

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
15 May 2008 (15.05.2008)

PCT

(10) International Publication Number
WO 2008/055976 A2

(51) **International Patent Classification:** Not classified

(21) **International Application Number:**

PCT/EP2007/062141

(22) **International Filing Date:**

9 November 2007 (09.11.2007)

(25) **Filing Language:**

English

(26) **Publication Language:**

English

(30) **Priority Data:**

06123806.9

10 November 2006 (10.11.2006)

EP

(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).

(72) **Inventors; and**

(75) **Inventors/Applicants** (for US only): **COLBOURNE, David** [GB/GB]; Pool Lane, Ince, Chester Cheshire CH2 4NU (GB). **WEDLOCK, David John** [GB/GB]; Pool Lane, Ince, Chester Cheshire CH2 4NU (GB).

(74) **Agent:** **SHELL INTERNATIONAL B.V.**; Intellectual Property Services, PO Box 384, NL-2501 CJ The Hague (NL).

(81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW

(84) **Designated States** (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, **DK**, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, **RO**, SE, SI, SK, TR), OAPI (BF, **BJ**, CF, CG, CI, CM, GA, GN, GQ, GW, ML, **MR**, NE, SN, TD, TG).

Declaration under Rule 4.17:

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(U))

Published:

— without international search report and to be republished upon receipt of that report

(54) **Title:** LUBRICANT COMPOSITION FOR USE THE REDUCTION OF PISTON RING FOULING IN AN INTERNAL COMBUSTION ENGINE

(57) **Abstract:** The present invention relates to a lubricant composition comprising a base oil or base oil blend and one or more additives, wherein the lubricant composition has a kinematic viscosity at 100°C of more than 5.0 mm²/s (cSt), a cold cranking simulated dynamic viscosity at -15°C according to ASTM D 5293 of less than 9500 mPas (cP) and a mini rotary viscosity test value of less than 60000 mPas at -20°C according to ASTM D 4684, and wherein the base oil or base oil blend has been obtained from a waxy paraffinic Fischer-Tropsch synthesized hydrocarbon fraction and comprises a continuous series of isoparaffins having n, n+1, n+2, n+3 and n+4 carbon atoms, wherein n is between 15 and 35, suitable for the reduction of piston ring fouling in an internal combustion engine.



WO 2008/055976 A2

- 1 -

LUBRICANT COMPOSITION FOR USE THE REDUCTION OF PISTON
RING FOULING IN AN INTERNAL COMBUSTION ENGINE

Field of invention

The present invention relates to a lubricant composition, and to the use of the lubricant composition for the reduction of piston ring deposits in a combustion engine.

Background of the invention

In the recent decades, use of internal combustion engines for transportation and other means of energy generation has become widespread. In particular compression ignited internal combustion engines which are also known as "Diesel engines" after Rudolf Diesel, who invented the first compression ignition engine in 1892, feature among the main type of engines employed for passenger cars in Europe, and globally for heavy duty applications, as well as for stationary power generation as a result of their high energy efficiency. In a compression-ignited internal combustion engine a fuel/air mixture is ignited by being compressed until it ignites due to the temperature increase due to compression, rather than by a separate source of ignition, such as a spark plug as in gasoline engines .

In recent years, compression-ignited internal combustion engines have been developed with a specific power output of as high as 60 kW/litre. Such engines have such high energy output that the heat can no longer be dissipated through heat exchange through the engine block

- 2 -

or cylinder head and the coolant or lubricant, while at the top ring groove, temperatures can exceed 250 °C. As a result, deposits on the piston and cylinder surfaces, such as soot and oil sludge are formed in increased amounts in such engines. This in turn can lead to ring-sticking or eventual failure of e.g. piston rings, and other related problems in their operation. A further issue at the high pressures and temperatures involved resides in the fact that the piston ring sealing performance may be compromised, resulting in gases from the combustion process to enter the lubricated parts of the engine. The result is enhanced oxidation and fouling of the lubricating oils employed. This one on hand will shorten the required exchange intervals, or can even lead to failure of the lubricating oil, and deposition of sludge in the engine.

Furthermore, sulphated ash, sulphur and phosphorus concentrations of lubricating oil compositions conventionally used in internal combustion engines may have adverse effects on engine cleanliness.

Hence, there is a need for a reduction of deposits formed on pistons and cylinders in diesel engine exhaust gases.

It has now surprisingly been found by applicants that when a lubricant composition based on highly paraffinic base oils comprising a continuous series of iso-paraffins having n , $n+1$, $n+2$, $n+3$ and $n+4$ carbon atoms, wherein n is between 15 and 35, and derived from a Fischer-Tropsch process, is employed to lubricate a compression-ignited internal combustion engine, deposits on the pistons and the piston ring grooves in the Nissan TD25 piston cleanliness tests are strongly diminished as compared to mineral oil based lubricants.

- 3 -

Summary of the invention

Accordingly, the present invention relates to a lubricant composition comprising a base oil or base oil blend and one or more additives, wherein the lubricant composition has a kinematic viscosity at 100 °C of more than 5.0 mm²/s (cSt), a cold cranking simulated dynamic viscosity at -15 °C according to ASTM D 5293 of less than 9500 mPas (cP) and a mini rotary viscosity test value of less than 60000 mPas at -20 °C according to ASTM D 4684, and wherein the base oil or base oil blend has been obtained from a waxy paraffinic Fischer-Tropsch synthesized hydrocarbon fraction and comprising a continuous series of iso-paraffins having n, n+1, n+2, n+3 and n+4 carbon atoms, wherein n is between 15 and 35, for the reduction of piston ring fouling in an internal combustion engine, having a Top Groove fill in of below 50 % vol. according to the Nissan TD25 Detergency Test (Japanese Automobile Standards Organization (JASO) M336:1998). Preferably, the lubricant composition has a residual carbon content of less than 4.8 % wt. according to the Nissan TD25 Detergency Test (Japanese Automobile Standards Organization (JASO) M336:1998).

The present invention accordingly relates to the use of a lubricant used to lubricate a compression-ignited internal combustion engine, i.e. a Diesel Engine, a reciprocating engine, Wankel engine and similar designed engine in which combustion is intermittent. As set out above, applicants have found that the use of a lubricant comprising a Fischer-Tropsch derived base oil leads to a significant and unexpected synergistic increase in piston cleanliness. Without wishing to be bound to any particular theory, it is believed that this may be related to the fact that the base oil properties result in a reduction

- 4 -

of the amounts of additives required to achieve a suitable viscosity behaviour of the lubricant composition, as well as due to physical properties such as thermal diffusion coefficient as compared to mineral oil derived base oils.

The engine for which the package according to the invention is to be employed is lubricated, i.e. the lubricant forms a film between surfaces of parts moving against each other so as to minimize direct contact between them. This lubricating film decreases friction, wearing, and production of excessive heat between the moving parts. Also as a moving fluid, the lubricant transposes heat from surfaces of lubricated parts due to friction from parts moving against each other or the oil film. Typically, an internal combustion engine has a crankcase, cylinder head, and cylinders. The lubricant is typically present in the crankcase, where crankshaft, bearings, and bottoms of rods connecting pistons to the crankshaft are submerged in the lubricant. The rapid motion of these parts causes the lubricant to splash and lubricate the contacting surfaces between the piston rings and interior surfaces of the cylinders. This lubricant film also serves as a seal between the piston rings and cylinder walls to separate the combustion volume in the cylinders from the space in the crankcase.

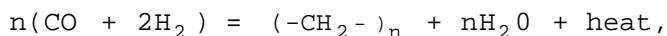
Without wishing to be bound to any particular theory, it is believed that the presence of the residual lubricant film reduces the temperature of the piston and interior surfaces of the cylinder, thereby reducing the formation of soot and sludge.

By "Fischer-Tropsch derived" is meant that a base oil is, or derives from, a synthesis product of a Fischer-Tropsch condensation process. The term

- 5 -

"non-Fischer-Tropsch derived" may be interpreted accordingly. A Fischer-Tropsch derived fuel may also be referred to as a GTL (Gas-To-Liquids) fuel.

The Fischer-Tropsch reaction converts carbon monoxide and hydrogen into longer chain, usually paraffinic, hydrocarbons :



in the presence of an appropriate catalyst and typically at elevated temperatures (eg, 125 to 300 °C, preferably

175 to 250°C) and/or pressures (eg, 5 to 100 bar, preferably 12 to 50 bar). Hydrogen :carbon monoxide ratios other than 2:1 may be employed if desired. The carbon monoxide and hydrogen may themselves be derived from organic or inorganic, natural or synthetic sources, typically either from natural gas or from organically derived methane.

An example of a Fischer-Tropsch based process is the SMDS (Shell Middle Distillate Synthesis) described in "The Shell Middle Distillate Synthesis Process", van der Burgt et al (supra) . This process (also sometimes referred to as the Shell "Gas-To-Liquids" or "GTL" technology) produces middle distillate range products by conversion of a natural gas (primarily methane) derived synthesis gas into a heavy long chain hydrocarbon (paraffin) wax which can then be hydroconverted and fractionated to produce liquid transport fuels such as the gas oils useable in diesel fuel compositions . A version of the SMDS process, utilising a fixed bed reactor for the catalytic conversion step, is currently in use in Bintulu, Malaysia and its gas oil products have been blended with petroleum derived gas oils in commercially available automotive fuels.

- 6 -

By virtue of the Fischer-Tropsch process, a Fischer-Tropsch derived base oil has essentially no, or undetectable levels of, sulphur and nitrogen. Compounds containing these heteroatoms tend to act as poisons for Fischer-Tropsch catalysts and are therefore removed from the synthesis gas feed. This can yield additional benefits, in terms of effect on catalyst performance, in fuel compositions in accordance with the present invention .

The lubricant compositions may be used to lubricate mechanical engine components, particularly an internal combustion, such as a compression-ignited, engine, by adding the lubricating oil thereto. The lubricant composition preferably comprises less than 10 wt% of an additional base oil not derived from Fischer-Tropsch process. Again more preferably, the lubricant composition comprises no additional base oil.

Preferably, the lubricant composition is a multigrade crankcase lubricating oil composition comprising, or made by admixing:

- (a) a major amount of a base oil having lubricating viscosity, comprised of at least 50% wt., more preferably at least 60% wt., yet more preferably at least 70% wt., again more preferably 80% wt., yet more preferably 90% wt., and most preferably 100 % wt. of a Fischer-Tropsch derived base oil; and minor amounts of:
 - (b) a dispersant, such as an ashless dispersant;
 - (c) a metal detergent, such as a calcium and/or magnesium detergent;
 - (e) one or more other lubricant additive components selected from anti-oxidants, anti-wear agents and friction modifiers; and
 - (f) a viscosity modifier.

- 7 -

Typical Fischer-Tropsch products comprise a continuous series of paraffins having n , $n+1$, $n+2$, $n+3$ and $n+4$ carbon atoms. The paraffins will be isomerized as set out below in order to achieve suitable viscometric properties for use as a lubricating oil. The base oils suitably employed in the present process comprise a continuous series of iso-paraffins having n , $n+1$, $n+2$, $n+3$ and $n+4$ carbon atoms, wherein n is between 15 and 35.

The base oil or base oil blend preferably has a paraffin content of greater than 80 wt% paraffins and a saturates content of greater than 98 wt%. Preferably, the base oil or base oil blend comprises at least 98 wt% saturates and wherein the saturates fraction consists of between 10 and 40 wt% of cyclo-paraffins.

The base oil may be a single base oil fraction, or a blend of base oil fractions of differing viscosity.

More preferably, the saturates fraction consists of more than 12 wt% of cyclo-paraffins.

The base oil preferably is a Fischer-Tropsch derived base oil, having a paraffin content of greater than 80 wt% paraffins, a saturates content of greater than 98 wt% and comprises a continuous series of iso-paraffins having n , $n+1$, $n+2$, $n+3$ and $n+4$ carbon atoms, wherein n is between 15 and 35, and wherein n is between 15 and 35.

The base oil further preferably comprises preferably at least 98 wt% saturates, more preferably at least 99.5 wt% saturates and most preferably at least 99.9 wt%. The saturates fraction in the base oil preferably comprises between 10 and 40 wt% of cyclo-paraffins. Again preferably, the content of cyclo-paraffins is less than 30 wt% and more preferably less than 20 wt%. Preferably the content of cyclo-paraffins is at least 12 wt% and more preferably at least 15 wt%. Such base oils are

- 8 -

further characterized in that the weight ratio of 1-ring cyclo-paraffins relative to cyclo-paraffins having two or more rings is greater than 3 preferably greater than 5. It was found that this ratio is suitably smaller than 15.

5 Any suitable method may be used to determine the content and the presence of the cyclo-paraffins and of a continuous series of the series of iso-paraffins having n , $n+1$, $n+2$, $n+3$ and $n+4$ carbon atoms in the base oil or base oil blend. A particularly suitable method comprises
10 the following steps:

The base oil sample is first separated into a polar (aromatic) phase and a non-polar (saturates) phase by making use of a high performance liquid chromatography (HPLC) method IP368/01, wherein as mobile phase pentane
15 is used instead of hexane as the method states. The saturates and aromatic fractions are then analyzed using a Finnigan MAT90 mass spectrometer equipped with a Field desorption/Field Ionisation (FD/FI) interface, wherein FI (a "soft" ionisation technique) is used for the semi-
20 quantitative determination of hydrocarbon types in terms of carbon number and hydrogen deficiency. The type classification of compounds in mass spectrometry is determined by the characteristic ions formed and is normally classified by "z number". This is given by the
25 general formula for all hydrocarbon species: C_nH_{2n+z} .

Because the saturates phase is analysed separately from the aromatic phase it is possible to determine the content of the different (cyclo)-paraffins having the same stoichiometry. The results of the mass spectrometer
30 are processed using commercial software (poly 32; available from Sierra Analytics LLC, 3453 Dragoo Park Drive, Modesto, California GA95350 USA) to determine the relative proportions of each hydrocarbon type and the

- 9 -

average molecular weight and polydispersity of the saturates and aromatics fractions.

The base oil composition preferably has a content of aromatic hydrocarbon compounds of less than 1 wt%, more preferably less than 0.5 wt% and most preferably less 0.1 wt%, a sulphur content of less than 20 ppm and a nitrogen content of less than 20 ppm. The pour point of the base oil is preferably less than -30 °C and more preferably lower than -40 °C. The viscosity index is preferably higher than 120. It has been found that the novel base oils typically have a viscosity index of below 140. The kinematic viscosity at 100 °C of the base oil is preferably between 2 and 25 mm²/s (cSt), preferably between 3 and 15 mm²/s, and more preferably between 4 and 8 mm²/s and the Noack volatility is preferably lower than 14 wt%.

The base oils as described above are suitably obtained by hydroisomerisation of a Fischer-Tropsch derived paraffinic wax, preferably followed by some type of dewaxing, such as solvent or catalytic dewaxing.

The base oils as derived from a Fischer-Tropsch wax as here described will be referred to in this description as Fischer-Tropsch derived base oils. Blends of different base oil grades or fractions having different viscosity may also be employed. This has the advantage that a large range of lubricant viscosity is available.

The base oil or base oil blend is suitably obtainable from a process comprising the following steps:

(a) hydrocracking/hydroisomerising a Fischer-Tropsch product having a weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms of at least 0.2 and wherein at

- 10 -

least 30 wt% of compounds in the Fischer-Tropsch product have at least 30 carbon atoms,

(b) separating the product of step (a) into at least one or more fuel fractions and a base oil precursor fraction, and

(c) performing a catalytic dewaxing step to the base oil precursor fraction obtained in step (b), and optionally

(d) separating the products obtained in step (c) into at least one or more base oil fractions, and a lower boiling fraction.

Preferably, the Fischer-Tropsch product used in step (a) has at least 50 wt%, and more preferably at least 55 wt% of compounds having at least 30 carbon atoms and wherein the weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms of the Fischer-Tropsch product is at least 0.4 and wherein the Fischer-Tropsch product comprises a C20+ fraction having an ASF-alpha value (Anderson-Schulz-Flory chain growth factor) of at least 0.925.

Examples of Fischer-Tropsch processes which for example can be used to prepare the above-described Fischer-Tropsch derived base oil are the so-called commercial Slurry Phase Distillate technology of Sasol, the Shell Middle Distillate Synthesis Process and the "AGC-21" Exxon Mobil process. These and other processes are for example described in more detail in US-A-4943672, US-A-5059299, WO-A-9934917 and WO-A-9920720. Typically these Fischer-Tropsch synthesis products will comprise hydrocarbons having 1 to 100 and even more than 100 carbon atoms. This hydrocarbon product will comprise normal paraffins, iso-paraffins, oxygenated products and unsaturated products. If base oils are one of the desired

- 11 -

iso-paraffinic products it may be advantageous to use a relatively heavy Fischer-Tropsch derived feed. The relatively heavy Fischer-Tropsch derived feed has at least 30 wt%, preferably at least 50 wt%, and more preferably at least 55 wt% of compounds having at least 30 carbon atoms. Furthermore the weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms of the Fischer-Tropsch derived feed is preferably at least 0.2, more preferably at least 0.4 and most preferably at least 0.55. Preferably the Fischer-Tropsch derived feed comprises a C₂₀+ fraction having an ASF-alpha value (Anderson-Schulz-Flory chain growth factor) of at least 0.925, preferably at least 0.935, more preferably at least 0.945, even more preferably at least 0.955. Such a Fischer-Tropsch derived feed can be obtained by any process, which yields a relatively heavy Fischer-Tropsch product as described above. Not all Fischer-Tropsch processes yield such a heavy product. An example of a suitable Fischer-Tropsch process is described in WO-A-9934917. The Fischer-Tropsch derived base oil will contain no or very little sulphur and nitrogen containing compounds. This is typical for a product derived from a Fischer-Tropsch reaction, which uses synthesis gas containing almost no impurities. Sulphur and nitrogen levels will generally be below the detection limits, which are currently 5 mg/kg for sulphur and 1 mg/kg for nitrogen respectively.

The process will generally comprise a Fischer-Tropsch synthesis, a hydroisomerisation step and an optional pour point reducing step, wherein said hydroisomerisation step and optional pour point reducing step are performed as:

(a) hydrocracking/hydroisomerising a Fischer-

- 12 -

Tropsch product, (b) separating the product of step (a) into at least one or more distillate fuel fractions and a base oil or base oil intermediate fraction.

5 If the viscosity and pour point of the base oil as obtained in step (b) is as desired no further processing is necessary and the oil can be used as the base oil according the invention. If required, the pour point of the base oil intermediate fraction is suitably further reduced in a step (c) by means of solvent or preferably
10 catalytic dewaxing of the oil obtained in step (b) to obtain oil having the preferred low pour point. The desired viscosity of the base oil may be obtained by isolating by means of distillation from the intermediate base oil fraction or from the dewaxed oil the a suitable
15 boiling range product corresponding with the desired viscosity. Distillation may be suitably a vacuum distillation step.

The hydroconversion/hydroisomerisation reaction of step (a) is preferably performed in the presence of
20 hydrogen and a catalyst, which catalyst can be chosen from those known to one skilled in the art as being suitable for this reaction of which some will be described in more detail below. The catalyst may in principle be any catalyst known in the art to be suitable
25 for isomerising paraffinic molecules. In general, suitable hydroconversion/hydroisomerisation catalysts are those comprising a hydrogenation component supported on a refractory oxide carrier, such as amorphous silica-
alumina (ASA), alumina, fluorided alumina, molecular
30 sieves (zeolites) or mixtures of two or more of these. One type of preferred catalysts to be applied in the hydroconversion/hydroisomerisation step in accordance with the present invention are

- 13 -

hydroconversion/hydroisomerisation catalysts comprising platinum and/or palladium as the hydrogenation component. A very much preferred hydroconversion/hydroisomerisation catalyst comprises platinum and palladium supported on an amorphous silica-alumina (ASA) carrier. The platinum and/or palladium is suitably present in an amount of from 0.1 to 5.0% by weight, more suitably from 0.2 to 2.0% by weight, calculated as element and based on total weight of carrier. If both present, the weight ratio of platinum to palladium may vary within wide limits, but suitably is in the range of from 0.05 to 10, more suitably 0.1 to 5. Examples of suitable noble metal on ASA catalysts are, for instance, disclosed in WO-A-9410264 and EP-A-0582347 . Other suitable noble metal-based catalysts, such as platinum on a fluorided alumina carrier, are disclosed in e.g. US-A-5059299 and WO-A-9220759 . A second type of suitable hydroconversion/hydroisomerisation catalysts are those comprising at least one Group VIB metal, preferably tungsten and/or molybdenum, and at least one non-noble Group VIII metal, preferably nickel and/or cobalt, as the hydrogenation component. Both metals may be present as oxides, sulphides or a combination thereof. The Group VIB metal is suitably present in an amount of from 1 to 35% by weight, more suitably from 5 to 30% by weight, calculated as element and based on total weight of the carrier. The non-noble Group VIII metal is suitably present in an amount of from 1 to 25 wt%, preferably 2 to 15 wt%, calculated as element and based on total weight of carrier. A hydroconversion catalyst of this type, which has been found particularly suitable, is a catalyst comprising nickel and tungsten supported on fluorided alumina .

- 14 -

The above non-noble metal-based catalysts are preferably used in their sulphided form. In order to maintain the sulphided form of the catalyst during use some sulphur needs to be present in the feed. Preferably at least 10 mg/kg and more preferably between 50 and 150 mg/kg of sulphur is present in the feed.

A preferred catalyst, which can be used in a non-sulphided form, comprises a non-noble Group VIII metal, e.g., iron, nickel, in conjunction with a Group IB metal, e.g., copper, supported on an acidic support. Copper is preferably present to suppress hydrogenolysis of paraffins to methane. The catalyst has a pore volume preferably in the range of 0.35 to 1.10 ml/g as determined by water absorption, a surface area of preferably between 200-500 m²/g as determined by BET nitrogen adsorption, and a bulk density of between 0.4-1.0 g/ml. The catalyst support is preferably made of an amorphous silica-alumina wherein the alumina may be present within wide range of between 5 and 96 wt%, preferably between 20 and 85 wt%. The silica content as SiO₂ is preferably between 15 and 80 wt%. Also, the support may contain small amounts, e.g., 20-30 wt%, of a binder, e.g., alumina, silica, Group IVA metal oxides, and various types of clays, magnesia, etc., preferably alumina or silica. The preparation of amorphous silica-alumina microspheres has been described in Ryland, Lloyd B., Tamele, M.W., and Wilson, J.N., Cracking Catalysts, Catalysis: volume VII, Ed. Paul H. Emmett, Reinhold Publishing Corporation, New York, 1960, pp. 5-9.

The catalyst is prepared by co-impregnating the metals from solutions onto the support, drying at 100-150 °C, and calcining in air at 200-550 °C. The Group VIII metal is present in amounts of about 15 wt% or

- 15 -

less, preferably 1-12 wt%, while the Group IB metal is usually present in lesser amounts, e.g., 1:2 to about 1:20 weight ratio respecting the Group VIII metal.

A typical catalyst is shown below:

5 Ni, wt% 2.5-3.5
Cu, wt% 0.25-0.35
Al₂O₃-SiO₂ wt% 65- 75
Al₂O₃ (binder) wt% 25-30
Surface Area 290-325 m²/g
10 Pore Volume (Hg) 0.35-0.45 ml/g
Bulk Density 0.58-0.68 g/ml

Another class of suitable hydroconversion/hydroisomerisation catalysts are those based on molecular sieve type materials, suitably comprising at least one Group VIII metal component, preferably Pt and/or Pd, as the hydrogenation component. Suitable zeolitic and other aluminosilicate materials, then, include Zeolite beta, Zeolite γ , Ultra Stable γ , ZSM-5, ZSM-12, ZSM-22, ZSM-23, ZSM-48, MCM-68, ZSM-35, SSZ-32, ferrierite, mordenite and silica-alumino-phosphates, such as SAPO-11 and SAPO-31.

Examples of suitable hydroisomerisation / hydroisomerisation catalysts are for instance described in WO-A-9201657 . Combinations of these catalysts are also possible. Very suitable ydroconversion/hydroisomerisation processes are those involving a first step wherein a zeolite beta or ZSM-48 based catalyst is used and a second step wherein a ZSM-5, ZSM-12, ZSM-22, ZSM-23, ZSM-48, MCM-68, ZSM-35, SSZ-32, ferrierite, mordenite based catalyst is used. Of the latter group ZSM-23, ZSM-22 and ZSM-48 are preferred. Examples of such processes are described in US-A-20040065581, which

- 16 -

disclose a process comprising a first step catalyst comprising platinum and zeolite beta and a second step catalyst comprising platinum and ZSM-48. These processes are capable of yielding a base oil product which does not require a further dewaxing step.

Combinations wherein the Fischer-Tropsch product is first subjected to a first hydroisomerisation step using the amorphous catalyst comprising a silica-alumina carrier as described above followed by a second hydroisomerisation step using the catalyst comprising the molecular sieve has also been identified as a preferred process to prepare the base oil to be used in the present invention. More preferred the first and second hydroisomerisation steps are performed in series flow. Most preferred the two steps are performed in a single reactor comprising beds of the above amorphous and/or crystalline catalyst.

In step (a) the feed is contacted with hydrogen in the presence of the catalyst at elevated temperature and pressure. The temperatures typically will be in the range of from 175 to 380 °C, preferably higher than 250 °C and more preferably from 300 to 370 °C. The pressure will typically be in the range of from 10 to 250 bar and preferably between 20 and 80 bar. Hydrogen may be supplied at a gas hourly space velocity of from 100 to 10000 Nl/l/hr, preferably from 500 to 5000 Nl/l/hr. The hydrocarbon feed may be provided at a weight hourly space velocity of from 0.1 to 5 kg/l/hr, preferably higher than 0.5 kg/l/hr and more preferably lower than 2 kg/l/hr. The ratio of hydrogen to hydrocarbon feed may range from 100 to 5000 Nl/kg and is preferably from 250 to 2500 Nl/kg.

The conversion in step (a) as defined as the weight percentage of the feed boiling above 370 °C which reacts

- 17 -

per pass to a fraction boiling below 370 °C, is at least 20 wt%, preferably at least 25 wt%, but preferably not more than 80 wt%, more preferably not more than 65 wt%. The feed as used above in the definition is the total hydrocarbon feed fed to step (a), thus also any optional recycle of a high boiling fraction which may be obtained in step (b) .

In step (b) the product of step (a) is preferably separated into one or more distillate fuels fractions and a base oil or base oil precursor fraction having the desired viscosity properties. If the pour point is not in the desired range the pour point of the base oil is further reduced by means of a dewaxing step (c), preferably by catalytic dewaxing. In such an embodiment it may be a further advantage to dewax a wider boiling fraction of the product of step (a) . From the resulting dewaxed product the base oil and oils having a desired viscosity can then be advantageously isolated by means of distillation. Dewaxing is preferably performed by catalytic dewaxing as for example described in WO-A-02070629, which publication is hereby incorporated by reference. The final boiling point of the feed to the dewaxing step (c) may be the final boiling point of the product of step (a) or lower if desired.

Suitably, the base oil or base oil blend has a kinematic viscosity at 100 °C of from 3 to 25 mm²/s. Preferably, it has a kinematic viscosity at 100 °C of from 3 to 15 mm²/sec, more preferably of from 3,5 to 9,5 mm²/sec, yet more preferably from 3,75 to 8,5 mm²/sec.

Preferably, the base oil has a pour point of less than -39 °C and a kinematic viscosity at 100 °C of

- 18 -

between 3.8 and 8.5 mm²/s (cSt), and wherein the lubricant composition has a kinematic viscosity at 100 °C of between 9.3 and 12.5 mm²/s (cSt). Yet more preferably, it has a kinematic viscosity at 100 °C below 15,5 mm²/s, more preferably below 14 mm²/s, most preferably below 13 mm²/s.

The pour point of the base oil is preferably below -30 °C. The flash point of the base oil as measured by ASTM D92 preferably is greater than 120 °C, more preferably even greater than 140 °C.

The base oil used in the lubricant composition in the package according to the invention preferably has a viscosity index in the range of from 100 to 600, more preferably a viscosity index in the range of from 110 to 200, and even more preferably a viscosity index in the range of from 120 to 150.

The lubricant used in the package according to the invention may comprise as the base oil component exclusively the paraffinic base oil, or a combination of the paraffinic base oils and ester as described above, or alternatively in combination with another additional base oil. The additional base oil will suitably comprise less than 20 wt%, more preferably less than 10 wt%, again more preferably less than 5 wt% of the total fluid formulation. Examples of such base oils are mineral based paraffinic and naphthenic type base oils and synthetic base oils, for example poly alpha olefins, poly alkylene glycols and the like. The amounts are limited by the nitrous oxide reduction that is to be attained. Preferably, the lubricant further comprises saturated cyclic hydrocarbons in an amount of from 5 to 10% by weight, based on the total lubricant since this improves

- 19 -

the low temperature compatibility of the different components in the lubricant.

The lubricant according to the invention further preferably comprises a viscosity improver in an amount of
5 from 0.01 to 30% by weight. Viscosity index improvers (also known as VI improvers, viscosity modifiers, or viscosity improvers) provide lubricants with high- and low-temperature operability. These additives impart shear stability at elevated temperatures and acceptable
10 viscosity at low temperatures. The lubricant used in the package according to the invention further preferably comprises at least one other additional lubricant component in effective amounts, such as for instance polar and/or non-polar lubricant base oils, and
15 performance additives such as for example, but not limited to, metallic and ashless oxidation inhibitors, metallic and ashless dispersants, metallic and ashless detergents, corrosion and rust inhibitors, metal deactivators, metallic and non-metallic, low-ash,
20 phosphorus- containing and non-phosphorus, sulphur- containing and non-sulphur-containing anti-wear agents, metallic and non-metallic, phosphorus-containing and non-phosphorus, sulphur-containing and non-sulphurous extreme pressure additives, anti-seizure agents, pour point
25 depressants, wax modifiers, viscosity modifiers, seal compatibility agents, friction modifiers, lubricity agents, anti-staining agents, chromophoric agents, anti foaming agents, demulsifiers, and other usually employed additive packages. For a review of many commonly used
30 additives, reference is made to D. Klamann in Lubricants and Related Products, Verlag Chemie, Deerfield Beach, FL; ISBN 0-89573-177-0, and to "Lubricant Additives" by M. W.

- 20 -

Ranney, published by Noyes Data Corporation of Parkridge, N.J. (1973) .

Preferably, the lubricant composition has low sulphated ash, sulphur and phosphorus concentrations, which will result in additional engine cleanliness such as piston cleanliness. More preferably, the lubricant composition has a sulphur content of in the range of from 0.01 to 0.3 wt. %, a phosphorus content in the range of from 0.01 to 0.1 wt. % and a sulphated ash content in the range of from 0.1 to 1.2 wt. %, based on the total weight of the lubricant composition, which comprises the synthetic base oil as described herein-above.

In a preferred embodiment of the present invention, R is an optionally substituted branched or straight chain alkyl group containing from 4 to 49 carbon atoms, more preferably from 6 to 40 carbon atoms; R₁ is hydrogen or an optionally substituted branched or straight chain alkyl group containing from 3 to 50 carbon atoms, more preferably from 4 to 49 carbon atom, even more preferably from 6 to 40 carbon atoms; and X is an integer from 10 to 9,000, more preferably from 20 to 8,000.

In the present invention, the phrase "optionally substituted branched or straight chain alkyl group" is used to describe alkyl groups optionally containing one or more "inert" heteroatom-containing functional groups. By "inert" is meant that the functional groups do not interact to any substantial degree with the other components of the lubricating oil composition. Non-limiting examples of such inert groups are amines and halides, such as fluoride and chloride.

Examples of compounds of formula I include those described in US-B1-6331510, US-B1-6204224 and US-B1-6372696 . Compounds of formula I include those

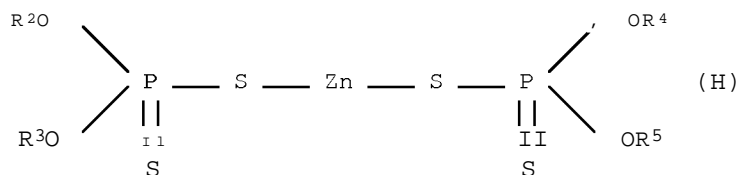
- 21 -

available ex. Rohmax under the trade designations "Acryloid 985", "Viscoplex 6-054", "Viscoplex 6-954" and "Viscoplex 6-565" and that available ex. The Lubrizol Corporation under the trade designation "LZ 7720C".

Compounds of formula I may be conveniently prepared by conventional methods. In particular, said compounds may be prepared according to the methods described in US-A-3506574 and EP-A2-0750031 .

The lubricating oil composition may comprise a single zinc dithiophosphate or a combination of two or more zinc dithiophosphates, the or each zinc dithiophosphate being selected from zinc dialkyl-, diaryl- or alkylaryl-dithiophosphates, provided that the total phosphorus content of the lubricating oil composition is in the range of from 0.01 to 0.1 wt. % .

Zinc dithiophosphate is a well known additive in the art and may be conveniently represented by general formula II;



wherein R² to R⁵ may be the same or different and are each a primary alkyl group containing from 1 to 20 carbon atoms preferably from 3 to 12 carbon atoms, a secondary alkyl group containing from 3 to 20 carbon atoms, preferably from 3 to 12 carbon atoms, an aryl group or an aryl group substituted with an alkyl group, said alkyl substituent containing from 1 to 20 carbon atoms preferably 3 to 18 carbon atoms.

Zinc dithiophosphate compounds in which R² to R⁵ are all different from each other can be used alone or in

- 22 -

admixture with zinc dithiophosphate compounds in which R2 to R5 are all the same.

Preferably, the or each zinc dithiophosphate used in the present invention is a zinc dialkyl dithiophosphate.

5 Suitable zinc dithiophosphates which are commercially available include primary zinc dithiophosphates such as those available ex. Lubrizol Corporation under the trade designations "Lz 1097" and "Lz 1395", those available ex. Chevron Oronite under the trade designations "OLOA 267" and "OLOA 269R", and that available ex. Ethyl under the trade designation "HITEC 7197"; secondary zinc

10 dithiophosphates such as those available ex. Lubrizol Corporation under the trade designations "Lz 677A", "Lz 1095" and "Lz 1371", that available ex. Chevron Oronite under the trade designation "OLOA 262" and that available ex. Ethyl under the trade designation "HITEC 7169"; and aryl type zinc dithiophosphates such as those available ex. Lubrizol Corporation under the trade designations "Lz 1370" and "Lz 1373" and that available ex. Chevron

15 Oronite under the trade designation "OLOA 260".

The lubricating oil composition according to the present invention may generally comprise in the range of from 0.1 to 1.0 wt. % of zinc dithiophosphate, (if primary or secondary alkyl type), preferably in the range

25 of from 0.2 to 0.8 wt. % and most preferably in the range of from 0.4 to 0.7 wt. %, based on total weight of the lubricating oil composition.

The amount of phosphorus in the lubricating oil composition of the present invention is therefore

30 generally in the range of from 0.01 to 0.10 wt. %, preferably in the range of from 0.02 to 0.08 wt. %, most preferably in the range of from 0.04 to 0.07 wt. %.

- 23 -

At phosphorus levels of 0.01 wt. % and below, there is insufficient anti-wear performance. At phosphorus levels of 0.1 wt. % and above, the phosphorus may have a detrimental effect on vehicle after-treatment devices .

5 The lubricating oil composition of the present invention generally has a sulphated ash content in the range of from 0.1 to 1.2 wt. %, preferably in the range of from 0.3 to 1.2 wt. %, more preferably in the range of from 0.5 to 1.1 wt. % and most preferably in the range of
10 from 0.6 to 1.0 wt. %, based on the total weight of the lubricating oil composition.

 The lubricating oil composition of the present invention generally has a sulphur content in the range of from 0.01 to 0.3 wt. %, preferably in the range of from
15 0.06 to 0.3 wt. %, more preferably in the range of from 0.1 to 0.25 wt. % and most preferably in the range of from 0.12 to 0.20 wt. %, based on the total weight of the lubricating oil composition.

 Preferred compositions according to the present invention have one or more of the following features:

- 20 (i) greater than 0.01 wt. % of phosphorus;
 (ii) greater than 0.035 wt. % of phosphorus;
 (iii) at least 0.035 wt. % of phosphorus;
 (iv) less than 0.07 wt. % of phosphorus;
25 (v) less than 0.10 wt. % of phosphorus;
 (vi) at most 0.08 wt. % of phosphorus;
 (vii) not greater than 1.0 wt. % of sulphated ash;
 (viii) not greater than 0.9 wt. % of sulphated ash;
 (ix) not greater than 0.7 wt. % of sulphated ash;
30 (x) not greater than 0.3 wt. % of sulphur;
 (xi) not greater than 0.1 wt. % of sulphur; and
 (xii) not greater than 0.05 wt. % of sulphur, based on the total weight of the lubricating oil composition.

- 24 -

In a further aspect, the present invention provides for a method of lubricating a compression-ignited internal combustion engine comprising operating the engine and lubricating the engine with a lubricating oil composition of the first aspect. In yet a further aspect, the present invention provides a method of improving piston cleanliness and reducing the ring-sticking tendencies of a compression-ignited internal combustion engine comprising adding to the engine a lubricating oil composition according to the present invention. In yet a further aspect, the present invention provides a combination comprising the crankcase of a compression-ignited internal combustion engine, preferably having a specific power output of 25 kW/ litre or greater, and a lubricating oil composition according to the invention.

The invention will be further illustrated by the following, non-limiting examples:

Example 1

Two low sulfur, low sulphated ash, and low phosphorus content 5W-40 lubricant compositions were prepared.

The lubricant formulation according to the present invention was formulated using two Fischer-Tropsch derived base oils having the properties as disclosed in Table 1.

For comparison, a lubricant formulation was prepared based on two mineral oil-derived Group III base oils commercially available as Yubase 4 and Yubase 6 from SK Corporation (Yubase is a registered trademark of SK Corporation). A "Group III" base oil is a base oil according to the definitions of American Petroleum Institute (API) category I and II. Such API categories are defined in API Publication 1509, 15th Edition, Appendix E, April 2002. Group III base oils contain

- 25 -

greater than or equal to 90 % saturates and less than or equal to 0.03 % sulphur and have a viscosity index of greater than 120, according to the afore-mentioned ASTM methods. The following additives were employed: VISCOPLEX 6-054, a commercially available dispersant and viscosity index improver (VISCOPLEX is a registered trademark of Rohm GmbH & Co. KG); a commercially available heavy duty diesel engine oil soot dispersant; Infineum SV200 and Infineum SV150, both commercially available viscosity index improvers ("Infineum" is a trademark of Infineum International Ltd.; SV, is an abbreviation for ShellVis, the latter is a trademark of Shell Chemical Company) , and a commercially available overbased detergent (Infineum C9371). Lubricant compositions were blended to comparable VdCCS (cold crank viscosity) at -30C and comparable Vk100C by appropriately balancing the pair of base oils in each case and also the viscosity modifier treat in each case.

Table 1 : Blends for Nissan TD25 piston cleanliness tests

Components [% m/m]	Example 1	Comparative Example
GTL base oil 1 (5 mm ² /s (cSt))	63,60	-
GTL base oil 2 [8 mm ² /s (cSt)]	7,50	-
Yubase 4	-	62,00
Yubase 6	-	6,36
Ashless dispersant	14,00	14,00
Overbased detergent	2,40	2,40
Viscosity modifier Viscoplex 6-054	1,50	1,50
Viscosity modifiers	11,00	13,76 (5.76+8.00)

- 26 -

(Infineum SV151 & 201)	(5.5+5.5)	
Antifoam agent [ppm]	264	264
Inspection Properties		
VK @ 100°C [mm ² /s (cSt)]	15.47	15.69
VK @ 40°C [mm ² /s (cSt)]	93.25	94.59
VdCCS @ -30°C [mPas (cP)]	6357	6583
Noack evaporative loss ASTM D-5800 [%m/m]	7.9, 8.0	12.3, 12.5

A Nissan TD25 Detergency Test (Japanese Automobile Standards Organization (JASO) M336:1998)) was performed which evaluates the detergency of automobile diesel oils under high temperature and high load, in a simulation of a high-speed highway service of a diesel-powered passenger car or light truck. JASO Specifications: The Nissan TD25 detergency procedure is part of JASO Specifications JASO DH-I and JASO DL-I.

The test engine was a 2.5L four-cylinder, in-line TD25 diesel engines manufactured by Nissan Diesel (Nissan Diesel is a registered trademark of Nissan Diesel Motor CO., LTD.) . The engine was mounted into an engine dynamometer test stand. As a test fuel, a class 2 light gas oil, as specified by JIS K 2202 was employed.

The engine test included running the engine continuously at a speed of 4,300 rpm under full load and maximal torque for a duration of 200 hours, with the exception of a complete oil change at 100 hours. The engine oil temperature was 120 °C, the coolant temperature 90 °C. After the test, piston state and sludge formed were rated. Equally, the wear amount of the piston rings

- 27 -

and metals bearings, of the oil rings, the camshaft and cylinder liners were determined. Furthermore, an analysis of the used oils was performed. Pistons and rings were evaluated for lacquer deposits, wear, and ring sticking. Oil rings were rated for clogging. Cylinder liners were evaluated for deposits and wear. Cylinder heads were rated for combustion chamber deposits. Oil-contact surfaces in the engine were rated for sludge formation. The used lubricant was evaluated for kinematic viscosity, soot content, sulphated ash, total acid number, total base number, insoluble matter, water, fuel dilution and wear metals. The results for piston ring deposits and top groove fill are depicted in Table 2 :

Table 2 : Nissan TD25 test results

Components	Example 1	Comparative Example
Piston detergency		
Residual carbon [% wt.]	4.75	4.94
Top Groove fill		
[% vol.]	37.0	57.1

Accordingly, the tests clearly illustrate the increased piston cleanliness and reduced top groove fill of a GTl-based formulation with respect to a mineral oil Group II base oil based formulation.

- 28 -

C L A I M S

1. Lubricant composition comprising a base oil or base oil blend and one or more additives, and having a kinematic viscosity at 100 °C of more than 5.0 mm²/s (cSt), a cold cranking simulated dynamic viscosity at -15 °C according to ASTM D 5293 of less than 9500 mPas (cP) and a mini rotary viscosity test value of less than 60000 mPas at -20 °C according to ASTM D 4684, and wherein the base oil or base oil blend has been obtained from a waxy paraffinic Fischer-Tropsch synthesized hydrocarbon fraction and comprises a continuous series of iso-paraffins having n, n+1, n+2, n+3 and n+4 carbon atoms, wherein n is between 15 and 35, having a Top Groove fill of below 50 % vol. according to the Nissan TD25 Detergency Test (Japanese Automobile Standards Organization (JASO) M336:1998).
2. Lubricant composition according to claim 1, having a residual carbon content of less than 4.8 % wt. according to the Nissan TD25 Detergency Test (Japanese Automobile Standards Organization (JASO) M336:1998).
3. Lubricant composition according to claim 1 or 2, wherein the base oil or base oil blend has a kinematic viscosity at 100 °C of from 3 to 25 mm²/s.
4. Lubricant composition according to any one of claims 1 to 3, wherein the base oil has a pour point of less than -39 °C and a kinematic viscosity at 100 °C of between 3.8 and 8.5 mm²/s (cSt), and wherein the lubricant composition has a kinematic viscosity at 100 °C of between 9.3 and 12.5 mm²/s (cSt).
5. Lubricant composition according to any one of claims 1 to 4, wherein the lubricant composition comprises less

- 29 -

than 10 wt% of an additional base oil not derived from Fischer-Tropsch process.

6. Lubricant composition according to any one of claims 1 to 5, wherein the lubricant composition comprises no additional base oil.

7. Lubricant composition according to any one of claims 1 to 6, wherein the base oil or base oil blend comprises at least 98 wt% saturates and wherein the saturates fraction consists of between 10 and 40 wt% of cyclo-paraffins.

8. Lubricant composition according to claim 7, wherein the saturates fraction consists of between 10 and 40 wt% of cyclo-paraffins.

9. Use of a lubricant composition comprising a base oil or base oil blend and one or more additives, and having a kinematic viscosity at 100 °C of more than 5.0

mm²/s (cSt), a cold cranking simulated dynamic viscosity at -15 °C according to ASTM D 5293 of less than 9500 mPas (cP) and a mini rotary viscosity test value of less than 60000 mPas at -20 °C according to ASTM D 4684, and wherein the base oil or base oil blend has been obtained from a waxy paraffinic Fischer-Tropsch synthesized hydrocarbon fraction and comprises a continuous series of iso-paraffins having n, n+1, n+2, n+3 and n+4 carbon atoms, wherein n is between 15 and 35 for the reduction of piston ring fouling in an internal combustion engine.

10. Use according to claim 9, wherein the base oil or base oil blend is obtainable from a process comprising the following steps:

(a) hydrocracking/hydroisomerising a Fischer-Tropsch product having a weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms of at least 0.2 and wherein at

- 30 -

least 30 wt% of compounds in the Fischer-Tropsch product have at least 30 carbon atoms,

(b) separating the product of step (a) into at least one or more fuel fractions and a base oil precursor fraction, and

(c) performing a catalytic dewaxing step to the base oil precursor fraction obtained in step (b), and optionally

(d) separating the products obtained in step (c) into at least one or more base oil fractions, and a lower boiling fraction.

11. Use according to claim 9, wherein the Fischer-Tropsch product used in step (a) has at least 50 wt%, and more preferably at least 55 wt% of compounds having at least 30 carbon atoms and wherein the weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms of the Fischer-Tropsch product is at least 0.4 and wherein the Fischer-Tropsch product comprises a C20+ fraction having an ASF-alpha value (Anderson-Schulz-Flory chain growth factor) of at least 0.925.

12. A method of lubricating a compression-ignited internal combustion engine comprising operating the engine and lubricating the engine with a lubricating oil composition comprising a base oil or base oil blend and one or more additives, wherein the lubricant composition has a kinematic viscosity at 100 °C of more than 5.0 mm²/s (cSt), a cold cranking simulated dynamic viscosity at -15 °C according to ASTM D 5293 of less than 9500 mPas (cP) and a mini rotary viscosity test value of less than 60000 mPas at -20 °C according to ASTM D 4684, and wherein the base oil or base oil blend has been obtained from a waxy paraffinic Fischer-Tropsch synthesized hydrocarbon

- 31 -

fraction and comprises a continuous series of iso-paraffins having n , $n+1$, $n+2$, $n+3$ and $n+4$ carbon atoms, wherein n is between 15 and 35.

13. A method of improving piston cleanliness and reducing the ring-sticking tendencies of a compression-ignited internal combustion engine comprising adding to the engine a lubricating oil composition comprising a base oil or base oil blend and one or more additives, wherein the lubricant composition has a kinematic viscosity at 100 °C of more than 5.0 mm²/s (cSt), a cold cranking simulated dynamic viscosity at -15 °C according to ASTM D 5293 of less than 9500 mPas (cP) and a mini rotary viscosity test value of less than 60000 mPas at -20 °C according to ASTM D 4684, and wherein the base oil or base oil blend has been obtained from a waxy paraffinic Fischer-Tropsch synthesized hydrocarbon fraction and comprises a continuous series of iso-paraffins having n , $n+1$, $n+2$, $n+3$ and $n+4$ carbon atoms, wherein n is between 15 and 35.