preferably a monocarboxylic acid having 8 to 14 carbon atoms, especially a mixture of octanoic and decanoic acids.

The antiwear additive system preferably further comprises a phosphorus-containing and/or sulphur-containing antiwear additive.

The phosphorus-containing and/or sulphur-containing antiwear additive may also contain other inorganic elements such as nitrogen and halogens, in particular chlorine, boron and silicon. Furthermore it may contain metallic elements such as zinc, molybdenum, tungsten and niobium.

Examples of phosphorus-containing additives include phosphate esters, acid phosphates, phosphites and dialkyl alkyl phosphonates. Examples of sulphur-containing additives include sulphurized olefins, sulphurized esters, sulphurized aromatics, trithianes and derivatives of thioglycolates. Examples of phosphorus and sulphur-containing additives include dithiophosphates, thiophosphates and phosphorothionates. Preferred examples of a dithiophosphate are molybdenum dialkyl dithiophosphates and ZDDP with ZDDP being especially preferred. Examples of phosphorus and nitrogen-containing additives include phosphoramides and amine phosphates. Examples of sulphur and nitrogen-containing additives include dithiocarbamates, for example molybdenum dithiocarbamates (MoDTC), ammonium salts of sulphonc acid, amine salts of thiocyanic acid, alkylidithiobenzoxazoles, derivatives of 2-mercaptobenzothiazole and 2,5-dimercapto-1,3,4-thiadiazole. Examples of sulphur, phosphorus and nitrogen-containing additives include amine thiophosphates and amine dithiophosphates.

Preferably the phosphorus-containing and/or sulphur-containing antiwear additive contains both phosphorus and sulphur. More preferably the phosphorus-containing and/or sulphur-containing antiwear additive also contains zinc or molybdenum, particularly the phosphorus-containing and/or sulphur-containing antiwear additive is ZDDP.

When the ester and the phosphorus-containing and/or sulphur-containing antiwear additive are both present in the antiwear additive system the ratio of ester to phosphorus-containing and/or sulphur-containing antiwear additive ranges from 80:20 to 20:80 weight percent, preferably from 70:30 to 30:70 and particularly from 60:40 to 40:60.

The antiwear additive system according to the invention has no more than 10 wt% phosphorus, preferably no more than 7wt%, more preferably no more than 6 wt% phosphorus.

The antiwear additive system according to the invention is present at levels between 0.1 and 5 % by weight, more preferably between 0.3 and 4%, even more preferably between 0.5 and 3% in the automotive engine oil.

A preferred antiwear additive system comprises 0.5% by weight in the automotive engine oil of an ester, which is the reaction product of trimethylol propane with dimer acid and a mixture of octanoic and decanoic acid with 0.5% by weight in the automotive engine oil of a ZDDP solution (for example Lubrizol L1371).

The automotive engine oil comprising the base oil and antiwear additive system preferably has no more than 0.08 wt% phosphorus, more preferably no more than 0.07 wt%, especially no more than 0.06 wt% phosphorus present.

The automotive engine oil also comprises other types of additives of known functionality at levels between 0.1 to 30%, more preferably between 0.5 to 20 % more especially between 1 to 10% of the total weight of the engine oil. These can include detergents, dispersants, oxidation inhibitors, corrosion inhibitors, rust inhibitors, friction modifiers, foam depressants, pour point depressants, viscosity index improvers and mixtures thereof. Viscosity index improvers include polyisobutenes,

polymethacrylate acid esters, polyacrylate acid esters, diene polymers, polyalkyl styrenes, alkenyl aryl conjugated diene copolymers and polyolefins. Foam depressants include silicones and organic polymers. Pour point depressants include polymethacrylates, polyacrylates, polyacrylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, terpolymers of dialkylfumarates, vinyl esters of fatty acids and alkyl vinyl ethers. Ashless detergents include carboxylic dispersants, amine dispersants, Mannich dispersants and polymeric dispersants. Friction modifiers include amides, amines and partial fatty acid esters of polyhydric alcohols. Ash-containing dispersants include neutral and basic alkaline earth metal salts of an acidic organic compound. Oxidation inhibitors include hindered phenols and alkyl diphenylamines. Additives may include more than one functionality in a single additive.

According to a further embodiment of the present invention an antiwear additive system comprising a complex ester which is obtained by an esterification reaction between at least one polyfunctional alcohol and at least one polyfunctional carboxylic acid and a chain-stopping agent, wherein:

- (a) said polyfunctional alcohol is an aliphatic polyol;
- (b) said at least one polyfunctional carboxylic acid is selected from an aliphatic dicarboxylic acid having from 5 to 18 carbon atoms and a dimer fatty acid or mixtures thereof;
- (c) said chain-stopping agent is selected from an aliphatic monocarboxylic acid having from 5 to 24 carbon atoms and an aliphatic monofunctional alcohol having from 5 to 24 carbon atoms

with the resultant complex ester having a kinematic viscosity at 100 °C ranging from 10 to 300 mm²/s and a non-polarity index (NPI)

$$\text{NPI} = \frac{\text{total number of carbon atoms} * \text{molecul. weight}}{\text{number of carboxylate groups} * 100}$$

ranging from 20 to 500.

The antiwear additive system preferably further comprises a phosphorus-containing and/or sulphur-containing antiwear additive.

According to a further embodiment of the present invention a method of reducing wear in an automotive engine by the use of an automotive engine oil comprising a

base oil and an antiwear additive system comprising a complex ester which is obtained by an esterification reaction between at least one polyfunctional alcohol and at least one polyfunctional carboxylic acid and a chain-stopping agent, wherein:

- (a) said polyfunctional alcohol is an aliphatic polyol;
- (b) said at least one polyfunctional carboxylic acid is selected from an aliphatic dicarboxylic acid having from 5 to 18 carbon atoms and a dimer fatty acid or mixtures thereof;
- (c) said chain-stopping agent is selected from an aliphatic monocarboxylic acid having from 5 to 24 carbon atoms and an aliphatic monofunctional alcohol having from 5 to 24 carbon atoms

with the resultant complex ester having a kinematic viscosity at 100 °C ranging from 10 to 300 mm²/s and a non-polarity index (NPI)

$$\text{NPI} = \frac{\text{total number of carbon atoms} * \text{molecul. weight}}{\text{number of carboxylate groups} * 100}$$

ranging from 20 to 500.

According to a further embodiment of the present invention use of an automotive engine oil comprising a base oil and an antiwear additive system comprising a complex ester which is obtained by an esterification reaction between at least one polyfunctional alcohol and at least one polyfunctional carboxylic acid and a chain-stopping agent, wherein:

- (a) said polyfunctional alcohol is an aliphatic polyol;
- (b) said at least one polyfunctional carboxylic acid is selected from an aliphatic dicarboxylic acid having from 5 to 18 carbon atoms and a dimer fatty acid or mixtures thereof;
- (c) said chain-stopping agent is selected from an aliphatic monocarboxylic acid having from 5 to 24 carbon atoms and an aliphatic monofunctional alcohol having from 5 to 24 carbon atoms

with the resultant complex ester having a kinematic viscosity at 100 °C ranging from 10 to 300 mm²/s and a non-polarity index (NPI)

$$\text{NPI} = \frac{\text{total number of carbon atoms} * \text{molecul. weight}}{\text{number of carboxylate groups} * 100}$$

ranging from 20 to 500

to reduce wear in an automotive engine.

According to a further embodiment of the present invention the use of an antiwear additive system comprising a complex ester which is obtained by an esterification reaction between at least one polyfunctional alcohol and at least one polyfunctional carboxylic acid and a chain-stopping agent, wherein:

- (a) said polyfunctional alcohol is an aliphatic polyol;
- (b) said at least one polyfunctional carboxylic acid is selected from an aliphatic dicarboxylic acid having from 5 to 18 carbon atoms and a dimer fatty acid or mixtures thereof;
- (c) said chain-stopping agent is selected from an aliphatic monocarboxylic acid having from 5 to 24 carbon atoms and an aliphatic monofunctional alcohol having from 5 to 24 carbon atoms

with the resultant complex ester having a kinematic viscosity at 100 °C ranging from 10 to 300 mm²/s and a non-polarity index (NPI)

$$\text{NPI} = \frac{\text{total number of carbon atoms} * \text{molecul. weight}}{\text{number of carboxylate groups} * 100}$$

ranging from 20 to 500

in an automotive engine oil.

According to a further embodiment of the present invention a method of reducing wear in an automotive engine by the addition of an automotive engine oil comprising a base oil and a complex ester which is obtained by an esterification reaction between at least one polyfunctional alcohol and at least one polyfunctional carboxylic acid and a chain-stopping agent, wherein:

- (a) said polyfunctional alcohol is an aliphatic polyol;
- (b) said at least one polyfunctional carboxylic acid is selected from an aliphatic dicarboxylic acid having from 5 to 18 carbon atoms and a dimer fatty acid or mixtures thereof;
- (c) said chain-stopping agent is selected from an aliphatic monocarboxylic acid having from 5 to 24 carbon atoms and an aliphatic monofunctional alcohol having from 5 to 24 carbon atoms

with the resultant complex ester having a kinematic viscosity at 100 °C ranging from 10 to 300 mm²/s and a non-polarity index (NPI)

$$\text{NPI} = \frac{\text{total number of carbon atoms} * \text{molecul. weight}}{\text{number of carboxylate groups} * 100}$$

ranging from 20 to 500.

wherein the automotive engine oil has a phosphorus level of no more than 0.08%.

According to a further embodiment of the present invention an automotive engine comprising an automotive engine oil comprising a base oil and an antiwear additive system comprising a complex ester which is obtained by an esterification reaction between at least one polyfunctional alcohol and at least one polyfunctional carboxylic acid and a chain-stopping agent, wherein:

- (a) said polyfunctional alcohol is an aliphatic polyol;
- (b) said at least one polyfunctional carboxylic acid is selected from an aliphatic dicarboxylic acid having from 5 to 18 carbon atoms and a dimer fatty acid or mixtures thereof;
- (c) said chain-stopping agent is selected from an aliphatic monocarboxylic acid having from 5 to 24 carbon atoms and an aliphatic monofunctional alcohol having from 5 to 24 carbon atoms

with the resultant complex ester having a kinematic viscosity at 100 °C ranging from 10 to 300 mm²/s and a non-polarity index (NPI)

$$\text{NPI} = \frac{\text{total number of carbon atoms} * \text{molecul. weight}}{\text{number of carboxylate groups} * 100}$$

ranging from 20 to 500.

The automotive engine comprising an automotive engine oil according to the invention exhibits abrasion scars, measured using the Reichert M2 friction and wear tester, of not more than 4mm², preferably not more than 3mm², more preferably not more than 2.5mm².

The invention will now be described further by way of example only with reference to the following Examples.

Example 1

Wear was measured for a formulated automotive engine oil having as base oil a mixture of NexbaseTM 3060 and NexbaseTM 3043 (colourless, catalytically hydroisomerised and dewaxed base oils comprising of hydrogenated, highly isoparaffinic hydrocarbons) with the addition of 1% levels of different antiwear additive systems using the Reichert M2 friction and wear tester under the following test conditions.

The tester basically consists of a test roll rigidly mounted in a holder, which is pressed against a revolving friction wheel, having a slip ring, by means of leverage. The friction wheel is immersed with its lower third in the sample lubricant under test and its rotation speed (known as friction speed) is such that a sufficient quantity of lubricant will always get to the contact surface of the test roll and the friction wheel. When the slip ring is rotated, abrasion areas (elliptical wear marks) are produced on the test roll.

Sample volume of formulated engine oil – 30 mL

Test roll and slip ring – hardened steel

Applied load – 1.5 kg

Friction speed at 1000 revolutions per minute of friction wheel -1.83 m/s

Friction length – 100m for each abrasion area to develop.

The slip ring was preconditioned by operating the tester using 30 mL Vitrea 22 (a mineral oil available ex Shell) in the oil reservoir. The test roll was then replaced for the testing of each individual formulated automotive engine oil. For each formulated engine oil a first test run was undertaken with the experimental conditions as described above. The test roll holder was then rotated so that a new face of the test roll could be abraded and the experiment repeated. This procedure was repeated a further 18 times to obtain 20 abrasion areas. The abrasion areas of each test roll were measured as follows. The length and width of each abrasion area were measured using a microscope (in mm). The calculation of each abrasion area was done using the following formula

Abrasion area (mm²) = width of abrasion (mm) * length of abrasion(mm) * 0.785

The results are in Table One below for averages of last 10 abrasion areas, last 5 abrasion areas and last 3 abrasion areas respectively.

Table One

Run Number	Antiwear additive system	Average of last 10 abrasion areas (mm ²)	Average of last 5 abrasion areas (mm ²)	Average of last 3 abrasion areas (mm ²)
1	Complex ester/ ZDDP solution (50/50)	2.02	1.74	1.67
2		1.93	1.72	1.79
3		1.81	1.74	1.75
4		1.80	1.74	1.61
5		2.91	2.07	2.09
6		4.55	2.27	2.23
7		1.89	1.77	1.80
8		1.73	1.64	1.68
9		9.93	11.76	13.17
10		9.64	9.71	8.80
11		2.90	1.72	1.68
12		1.80	1.77	1.72
C1	Comparative ZDDP solution	1.79	1.71	1.64
C2		2.07	1.60	1.59
C3		1.82	1.76	1.77
C4		1.83	1.77	1.82
C5		1.90	1.89	1.90
C6		2.74	1.78	1.70

The ester is the reaction product of trimethylolpropane (228kg) with dimer acid with at least 75% dimer present (383kg) and a mixture of C8/ C10 saturated monocarboxylic acid (522kg). The ester has a viscosity at 100°C of about 35mm²/s and an NPI of typically about 100.

The ZDDP solution is Lubrizol L1371.

The automotive engine oil with ZDDP as antiwear additive system contains 0.1% phosphorus. The automotive engine oil with the complex ester/ZDDP blend as the antiwear additive system contains 0.05% phosphorus.

It is clear from the results that runs 9 and 10 are outliers and are therefore not considered in the data analysis.

The data in Table One clearly illustrates that an antiwear additive system according to the present invention has similar wear properties compared to the commercially available ZDDP and has much lower phosphorus, sulphur and metal content.

Claims

1. An automotive engine oil comprising a base oil and an antiwear additive system comprising a complex ester which is obtained by an esterification reaction between at least one polyfunctional alcohol and at least one polyfunctional carboxylic acid and a chain-stopping agent, wherein:

- (a) said polyfunctional alcohol is an aliphatic polyol;
- (b) said at least one polyfunctional carboxylic acid is selected from an aliphatic dicarboxylic acid having from 5 to 18 carbon atoms and a dimer fatty acid or mixtures thereof;
- (c) said chain-stopping agent is selected from an aliphatic monocarboxylic acid having from 5 to 24 carbon atoms and an aliphatic monofunctional alcohol having from 5 to 24 carbon atoms

with the resultant complex ester having a kinematic viscosity at 100 °C ranging from 10 to 300 mm²/s and a non-polarity index (NPI)

$$\text{NPI} = \frac{\text{total number of carbon atoms} * \text{molecul. weight}}{\text{number of carboxylate groups} * 100}$$

number of carboxylate groups x 100

ranging from 20 to 500.

2. An automotive engine oil as claimed in claim 1 wherein the aliphatic polyol is of formula R(OH)_n where n is an integer, which ranges from 1-10 and R is a hydrocarbon chain, either branched or linear, of 2 to 15 carbon atoms.

3. An automotive engine oil as claimed in either of claims 1 or 2 wherein the polyfunctional carboxylic acid is an aliphatic dicarboxylic acid which has from 7 to 16 carbon atoms, more preferably from 8 to 14 carbon atoms.

4. An automotive engine oil as claimed in any of claims 1 to 3 wherein the chain stopping agent is an aliphatic monocarboxylic acid which has 7 to 20 carbon atoms, more preferably 8 to 18 carbon atoms.

5. An automotive engine oil as claimed in any of claims 1 to 3 wherein the chain stopping agent is an aliphatic monofunctional alcohol which has 7 to 16 carbon atoms, more preferably 8 to 14 carbon atoms.

6. An automotive engine oil as claimed in any of claims 1 to 5 wherein the complex ester has a kinematic viscosity at 100°C of 15 to 250, more preferably 20-200 and especially 25-100 mm²/s.
7. An automotive engine oil as claimed in any of claims 1 to 6 wherein the complex ester has a NPI value in the range 30 to 480, more preferably 40 to 300 and especially 40 to 150.
8. An automotive engine oil as claimed in any of claims 1 to 7 wherein the complex ester has an average molecular weight in the range 500 to 2500, more preferably 550 to 2000, especially 800 to 1500.
9. An automotive engine oil as claimed in any of claims 1 to 7 wherein the antiwear additive system further comprises a phosphorus-containing and/or sulphur-containing antiwear additive.
10. An automotive engine oil as claimed in claim 9 wherein the phosphorus-containing and/or sulphur-containing antiwear additive is zinc dialkyl dithiophosphate.
11. An automotive engine oil as claimed in either of claims 9 or 10 wherein the ratio of complex ester to phosphorus-containing and/or sulphur-containing antiwear additive is from 80:20 to 20:80 weight percent, preferably from 70:30 to 30:70 and particularly from 60:40 to 40:60.
12. An automotive engine oil as claimed in any of claims 1 to 11 wherein the antiwear additive system has no more than 10 wt% , preferably no more than 7wt%, more preferably no more than 6 wt% phosphorus.
13. An automotive engine oil as claimed in any of claims 1 to 12 wherein the antiwear additive system is present at levels between 0.1 and 5 % by weight, more preferably between 0.3 and 4%, even more preferably between 0.5 and 3% in the automotive engine oil.
14. An automotive engine oil as claimed in any one of claims 1 to 13 wherein the automotive engine oil has no more than 0.08 wt% phosphorus, more preferably no

more than 0.07 wt%, especially no more than 0.06 wt% phosphorus present.

15. An antiwear additive system comprising a complex ester which is obtained by an esterification reaction between at least one polyfunctional alcohol and at least one polyfunctional carboxylic acid and a chain-stopping agent, wherein:

- (a) said polyfunctional alcohol is an aliphatic polyol;
- (b) said at least one polyfunctional carboxylic acid is selected from an aliphatic dicarboxylic acid having from 5 to 18 carbon atoms and a dimer fatty acid or mixtures thereof;
- (c) said chain-stopping agent is selected from an aliphatic monocarboxylic acid having from 5 to 24 carbon atoms and an aliphatic monofunctional alcohol having from 5 to 24 carbon atoms

with the resultant complex ester having a kinematic viscosity at 100 °C ranging from 10 to 300 mm²/s and a non-polarity index (NPI)

$$\text{NPI} = \frac{\text{total number of carbon atoms} * \text{molecul. weight}}{\text{number of carboxylate groups} * 100}$$

ranging from 20 to 500.

16. A method of reducing wear in an automotive engine by the use of an automotive engine oil comprising a base oil and an antiwear additive system comprising a complex ester which is obtained by an esterification reaction between at least one polyfunctional alcohol and at least one polyfunctional carboxylic acid and a chain-stopping agent, wherein:

- (a) said polyfunctional alcohol is an aliphatic polyol;
- (b) said at least one polyfunctional carboxylic acid is selected from an aliphatic dicarboxylic acid having from 5 to 18 carbon atoms and a dimer fatty acid or mixtures thereof;
- (c) said chain-stopping agent is selected from an aliphatic monocarboxylic acid having from 5 to 24 carbon atoms and an aliphatic monofunctional alcohol having from 5 to 24 carbon atoms

with the resultant complex ester having a kinematic viscosity at 100 °C ranging from 10 to 300 mm²/s and a non-polarity index (NPI)

$$\text{NPI} = \frac{\text{total number of carbon atoms} * \text{molecul. weight}}{\text{number of carboxylate groups} * 100}$$

ranging from 20 to 500.

17. Use of an automotive engine oil comprising a base oil and an antiwear additive system comprising a complex ester which is obtained by an esterification reaction between at least one polyfunctional alcohol and at least one polyfunctional carboxylic acid and a chain-stopping agent, wherein:

- (a) said polyfunctional alcohol is an aliphatic polyol;
- (b) said at least one polyfunctional carboxylic acid is selected from an aliphatic dicarboxylic acid having from 5 to 18 carbon atoms and a dimer fatty acid or mixtures thereof;
- (c) said chain-stopping agent is selected from an aliphatic monocarboxylic acid having from 5 to 24 carbon atoms and an aliphatic monofunctional alcohol having from 5 to 24 carbon atoms

with the resultant complex ester having a kinematic viscosity at 100 °C ranging from 10 to 300 mm²/s and a non-polarity index (NPI)

$$\text{NPI} = \frac{\text{total number of carbon atoms} * \text{molecul. weight}}{\text{number of carboxylate groups} * 100}$$

ranging from 20 to 500

to reduce wear in an automotive engine.

18. A method of reducing wear in an automotive engine by the addition of an automotive engine oil comprising a base oil and a complex ester which is obtained by an esterification reaction between at least one polyfunctional alcohol and at least one polyfunctional carboxylic acid and a chain-stopping agent, wherein:

- (a) said polyfunctional alcohol is an aliphatic polyol;
- (b) said at least one polyfunctional carboxylic acid is selected from an aliphatic dicarboxylic acid having from 5 to 18 carbon atoms and a dimer fatty acid or mixtures thereof;
- (c) said chain-stopping agent is selected from an aliphatic monocarboxylic acid having from 5 to 24 carbon atoms and an aliphatic monofunctional alcohol having from 5 to 24 carbon atoms

with the resultant complex ester having a kinematic viscosity at 100 °C ranging from 10 to 300 mm²/s and a non-polarity index (NPI)

$$\text{NPI} = \frac{\text{total number of carbon atoms} * \text{molecul. weight}}{\text{number of carboxylate groups} * 100}$$

ranging from 20 to 500.

wherein the automotive engine oil has a phosphorus level of no more than 0.08%.

19. An automotive engine comprising an automotive engine oil comprising a base oil and an antiwear additive system comprising a complex ester which is obtained by an esterification reaction between at least one polyfunctional alcohol and at least one polyfunctional carboxylic acid and a chain-stopping agent, wherein:

- (a) said polyfunctional alcohol is an aliphatic polyol;
- (b) said at least one polyfunctional carboxylic acid is selected from an aliphatic dicarboxylic acid having from 5 to 18 carbon atoms and a dimer fatty acid or mixtures thereof;
- (c) said chain-stopping agent is selected from an aliphatic monocarboxylic acid having from 5 to 24 carbon atoms and an aliphatic monofunctional alcohol having from 5 to 24 carbon atoms

with the resultant complex ester having a kinematic viscosity at 100 °C ranging from 10 to 300 mm²/s and a non-polarity index (NPI)

$$\text{NPI} = \frac{\text{total number of carbon atoms} * \text{molecul. weight}}{\text{number of carboxylate groups} * 100}$$

ranging from 20 to 500.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2005/001771

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10M161/00 C10M141/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 503 762 A (BONGARDT ET AL) 2 April 1996 (1996-04-02) column 2, line 39 - column 3, line 56 column 4, line 28 - line 56 claims; examples	1-4, 6-8, 12, 14, 15
X	WO 98/10041 A (EXXON CHEMICAL PATENTS INC) 12 March 1998 (1998-03-12) page 11, line 4 - page 14, line 10 page 18, line 7 - page 22, line 20 page 25, line 5 - line 20 claims; tables 4, 10-13	1-3, 5-10, 12, 14-19
X	US 6 462 001 B1 (KENBEEK DIRK ET AL) 8 October 2002 (2002-10-08) column 2, line 27 - column 5, line 12 claims; examples	1-9, 14-19
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 98/10042 A (EXXON CHEMICAL PATENTS INC) 12 March 1998 (1998-03-12) page 7, line 5 - page 11, line 29 page 13, line 1 - page 20, line 22 claims; examples	1-3, 5-10, 12-15
A	US 3 390 083 A (LION CHARLOTTE) 25 June 1968 (1968-06-25) column 2, line 11 - column 3, line 73 column 4, line 27 - column 5, line 13 claims; examples 1-5	1-19

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