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(71) Applicant *(for all designated States except US)*: **SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(71) Applicant *(for US only)*: **SHELL OIL COMPANY** [US/US]; PO Box 2463, One Shell Plaza, Houston, Texas 77252-2463 (US).

(72) Inventors: **WILLARS, Malcom J**; Pool Lane, Ince, Chester Cheshire CH2 4NU (GB). **DIXON, Richard Thomas**; Pool Lane, Ince, Chester Cheshire CH2 4NU (GB).

(74) Agent: **MATTHEZING, Robert Maarten**; PO Box 384, NL-2501 CJ The Hague (NL).

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(54) Title: LUBRICATING COMPOSITION

(57) Abstract: A lubricating composition for use in the crankcase of an engine comprising a base oil and one or more additives, wherein the base oil comprises a Fischer-Tropsch derived base oil and wherein the lubricating composition comprises one or more comb polymers. The lubricating composition of the present invention has been found to improve sustained fuel economy properties whilst obtaining improved piston cleanliness properties and improved dispersancy properties.

LUBRICATING COMPOSITION

Field of the Invention

The present invention relates to a lubricating composition comprising a base oil and one or more additives for particular use in the crankcase of an engine. In particular, the present invention relates to a lubricating composition comprising a base oil and one or more additives for use in the crankcase of an engine for providing improved sustained fuel economy in a diesel engine, as well as improved dispersancy and piston cleanliness.

Background of the Invention

Government regulations and market demands continue to emphasize conservation of fossil fuels in the transportation industry. There is increasing demand for more fuel-efficient vehicles in order to meet CO_2 emissions reductions targets. Therefore, any incremental improvement in fuel economy (FE) is of great importance in the automotive sector. Lubricants can play an important role in reducing a vehicle’s fuel consumption and there is a continuing need for improvements in fuel economy performance, in particular long term or sustained fuel economy performance, of lubricant compositions contained within an internal combustion engine.

Various attempts have been made to improve the fuel economy performance of lubricating engine oils. US2010/0190671 relates to the use of comb polymers for reducing fuel consumption. In particular, the comb polymer disclosed therein comprises, in the main chain, at least one repeat unit which is obtained from at least one polyolefin-based macromonomer, and at least one repeat unit which is obtained from at least one low molecular weight monomer selected from the group consisting of styrene monomers having 8 to 17 carbon atoms, alkyl(meth)acrylates having 1 to 10 carbon atoms in the alcohol group, vinyl esters having from 1 to 11 carbon atoms in the acyl group, vinyl ethers having 1 to 10 carbon atoms in the alcohol group, (di)alkyl fumurates having 1 to 10 carbon atoms in the alcohol group, (di)alkyl maleates having 1 to 10 carbon atoms in the alcohol group and mixtures thereof, where the molar degree of branching is in the range of 0.1 to 10 mol% and the comb polymer comprises a total of at least 80% by weight, based on the total weight of repeat units of the comb polymer, of the at least one repeat unit which is obtained from the at least one polyolefin-based macromonomer and the at least one repeat unit which is obtained from the at least one low molecular weight monomer. There is no disclosure in US2010/0190671, however, of the use of such comb polymers for providing improved long-term or sustained fuel economy.

There is also a need to provide lubricating compositions for use in the crankcase of an engine, wherein the compositions provide improved dispersancy and piston cleanliness benefits as well as long term or sustained fuel economy benefits.

Summary of the Invention

According to the present invention there is provided a lubricating composition for use in the crankcase of an engine comprising a base oil and one or more additives, wherein the base oil comprises a Fischer-Tropsch derived base oil and wherein the lubricating composition comprises one or more comb polymers. The lubricating composition of the present invention provides improved dispersancy and improved piston cleanliness in addition to improved long term or sustained fuel economy.

According to another aspect of the present invention there is provided the use of a lubricating composition as described herein, in the crankcase of an engine, in order to improve sustained fuel economy properties whilst obtaining improved piston cleanliness properties.

According to a further aspect of the present invention there is provided the use of a lubricating composition in the crankcase of an engine, in order to improve sustained fuel economy properties whilst obtaining improved dispersancy properties.

Detailed Description of the Invention

As used herein, the term “sustained fuel economy” means good fuel economy throughout the oil drain interval. A lubricant exhibiting sustained fuel economy has comparable good fuel economy performance throughout the oil drain interval as at the start.

While not wishing to be limited by theory it is believed that the improved soot dispersancy exhibited by the lubricating compositions of the present invention leads to a lower viscosity increase in the lubricating oil compositions over the oil drain interval and hence an improvement in sustained fuel economy properties.

There are no particular limitations regarding the base oil used in lubricating composition according to the present invention (provided that the base oil comprises at least a Fischer-Tropsch derived base oil), and various conventional mineral oils, synthetic oils as well as naturally derived esters such as vegetable oils may be conveniently used.

The base oil used in the present invention may - in addition to the Fischer-Tropsch derived base oil -

conveniently comprise mixtures of one or more mineral oils and/or one or more synthetic oils; thus, according to the present invention, the term "base oil" may refer to a mixture containing more than one base oil, including at least one Fischer-Tropsch derived base oil. Mineral oils include liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oil of the paraffinic, naphthenic, or mixed paraffinic/naphthenic type which may be further refined by hydrofinishing processes and/or dewaxing.

Suitable base oils for use in the lubricating oil composition of the present invention are Group I-III mineral base oils (preferably Group III), Group IV poly-alpha olefins (PAOs), Group II-III Fischer-Tropsch derived base oils (preferably Group III), Group V ester base oils, and mixtures thereof.

By "Group I", "Group II" "Group III" and "Group IV" and "Group V" base oils in the present invention are meant lubricating oil base oils according to the definitions of American Petroleum Institute (API) for categories I, II, III, IV and V. These API categories are defined in API Publication 1509, 15th Edition, Appendix E, April 2002.

Fischer-Tropsch derived base oils are known in the art. By the term "Fischer-Tropsch derived" is meant that a base oil is, or is derived from, a synthesis product of a Fischer-Tropsch process. A Fischer-Tropsch derived base oil may also be referred to as a GTL (Gas-To-Liquids) base oil. Suitable Fischer-Tropsch derived base oils that may be conveniently used as the base oil in the lubricating composition of the present invention are those as for example disclosed in EP 0 776 959, EP 0 668 342, WO 97/21788, WO 00/15736, WO 00/14188, WO 00/14187, WO

00/14183, WO 00/14179, WO 00/08115, WO 99/41332, EP 1 029 029, WO 01/18156 and WO 01/57166.

Typically, the aromatics content of a Fischer-Tropsch derived base oil, suitably determined by ASTM D 4629, will typically be below 1 wt.%, preferably below 0.5 wt.% and more preferably below 0.1 wt.%. Suitably, the base oil has a total paraffin content of at least 80 wt.%, preferably at least 85, more preferably at least 90, yet more preferably at least 95 and most preferably at least 99 wt.%. It suitably has a saturates content (as measured by IP-368) of greater than 98 wt.%. Preferably the saturates content of the base oil is greater than 99 wt.%, more preferably greater than 99.5 wt.%. It further preferably has a maximum n-paraffin content of 0.5 wt.%. The base oil preferably also has a content of naphthenic compounds of from 0 to less than 20 wt.%, more preferably of from 0.5 to 10 wt.%.

Typically, the Fischer-Tropsch derived base oil or base oil blend has a kinematic viscosity at 100°C (as measured by ASTM D 7042) in the range of from 1 to 30 mm^2/s (cSt), preferably from 1 to 25 mm^2/s (cSt), and more preferably from 2 mm^2/s to 12 mm^2/s. Preferably, the Fischer-Tropsch derived base oil has a kinematic viscosity at 100°C (as measured by ASTM D 7042) of at least 2.5 mm^2/s, more preferably at least 3.0 mm^2/s. In one embodiment of the present invention, the Fischer-Tropsch derived base oil has a kinematic viscosity at 100°C of at most 5.0 mm^2/s, preferably at most 4.5 mm^2/s, more preferably at most 4.2 mm^2/s (e.g. “GTL 4”). In another embodiment of the present invention, the Fischer-Tropsch derived base oil has a kinematic viscosity at 100°C of at most 8.5 mm^2/s, preferably at most 8 mm^2/s (e.g. “GTL 8”).

Further, the Fischer-Tropsch derived base oil typically has a kinematic viscosity at 40°C (as measured by ASTM D 7042) of from 10 to 100 mm^2/s (cSt), preferably from 15 to 50 mm^2/s.

Also, the Fischer-Tropsch derived base oil preferably has a pour point (as measured according to ASTM D 5950) of below -30°C, more preferably below -40°C, and most preferably below -45°C.

The flash point (as measured by ASTM D92) of the Fischer-Tropsch derived base oil is preferably greater than 120°C, more preferably even greater than 140°C.

The Fischer-Tropsch derived base oil preferably has a viscosity index (according to ASTM D 2270) in the range of from 100 to 200. Preferably, the Fischer-Tropsch derived base oil has a viscosity index of at least 125, preferably 130. Also it is preferred that the viscosity index is below 180, preferably below 150.

In the event the Fischer-Tropsch derived base oil contains a blend of two or more Fischer-Tropsch derived base oils, the above values apply to the blend of the two or more Fischer-Tropsch derived base oils.

The lubricating oil composition preferably comprises 80 wt% or greater of Fischer-Tropsch derived base oil.

Synthetic oils include hydrocarbon oils such as olefin oligomers (including polyalphaolefin base oils; PAOs), dibasic acid esters, polyol esters, polyalkylene glycols (PAGs), alkyl naphthalenes and dewaxed waxy isomerates. Synthetic hydrocarbon base oils sold by the Shell Group under the designation "Shell XHVI" (trade mark) may be conveniently used.

Poly-alpha olefin base oils (PAOs) and their manufacture are well known in the art. Preferred poly-alpha olefin base oils that may be used in the lubricating compositions of the present invention may be derived from linear C_2 to C_{32}, preferably C_6 to C_{16}, alpha olefins. Particularly preferred feedstocks for said poly-alpha olefins are 1-octene, 1-decene, 1-dodecene and 1-tetradecene.

There is a strong preference for using a Fischer-Tropsch derived base oil over a PAO base oil, in view of the high cost of manufacture of the PAOs. Thus, preferably, the base oil contains more than 50 wt.%, preferably more than 60 wt.%, more preferably more than 70 wt.%, even more preferably more than 80 wt.%. most preferably more than 90 wt.% Fischer-Tropsch derived base oil. In an especially preferred embodiment not more than 5 wt.%, preferably not more than 2 wt.%, of the base oil is not a Fischer-Tropsch derived base oil. It is even more preferred that 100 wt% of the base oil is based on one or more Fischer-Tropsch derived base oils.

The total amount of base oil incorporated in the lubricating composition of the present invention is preferably in the range of from 60 to 99 wt.%, more preferably in the range of from 65 to 90 wt.% and most preferably in the range of from 70 to 85 wt.%, with respect to the total weight of the lubricating composition.

Typically the base oil (or base oil blend) as used according to the present invention has a kinematic viscosity at 100°C (according to ASTM D445) of above 2.5 cSt and below 5.6 cSt. According to a preferred embodiment of the present invention the base oil has a kinematic viscosity at 100°C (according to ASTM D445) of between 3.5 and 4.5 cSt. In the event the base oil contains a blend of two or more base oils, it is preferred that the blend has a kinematic viscosity at

100°C of between 3.5 and 4.5 cSt.

Typically the lubricating compositions of the present invention would be utilised in, but not necessarily limited to, SAE J300 viscosity grades 0W-20, 0W-30, 0W-40, 5W-20, 5W-30 and 5W-40 as these are the grades which target fuel economy. As new SAE J300 viscosity grades are published, with lower viscosities than the current 0W-20, the present invention would also be very much applicable to these new viscosity lower grades. It is conceivable that the present invention could also be used with higher viscosity grades.

The lubricating composition according to the present invention preferably has a Noack volatility (according to ASTM D 5800) of below 15 wt.%. Typically, the Noack volatility (according to ASTM D 5800) of the composition is between 1 and 15 wt.%, preferably below 14.6 wt.% and more preferably below 14.0 wt.%.

The lubricating composition according to the present invention comprises one or more comb polymers, preferably in a solid polymer amount of from 0.1 wt% to 10 wt%, more preferably from 0.25 wt% to 7 wt%, and even more preferably from 0.5 wt% to 4 wt%, by weight of the total lubricating composition.

Preferably for use herein the comb polymer comprises, in the main chain, at least one repeat unit which is obtained from at least one polyolefin-based macromonomer, and at least one repeat unit which is obtained from at least one low molecular weight monomer selected from the group consisting of styrene monomers having 8 to 17 carbon atoms, alkyl(meth)acrylates having 1 to 10 carbon atoms in the alcohol group, vinyl esters having from 1 to 11 carbon atoms in the acyl group, vinyl ethers having 1 to 10 carbon atoms in the alcohol group, (di)alkyl fumurates having 1 to 10 carbon atoms in the alcohol group, (di)alkyl maleates having 1 to 10 carbon atoms in the alcohol group and mixtures thereof, where the molar degree of branching is in the range of 0.1 to 10 mol% and the comb polymer comprises a total of at least 80% by weight, based on the total weight of repeat units of the comb polymer, (or in another aspect based on the total weight of the comb polymer), of the at least one repeat unit which is obtained from the at least one polyolefin-based macromonomer and the at least one repeat unit which is obtained from the at least one low molecular weight monomer.

Preferably, the comb polymer used herein has 8% to 30% by weight of repeat units which are derived from polyolefin-based macromonomers, and the molar degree of branching of the comb polymer is in the range of 0.3% to 1.1%.

The term "comb polymer" as used herein means that relatively long side chains are bonded to a polymeric main chain, frequently also known as the backbone. The comb polymers used in the present invention have at least one repeat unit which is derived from polyolefin-based macromonomers. The exact proportion is evident via the molar degree of branching. The term "main chain" as used herein does not necessarily mean that the chain length of the main chain is greater than that of the side chains. Instead, this term relates to the composition of this chain. While the side chain has very high proportions of olefinic repeat units, especially units which are derived from alkenes or alkadienes, for example ethylene, propylene, n-butene, isobutene, butadiene, isoprene, the main chain comprises relatively large proportions of polar unsaturated monomers which have been detailed above.

The term “repeat unit” is known to those skilled in the art. The present comb polymers can be obtained by a process which involves the free-radical polymerisation of macromonomers and low molecular weight monomers, wherein double bonds are opened up to form covalent bonds. Accordingly, the repeat unit arises from the monomers used. However, the comb polymers can also be prepared by polymer-analagous reactions and graft copolymerisation. In this case, the converted repeat unit of the main chain is counted as a repeat unit which is derived from a polyolefin-based macromonomer. The same applies in the case of preparation of the comb polymers by graft polymerization.

Further details of preparation methods of the comb polymers use herein can be found in US2010/0190671 and US2008/0194443, which are incorporated herein by reference.

The comb polymers used in the present invention comprise repeat units which are derived from polyolefin-based macromonomers. These repeat units comprise at least one group which is derived from polyolefins. Examples of suitable polyolefins include C_2-C_{10} alkenes, such as ethylene, propylene, n-butene, isobutene, norbornene, and/or C_4-C_{10} alkadienes such as butadiene, isoprene, norbornadiene, and the like.

The repeat units derived from polyolefin-based macromonomers preferably comprise at least 70% by weight and more preferably at least 80% by weight and most preferably at least 90% by weight of groups which are derived from alkene and/or alkadienes, based on the weight of the repeat units derived from polyolefin-based macromonomers.

The polyolefinic groups may also be present in hydrogenated form. In addition to the groups which are derived from alkenes and/or alkadienes, the repeat units derived from polyolefin-based macromonomers may comprise further groups. These include small proportions of copolymerizable monomers, including among others, alkyl (meth)acrylates, styrene monomers, fumurates, maleates, vinyl esters and/or vinyl ethers. The proportion of these groups based on copolymerizable monomers is preferably at most 30% by weight, more preferably at most 15% by weight, based on the weight of the repeat units derived from polyolefin-based macromonomers. The repeat units derived from polyolefin-based macromonomers may comprise start groups and/or end groups which serve from functionalization or are caused by the preparation of the repeat units derived from polyolefin-based macromonomers. The proportion of these start groups and/or end groups is preferably at most 30% by weight, more preferably at most 15% by weight, based on the weight of the repeat units derived from polyolefin-based macromonomers.

The number-average molecular weight of the repeat units which are derived from polyolefin-based macromonomers is preferably in the range from 500 to 50000g/mol,more preferably from 700 to 10000g/mol, even more preferably from 1500 to 4900 g/mol and most preferably from 2000 to 3000 g/mol.

The melting point of the repeat units derived from the polyolefin-based macromonomers is preferably less than or equal to -10°C, more preferably less than or equal to -20°C, even more preferably less than or equal to -40°C, as measured by DSC. Most preferably, no DSC melting point can be measured for the repeat units derived from the polyolefin-based macromonomers.

In addition to the repeat units which are derived from the polyolefin-based macromonomers, the comb polymers used in the present invention comprise repeat units which are derived from low molecular weight monomers selected from the group consisting of styrene monomers having 8 to 17 carbon atoms, alkyl(meth)acrylates having 1 to 10 carbon atoms in the alcohol group, vinyl esters having 1 to 11 carbon atoms in the acyl group, vinyl ethers having 1 to 10 carbon atoms in the alcohol group, di(alkyl) fumurates having 1 to 10 carbon atoms in the alcohol group, (di)alkyl maleates having 1 to 10 carbon atoms in the alcohol group, and mixtures of these monomers.

The molecular weight of the low molecular weight repeat units or of the low molecular weight monomers is preferably at most 400g/mol, more preferably at most 200 g/mol and most preferably at most 150g/mol.

Examples of styrene monomers having 8 to 17 carbon atoms are styrene, substituted styrenes having an alkyl substituent in the side chain, for example, alpha-methyl-styrene and alpha-ethyl-styrene, substituted styrenes having an alkyl substituent on the ring, such as vinyltoluene p-methylstyrene, halogenated styrenes, for example monochlorostyrenes, dichlorostyrenes, tribromostyrenes, and tetrabromostyrenes.

The term “(meth)acrylates” encompasses acrylates and methacrylates, and also mixtures of acrylates and methacrylates. The alkyl (meth)acrylates having 1 to 10 carbon atoms in the alcohol group include (meth)acrylates which are derived from saturated alcohols, such as methyl(meth)acrylate, ethyl(meth)acrylate, n-propyl(meth)acrylate, isopropyl(meth)acrylate, n-butyl(meth)acrylate, tert-butyl(meth)acrylate, pentyl(meth)acrylate, hexyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, heptyl(meth)acrylate, 2-tert-butylheptyl(meth)acrylate, octyl(meth)acrylate, 3-isopropylheptyl(meth)acrylate, nonyl(meth)acrylate, decyl(meth)acrylate; (meth)acrylates which derive from unsaturated alcohols, for example 2-propynyl (meth)acrylate, allyl(meth)acrylate, vinyl(meth)acrylate, oleyl(meth)acrylate; cycloalkyl(meth)acrylates such as cyclpentyl(meth)acrylate, and 3-vinylcyclohexyl(meth)acrylate.

Preferred alkyl(meth)acrylates include 1 to 8, more preferably 1 to 4 carbon atoms in the alcohol group. The alcohol group here may be linear or branched.

Examples of vinyl esters having 1 to 11 carbon atoms in the acyl group include vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate. Preferred vinyl esters include 2 to 9, more preferably 2 to 5 carbon atoms in the acyl group. The acyl group may be linear or branched.

Examples of vinyl ethers having 1 to 10 carbon atoms in the alcohol group include vinyl methyl ether, vinyl ethyl ether, vinyl propyl ether, vinyl butyl ether. Preferred vinyl ethers include 1 to 8, more preferably 1 to 4 carbon atoms in the alcohol group. The alcohol group may be linear or branched.

The term “(di)ester” as used herein means that monoesters, diesters and mixtures of esters, especially of fumaric acid and/or of maleic acid may be used. The (di) alkyl fumurates having 1 to 10 carbon atoms in the alcohol group include monomethyl fumurate, dimethyl fumurate, monoethyl fumurate, diethyl fumurate, methyl ethyl fumurate, monobutyl fumurate, dibutyl fumurate, dipentyl fumurate and dihexyl fumurate. Preferred (di)alkyl fumurates comprise 1 to 8, more preferably 1 to 4, carbon atoms in the alcohol group. The alcohol group may be linear or branched.

The di(alkyl) maleates having 1 to 10 carbon atoms in the alcohol group include monomethyl maleate, dimethyl maleate, monoethyl maleate, diethyl maleate, methyl ethyl maleate, monobutyl maleate, dibutyl maleate. Preferred (di)alkyl maleates comprise 1 to 8, more preferably 1 to 4 carbon atoms in the alcohol group. The alcohol group herein may be linear or branched.

In addition to the repeat units detailed above, the comb polymers used herein may comprise further repeat units which are derived from further comonomers, their proportion being at most 20% by weight, preferably at most 10% by weight and more preferably at most 5% by weight, based on the weight of the repeat units.

These also include repeat units which are derived from alkyl(meth)acrylates having 11 to 30 carbon atoms in the alcohol group, especially undecyl(meth)acrylate, 5-methylundecyl(meth)acrylate, dodecyl(meth)acrylate, 2-methyldodecyl(meth)acrylate, tridecyl(meth)acrylate, 5-methyltridecyl(meth)acrylate, tetradecyl(meth)acrylate, pentadecyl(meth)acrylate, hexadecyl(meth)acrylate, 2-methylhexadecyl(meth)acrylate, heptadecyl(meth)acrylate, 5-isopropylheptadecyl(meth)acrylate, 4-tert-butyloctadecyl(meth)acrylate, 5-ethyloctadecyl(meth)acrylate, 3-isopropyloctadecyl(meth)acrylate, octadecyl(meth)acrylate, nonadecyl(meth)acrylate, eicosyl(meth)acrylate, cetyleicosyl(meth)acrylate, stearyleicosyl(meth)acrylate, docosyl(meth)acrylate and/or eicosyltetratriacontyl(meth)acrylate.

These also include repeat units which are derived from dispersing oxygen- and nitrogen-functionalized monomers such as those listed in paragraphs [0036] - [0059] of US2010/0190671, incorporated herein by reference.

The comb polymers used herein preferably have a molar degree of branching in the range of from 0.1 to 10 mol%, more preferably from 0.3 to 6 mol%, even more preferably from 0.3 to 1.1 mol%, especially from 0.4 to 1.0 mol% and most preferably from 0.4 to 0.6 mol%.

The molar degree of branching of the comb polymers f_{branch} is calculated by the formula:

$$f_{branch} = \frac{\sum_{a=1}^{A} n_a}{\sum_{a=1}^{A} n_a + \sum_{b=1}^{B} n_b}$$

where:

A is the number of types of repeat units which are derived from polyolefin-based macromonomers,

B is the number of types of repeat units which are derived from low molecular weight monomers selected from the group consisting of styrene monomers having 8 to 17 carbon atoms, alkyl(meth)acrylates having 1 to 10 carbon atoms in the alcohol group, vinyl esters having 1 to 11 carbon atoms in the acyl group, vinyl ethers having 1 to 10 carbon atoms in the alcohol group, (di)alkyl fumurates having 1 to 10 carbon atoms in the alcohol group, (di)alkyl maleates having 1 to 10 carbon atoms in the alcohol group, and mixtures of these monomers,

n_a is the number of repeat units which are derived from polyolefin-based macromonomers of the type a in the comb polymer molecule,

n_b is the number of repeat units which are derived from low molecular weight monomers selected from the group consisting of styrene monomers having 8 to 17 carbon atoms, alkyl(meth)acrylates having 1 to 10 carbon atoms in the alcohol group, vinyl esters having 1 to 11 carbon atoms in the acyl group, vinyl ethers having 1 to 10 carbon atoms in the alcohol group, (di)alkyl fumurates having 1 to 10 carbon atoms in the alcohol group, (di)alkyl maleates having 1 to 10 carbon atoms in the alcohol group, and mixtures of these monomers, of type b in the comb polymer molecule.

The molar degree of branching arises generally from the ratio of the monomers used if the comb polymer has been prepared by copolymerization of low molecular weight and macromolecular monomers. For the calculation, it is possible here to use the number-average molecular weight of the macromonomer.

If the comb polymer has been obtained by polymer-analogous reaction or by grant copolymerization, the molar degree of branching is found by known methods of determining the conversion.

The proportion of at least 80% by weight, preferably at least 90% by weight, of low molecular weight repeat units which are derived from monomers selected from the group consisting of styrene monomers having 8 to 17 carbon atoms, alkyl (meth)acrylates having 1 to 10 carbon atoms in the alcohol group, vinyl esters having 1 to 11 carbon atoms in the acyl group, vinyl ethers having 1 to 10 carbon atoms in the alcohol group, (di)alkyl fumurates having 1 to 10 carbon atoms in the alcohol group, (di)alkyl maleates having 1 to 10 carbon atoms in the alcohol group, and mixtures of these monomers, and of repeat units which are derived from polyolefin-based macromonomers, is based on the weight of the repeat units. In addition to the repeat units, polymers generally also comprise start groups and end groups which can form through initiation reactions and termination reactions. In one aspect of the present invention, the statement of at least 80% by weight, preferably at least 90% by weight, of low molecular weight repeat units which are derived from monomers selected from the group consisting of styrene monomers having 8 to 17 carbon atoms, alkyl (meth)acrylates having 1 to 10 carbon atoms in the alcohol group, vinyl esters having 1 to 11 carbon atoms in the acyl group, vinyl ethers having 1 to 10 carbon atoms in the alcohol group, (di)alkyl fumurates having 1 to 10 carbon atoms in the alcohol group, (di)alkyl maleates having 1 to 10 carbon atoms in the alcohol group, and mixtures of these monomers, and of repeat units which are derived from polyolefin-based macromonomers, is based on the weight of the comb polymers.

The comb polymer used herein preferably has 8 to 30% by weight, more preferably 10 to 26% by weight, of repeat units which are derived from polyolefin-based macromonomers, based on the total weight of the repeat units.

Preferred comb polymers for use herein include those which have a weight average molecular weight Mw in the range of 500,000 to 1,000,000g/mol, more preferably 100,000 to 500,000 g/mol and most preferably 150,000 to 450,000 g/mol.

The number-average molecular weight Mn, may preferably be in the range of 20,000 to 800,000 g/mol, more preferably 40,000 to 200,000 g/mol and most preferably 50,000 to 150,000 g/mol.

Preferably the comb polymers used herein have a polydipersity index Mw/Mn in the range of 1 to 5, more preferably in the range of from 2.5 to 4.5. The number average and the weight average molecular weight can be determined by known processes such as Gas Permeation Chromatography (GPC).

In a particular aspect of the present invention, the comb polymer has a low proportion of olefinic double bonds. The iodine number is preferably less than or equal to 0.2g per g of comb polymer, more preferably less than or equal to 0.1g per g of comb polymer. This proportion can be determined according to DIN 53241 after drawing off carrier oil and low molecular weight residual monomers at 180°C under reduced pressure for 24 hours.

In a preferred embodiment herein the comb polymer has repeat units which are derived from n-butyl methacrylate and/or from n-butyl acrylate. Preferably, the proportion of repeat units which are derived from n-butyl methacrylate and/or from n-butyl acrylate is at least 50% by weight, more preferably at least 60% by weight, based on the total weight of repeat units.

In a preferred embodiment herein the comb polymer has repeat units which are derived from styrene. The proportion of repeat units which are derived from styrene are preferably in the range of 0.1 to 30% by weight, more preferably 5 to 25% by weight.

In a preferred embodiment herein, the comb polymers have repeat units which are derived from alkyl(meth)acrylate having 11-30 carbon atoms in the alkyl radical, preferably in an amount in the range of 0.1% to 15% by weight, more preferably in the range of 1 to 10% by weight.

In a preferred embodiment herein the comb polymer has repeat units which are derived from styrene and repeat units which are derived from n-butyl methacrylate. The weight ratio of styrene repeat units and n-butylmethacrylate repeat units is preferably in the range of 1:1 to 1:9, more preferably 1:2 to 1:8.

In another preferred embodiment, the comb polymer has repeat units which are derived from methyl methacrylate and repeat units which are derived from n-butyl methacrylate, preferably in a weight ratio of 1:1 to 0:100, more preferably 3:7 to 0:100.

A commercially available comb polymer suitable for use herein is available from Evonik under the tradename Viscoplex 3-201.

The lubricating composition according to the present invention further comprises one or more additives such as anti-oxidants, anti-wear additives, dispersants, detergents, overbased detergents, extreme pressure additives, friction modifiers, viscosity index improvers, pour point depressants, metal passivators, corrosion inhibitors, demulsifiers, anti-foam agents, seal compatibility agents and additive diluent base oils, etc.

As the person skilled in the art is familiar with the above and other additives, these are not further discussed here in detail. Specific examples of such additives are described in for example Kirk-Othmer Encyclopedia of Chemical Technology, third edition, volume 14, pages 477-526.

Anti-oxidants that may be conveniently used include phenyl-naphthylamines (such as “IRGANOX L-06” available from Ciba Specialty Chemicals) and diphenylamines (such as “IRGANOX L-57” available from Ciba Specialty Chemicals) as e.g. disclosed in WO 2007/045629 and EP 1 058 720 B1, phenolic anti-oxidants, etc. The teaching of

WO 2007/045629 and EP 1 058 720 B1 is hereby incorporated by reference.

Anti-wear additives that may be conveniently used include zinc-containing compounds such as zinc dithiophosphate compounds selected from zinc dialkyl-, diaryl- and/or alkylaryl- dithiophosphates, molybdenum-containing compounds, boron-containing compounds and ashless anti-wear additives such as substituted or unsubstituted thiophosphoric acids, and salts thereof.

Examples of such molybdenum-containing compounds may conveniently include molybdenum dithiocarbamates, trinuclear molybdenum compounds, for example as described in WO 98/26030, sulphides of molybdenum and molybdenum dithiophosphate.

Boron-containing compounds that may be conveniently used include borate esters, borated fatty amines, borated epoxides, alkali metal (or mixed alkali metal or alkaline earth metal) borates and borated overbased metal salts.

The dispersant used is preferably an ashless dispersant. Suitable examples of ashless dispersants are polybutylene succinimide polyamines and Mannich base type dispersants.

The detergent used is preferably an overbased detergent or detergent mixture containing e.g. salicylate, sulphonate and/or phenate-type detergents.

Examples of viscosity index improvers which may conveniently be used in the lubricating composition of the present invention include the styrene-butadiene stellate copolymers, styrene-isoprene stellate copolymers and the polymethacrylate copolymer and ethylene-propylene copolymers (also known as olefin copolymers) of the crystalline and non-crystalline type. Dispersant-viscosity index improvers may be used in the lubricating composition of the present invention. However, preferably the composition according to the present invention contains less than 1.0 wt.%, preferably less than 0.5 wt.%, of a Viscosity Index improver concentrate (i.e. VI improver plus "carrier oil" or "diluent"), based on the total weight of the composition. Most preferably, the composition is free of Viscosity Index improver concentrate. The term "Viscosity Modifier" as used hereafter (such as in Table 2) is meant to be the same as the above-mentioned term "Viscosity Index improver concentrate".

Preferably, the composition contains at least 0.1 wt.% of a pour point depressant. As an example, alkylated naphthalene and phenolic polymers, polymethacrylates, maleate/fumarate copolymer esters may be conveniently used as effective pour point depressants. Preferably not more than 0.3 wt.% of the pour point depressant is used.

Furthermore, compounds such as alkenyl succinic acid or ester moieties thereof, benzotriazole-based compounds and thiodiazole-based compounds may be conveniently used in the lubricating composition of the present invention as corrosion inhibitors.

Compounds such as polysiloxanes, dimethyl polycyclohexane and polyacrylates may be conveniently used in the lubricating composition of the present invention as defoaming agents.

Compounds which may be conveniently used in the lubricating composition of the present invention as seal fix or seal compatibility agents include, for example, commercially available aromatic esters.

The lubricating compositions of the present invention may be conveniently prepared by admixing the comb polymer with the base oil(s), and one or more additives.

The above-mentioned additives are typically present in an amount in the range of from 0.01 to 35.0 wt.%, based on the total weight of the lubricating composition, preferably in an amount in the range of from 0.05 to 25.0 wt.%, more preferably from 1.0 to 20.0 wt.%, based on the total weight of the lubricating composition.

Preferably, the composition contains at least 9.0 wt.%, preferably at least 10.0 wt.%, more preferably at least 11.0 wt% of an additive package comprising an anti-wear additive, a metal detergent, an ashless dispersant and an anti-oxidant.

The lubricating compositions according to the present invention may be so-called “low SAPS” (SAPS = sulphated ash, phosphorus and sulphur), “mid SAPS” or “regular SAPS” formulations.

For Passenger Car Motor Oil (PCMO) engine oils the above ranges mean:

- a sulphated ash content (according to ASTM D 874) of up to 0.5 wt.%, up to 0.8 wt.% and up to 1.5 wt.%, respectively;
- a phosphorus content (according to ASTM D 5185) of up to 0.05 wt.%, up to 0.08 wt.% and typically up to 0.1 wt.%, respectively; and
- a sulphur content (according to ASTM D 5185) of up to 0.2 wt.%, up to 0.3 wt.% and typically up to 0.5 wt.%, respectively.

For Heavy Duty Diesel Engine Oils the above ranges mean:

- a sulphated ash content (according to ASTM D 874) of up to 1 wt.%, up to 1 wt.% and up to 2 wt.%, respectively;
- a phosphorus content (according to ASTM D 5185) of up to 0.08 wt.% (low SAPS) and up to 0.12 wt.% (mid SAPS),

respectively; and

- a sulphur content (according to ASTM D 5185) of up to 0.3 wt.% (low SAPS) and up to 0.4 wt.% (mid SAPS), respectively.

In another aspect, the present invention provides the use of a lubricating composition according to the present invention as an engine oil in the crankcase of an engine, in order to improve sustained fuel economy properties whilst also improving dispersancy and piston cleanliness properties. The engine oil may include a heavy duty diesel engine oil, a passenger car motor engine oil, as well as other types of engine oils.

The present invention is described below with reference to the following Examples, which are not intended to limit the scope of the present invention in any way.

Examples

Lubricating Oil Compositions

Various engine oils for use in a crankcase engine were formulated.

Table 1 indicates the properties for the base oils used. Table 2 indicates the composition and properties of the fully formulated engine oil formulations that were tested; the amounts of the components are given in wt.%, based on the total weight of the fully formulated formulations.

“Base oil 1” was a commercially available Group III base oils having a kinematic viscosity at 100°C (ASTM D445) of 4.2 cSt (average value). Base oil 1 is commercially available from e.g. SK Energy (Ulsan, South Korea) (under the trade designation “Yubase 4”).

“Base oil 2” was a commercially available Group III base oils having a kinematic viscosity at 100°C (ASTM

D445) of 6.5 cSt (average value). Base oil 2 is commercially available from e.g. SK Energy (Ulsan, South Korea) (under the trade designation "Yubase 6").

"Base oil 3" was a Fischer-Tropsch derived base oil ("GTL 4") having a kinematic viscosity at 100°C (ASTM D445) of approx. 4 cSt (mm^2s^{-1}). This GTL 4 base oil may be conveniently manufactured by the process described in e.g. WO 02/070631, the teaching of which is hereby incorporated by reference.

"Base oil 4" was a Fischer-Tropsch derived base oil ("GTL 8") having a kinematic viscosity at 100°C (ASTM D445) of approx. 8 cSt (mm^2s^{-1}). This GTL 8 base oil may be conveniently manufactured by the process described in e.g. WO 02/070631, the teaching of which is hereby incorporated by reference.

All tested engine oil formulations contained a combination of a base oil, a comb polymer (or other Viscosity Modifier in the case of Comparative Example 1), an additive package, optionally a pour point depressant, and optionally a friction modifier which additive package was the same in all tested compositions.

The additive package was a so-called "mid SAPS" (medium sulphated ash, phosphorus and sulphur) formulation.

The additive package contained a combination of additives including anti-oxidants, a zinc-based anti-wear additive, an ashless dispersant, an overbased detergent mixture and about 10 ppm of an anti-foaming agent.

The comb polymer was a commercially available comb polymer available from Evonik under the tradename "Viscoplex 3-201".

The pour point depressant in Comparative Example 1 was Viscoplex 6-054 which is a dispersant PMA commercially available from Evonik.

The viscosity modifier in Comparative Example 1 was a conventional styrene-hydrogenated isoprene co-polymer viscosity modifier concentrate, commercially available from Infineum under the trade designation “SV 201”.

The friction modifier was a conventional friction modifier, commercially available from Lubrizol under the tradename LZ8621.

The compositions of the Examples and the Comparative Examples were obtained by mixing the base oils with the other components, using conventional lubricant blending procedures.

In order to demonstrate the fuel economy properties of the compositions of the present invention, fuel economy measurements were performed on the examples and comparative examples according to the industry standard M111 Fuel Economy Test Method (according to CEC-L-054-96). The results of these tests are shown in Table 2.

In order to demonstrate the piston cleanliness properties of the compositions of the present invention, piston cleanliness measurements were performed on the examples and comparative examples according to the industry standard VW TDI Test Method (according to CEC-L-078-99). A “pass” for this method is deemed to be a value of greater than or equal to the reference oil (which in this case is 65 merits). The results of these tests are shown in Table 2.

In order to demonstrate the diesel soot dispersancy properties of the compositions of the present invention, measurements were performed on the examples and comparative examples according to the industry standard DV4 test (according to CEC-L-093-04). The results of these tests are shown in Table 2.

In order to demonstrate the propensity of the lubricating compositions of the present invention to form deposits when subjected to high temperatures (thermal stability) the examples and comparative examples were subjected to Microcoking Test (MCT) Method. In the MCT Method 0.6 cm^3 of the lubricating composition was put in the trough of an aluminium-alloy plate heated at one end (hot spot) and regulated at the other end (cold spot). The measurement of the temperature between these two spots allows to establish a thermal gradient, estimated to be linear, between the two ends of the trough. The standard duration of the test is 90 minutes. At the end of the test, the initiating temperature of deposit formation is determined and rated according to the CEC M-02-A-78 Code of Practice. The results of these tests are shown in Table 2.

Table 1

	Base oil 1 (Yubase 4)	Base oil 2 (Yubase 6)	Base oil 3 (GTL 4)	Base oil 4 (GTL 8)
Kinematic viscosity at 100°C[1] [cSt]	4.2	6.5	4.0	8
VI Index[2]	120	125	120	120
Pour point[3] [°C]	-15	-12	-30	-30
Noack volatility[4] [wt.%]	15.3	8	14.0	5

[1] According to ASTM D 445. Average figures quoted

[2] According to ASTM D 2270. Minimum values quoted.

[3] According to ASTM D 5950. Maximum values quoted.

[4] According to CEC L-40-A-93 / ASTM D 5800. Maximum values quoted

Table 2

Component [wt.%]	Comp. Example 1	Comp. Example 2	Example 1	Comp. Example. 3	Example 2
Base oil 1(Yubase 4)	49.5	76	-	78.1	-
Base oil 2(Yubase 6)	33.0	-	-	-	-
Base oil 3 (GTL 4)	-	-	55	-	53
Base oil 4 (GTL 8)	-	-	21	-	26
Viscoplex 3-201	-	11.5	11.5	9.4	8.5
Viscosity Modifier	5	-	-	-	-
Additive package	12	12	12	12	12
Pour point depressant	0.5	-	-	-	-
Friction Modifier	-	0.5	0.5	0.5	0.5
TOTAL	100	100	100	100	100
Properties of the total composition					
Kinematic viscosity at 100°C[1] [cSt]	11.83	11.31	10.88	9.853	9.707
Kinematic viscosity at 40°C[1] [cSt]	71.2	41.6	44.21	38.62	43.75
VI	165	281	247	255	216
HTHS 150[2] [cP]	3.53	3.45	3.49	3.15	3.24
M111	2.17	2.97	Not measured	3.45/3.32 (two measurements were taken)	3.07
VW TDI	65	Not measured	65	60 (average measurement) (fail)	65
MCT	6.3	4.1	6.6	5.2	7.5
DV4	9.5%	2.14%	2.22%	1.08%	Not measured

[1] According to ASTM D 445

[2] According to ASTM D 4683

Discussion

The results in Table 2 demonstrate that the lubricating compositions of the present invention surprisingly exhibit improved fuel economy, improved piston cleanliness, reduced high temperature deposit formation and improved soot dispersancy. Only when there is a combination of both GTL and comb polymer do we see fuel economy benefits together with piston cleanliness and reduced high temperature deposit formation.

CLAIMS

1. Lubricating composition for use in the crankcase of an engine comprising a base oil and one or more additives, wherein the base oil comprises a Fischer-Tropsch derived base oil and wherein the lubricating composition comprises one or more comb polymers.

2. Lubricating composition according to claim 1, wherein the comb polymer comprises, in the main chain, at least one repeat unit which is obtained from at least one polyolefin-based macromonomer, and at least one repeat unit which is obtained from at least one low molecular weight monomer selected from the group consisting of styrene monomers having 8 to 17 carbon atoms, alkyl(meth)acrylates having 1 to 10 carbon atoms in the alcohol group, vinyl esters having from 1 to 11 carbon atoms in the acyl group, vinyl ethers having 1 to 10 carbon atoms in the alcohol group, (di)alkyl fumurates having 1 to 10 carbon atoms in the alcohol group, (di)alkyl maleates having 1 to 10 carbon atoms in the alcohol group and mixtures thereof, where the molar degree of branching is in the range of 0.1 to 10 mol% and the comb polymer comprises a total of at least 80% by weight, based on the total weight of repeat units of the comb polymer, of the at least one repeat unit which is obtained from the at least one polyolefin-based macromonomer and the at least one repeat unit which is obtained from the at least one low molecular weight monomer.

3. Lubricating composition according to Claim 2, wherein the comb polymer has a molar degree of branching in the range of 0.3 to 3.6 mol%.

4. Lubricating composition according to claim 2 or 3

wherein the comb polymer has 8 to 30% by weight of the at least one repeat unit which is derived from the at least one polyolefin-based macromonomer, and the molar degree of branching of the comb polymer is in the range of 0.3% to 1.1%.

5. Lubricating composition according to any of claims 2 to 4 wherein the comb polymer has 11 to 26% by weight of the at least one repeat unit which is obtained from the at least one polyolefin-based macromonomer.

6. Lubricating composition according to any of claims 2 to 5, wherein the at least one repeat unit which is obtained from the at least one polyolefin-based macromonomer has a number-average molecular weight in the range of 700 to 10000 g/mol.

7. Lubricating composition according to any of claims 2 to 6 wherein the comb polymer comprises at least 90% by weight of repeat units which are obtained from at least one polyolefin-based macromonomer and from at least one low molecular weight monomer selected from the group consisting of styrene monomers having 8 to 17 carbon atoms, alkyl(meth)acrylates having 1 to 10 carbon atoms in the alcohol group, vinyl esters having from 1 to 11 carbon atoms in the acyl group, vinyl ethers having 1 to 10 carbon atoms in the alcohol group, (di)alkyl fumurates having 1 to 10 carbon atoms in the alcohol group, (di)alkyl maleates having 1 to 10 carbon atoms in the alcohol group and mixtures thereof.

8. Lubricating composition according to any of claims 2 to 7 wherein the polydispersity index Mw/Mn is in the range of from 1 to 5.

9. Lubricating composition according to any of claims 2 to 8 wherein the molar degree of branching of the comb polymer is in the range of from 0.4% to 1.0%, preferably

in the range of from 0.4% to 0.6%.

10. Lubricating composition according to any of claims 2 to 9 wherein the at least one repeat unit obtained from the at least one polyolefin-based macromonomer comprises a group which is obtained from monomers selected from the group consisting of C_2-C_{10} alkenes and C_4-C_{10} alkadienes.

11. Lubricating composition according to any of Claims 2 to 10 wherein the at least one repeat unit obtained from the at least one polyolefin-based macromonomer comprises at least 80% by weight of groups which are derived from monomers selected from the group consisting of C_2-C_{10} alkenes and C_4-C_{10} alkadienes, based on the weight of the at least one repeat unit derived from the at least one polyolefin-based macromonomer.

12. Lubricating composition according to any of claims 2 to 11 wherein the melting point of the at least one repeat unit obtained from the at least one polyolefin-based macromonomers is less than or equal to 10°C.

13. Lubricating composition according to any of claims 2 to 12 wherein no melting point of the at least one repeat unit obtained from the at least one polyolefin-based macromonomer is measured.

14. Lubricating composition according to any of claims 2 to 13 wherein the comb polymer has repeat units, preferably in a proportion of at least 50% by weight, which are obtained from at least one of n butyl methacrylate and n butyl acrylate.

15. Lubricating composition according to any of claims 2 to 14 wherein the comb polymer has repeat units which are obtained from styrene, preferably in a proportion in the range of from 5 to 25% by weight.

16. Lubricating composition according to any of claims 2 to 15 wherein the comb polymer has a weight-average

molecular weight in the range of 100,000 to 500,000 g/mol.

17. Lubricating composition according to any of claims 2 to 16 wherein the comb polymer has repeat units which are obtained from alkyl(meth)acrylates having 11—30 carbon atoms in the alkyl radical, preferably in a proportion in the range of from 1 to 10% by weight.

18. Lubricating composition according to any of claims 1 to 17 wherein the Fischer-Tropsch derived base oil has a kinematic viscosity at 100°C in the range of 2 mm^2/s to 10 mm^2/s.

19. Use of a lubricating composition according to any one of claims 1 to 18 in the crankcase of an engine, in order to improve sustained fuel economy properties whilst obtaining improved piston cleanliness properties.

20. Use of a lubricating composition according to any one of claims 1 to 18 in the crankcase of an engine, in order to improve sustained fuel economy properties whilst obtaining improved dispersancy properties.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/062666

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M169/04
ADD. C10N20/04 C10N30/04 C10N40/25

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)
C10M C10N

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 practicable, search terms used)

EPO-Internal, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010/190671 A1 (STOEHR TORSTEN [DE] ET AL) 29 July 2010 (2010-07-29) cited in the application the whole document -----	1-20
X	WO 2012/025901 A1 (TOTAL RAFFINAGE MARKETING [FR]; TRUONG-DINH NGUYEN [FR]) 1 March 2012 (2012-03-01) claims 1,13 -----	1
X	WO 2009/026201 A1 (LUBRIZOL CORP [US]; AL-AHMAD SALEEM [SA]) 26 February 2009 (2009-02-26) claims 1,12,13-15 -----	1
A	EP 2 186 872 A1 (SHELL INT RESEARCH [NL]) 19 May 2010 (2010-05-19) claim 9 ----- -/--	1-20

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 24 July 2013	Date of mailing of the international search report 05/08/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Greß, Tobias

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/062666

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2008/055976 A2 (SHELL INT RESEARCH [NL]; COLBOURNE DAVID [GB]; WEDLOCK DAVID JOHN [GB]) 15 May 2008 (2008-05-15) claim 13 -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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