

(19)



(11)

EP 1 996 684 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

24.04.2019 Bulletin 2019/17

(51) Int Cl.:

C10M 169/04 ^(2006.01) **C10M 105/04** ^(2006.01)

(21) Application number: **07726974.4**

(86) International application number:

PCT/EP2007/052492

(22) Date of filing: **16.03.2007**

(87) International publication number:

WO 2007/107506 (27.09.2007 Gazette 2007/39)

(54) **FUNCTIONAL FLUID COMPOSITIONS**

FUNKTIONELLE FLÜSSIGKEITZUSAMMENSETZUNGEN

COMPOSITIONS DE FLUIDE FONCTIONNEL

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE
SI SK TR**

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(30) Priority: **22.03.2006 EP 06111569**

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(43) Date of publication of application:

03.12.2008 Bulletin 2008/49

(56) References cited:

WO-A-01/57166 WO-A-02/070636

FR-A- 2 501 224

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DescriptionField of invention

[0001] The present invention relates to functional fluid compositions. More specifically, the subject invention relates to fluid compositions useful as shock absorbers fluids or hydraulic fluids, and to shock absorbers comprising the fluids and suspension systems for vehicles, and to hydraulic systems comprising the fluids.

Background of the invention

[0002] WO-A-2004/053030 describes functional fluids comprising a base stock or base oil, and at least one additive, and their use as Automatic Transmission Fluids (further referred to as ATF fluids herein). According to this publication, the base oils should have a viscosity index (VI) of about 130 or greater; a pour point of -10°C, and a ratio of measured to theoretical low temperature viscosity equal to about 1.2 or less at a temperature of -30°C, where the measured viscosity is cold-crank-case simulator viscosity, and where the theoretical viscosity is calculated at the same temperature using the Walther-MacCoull equation, and wherein said base stock or base oil is not a Group IV base stock or base oil. A disadvantage of the described compositions is the limited biodegradability of such formulations. A further disadvantage is that the highly paraffinic base oils described only have a limited compatibility with additives such as viscosity improvers at low temperatures, impairing the usability of such fluids.

[0003] FR-A-2501224 discloses a hydraulic fluid based on a polyalphaolefin polymer blend and a complex esters of neopolyol, which has a very low biodegradability as compared to paraffinic blends, as for instance disclosed in WO-A-01/57166.

[0004] ATF or shock absorber fluids can come into contact with soil and/or surface and subsurface water upon scrapping or replacement of for instance car parts, or when the used fluids are exchanged. There is hence the need to formulate specific functional base oil compositions that have a high biodegradability while providing a satisfactory performance, in particular a sufficiently high compatibility with viscosity index improvers at low temperatures. There is furthermore a need to have functional base oil compositions that have a very low viscosity and high compatibility at low temperatures.

Summary of the invention

[0005] Accordingly, the present invention relates to a fluid composition comprising

(a) from 70 to 99.99% by weight, based on the total hydraulic fluid composition, of a base oil composition qualified as readily biodegradable according to ISO 14593, the base oil composition comprising

(i) from 80 to 100% by weight of a base oil or base stock having a paraffin content of greater than 80% by weight paraffins and a saturates content of greater than 98% by weight and comprising a series of iso-paraffins having n, n+1, n+2, n+3 and n+4 carbon atoms and wherein n is between 15 and 35, and having a kinematic viscosity at 100 °C of at most 3 mm²/s; and

(ii) of from 0 to 20% by weight of an ester of a polyhydroxy compound, calculated on the base oil composition; and

(b) a viscosity index improver that is a polymethylmethacrylate polymer in an amount of from 0.01 to 30% by weight, based on the total hydraulic fluid composition,

wherein the hydraulic fluid composition has a viscosity index in the range of from 50 to 1000, a kinematic viscosity at 40°C of at least 7 mm²/s and a pour point of below or at -30°C.

[0006] Applicants have found that the compositions according to the invention offer a high biological degradability, since the base oil composition is still biodegradable in spite of the high viscosity index. At the same time, the compositions were found to have a high compatibility with viscosity improvers, specifically at low temperatures.

[0007] The base oil or base stock component (i) is a paraffin base oil having a paraffin content of greater than 80% by weight paraffins and a saturates content of greater than 98% by weight and comprising a series of iso-paraffins having n, n+1, n+2, n+3 and n+4 carbon atoms and wherein n is between 15 and 35. Preferably, the base oil (i) comprises a series of iso-paraffins having n, n+1, n+2, n+3 and n+4 carbon atoms and wherein n is between 19 and 35.

[0008] The saturates content of the base oil as measured by IP386 is greater than 98% by weight, preferably greater than 99% by weight and even more preferably greater than 99.5% by weight.

[0009] The base oil component (i) may suitably have a kinematic viscosity at 100 °C of at most 3 mm²/sec. The pour point of the base oil is preferably below -30 °C.

[0010] The fluid composition according to the invention preferably has a viscosity index in the range of from 100 to

600. The fluid composition according to the invention has a kinematic viscosity at 40 °C of at least 7 mm²/s.

[0011] The flash point of the base oil (i) as measured by ASTM D92 may be even greater than 120 °C, or even greater than 140 °C. The flash point of the base oil will depend on the application of the oil. Applicants have found that the flash points of the base oils as claimed are advantageously higher compared to mineral oil derived base oils. Preferably, the fluid composition has a flashpoint of at or greater than 80 °C according to ISO 2592.

[0012] The content and the presence of the 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 stock (i) may be measured by Field desorption/Field Ionisation (FD/FI) technique. In this technique the oil sample is first separated into a polar (aromatic) phase and a nonpolar (saturates) phase by making use of a high performance liquid chromatography (HPLC) method IP368/01, wherein as mobile phase pentane 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 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 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 iso-paraffins having the same stoichiometry or n-number. The results of the mass spectrometer 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.

[0013] The base oil component (i) having the continuous iso-paraffinic series as described above is preferably obtained by hydroisomerisation of a paraffinic wax, preferably followed by some type of dewaxing, such as solvent or catalytic dewaxing. The paraffinic wax may be a slack wax. More preferably the paraffinic wax is a Fischer-Tropsch derived wax, because of its purity and high paraffinic content. 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. 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 EP-A-776959, EP-A-668342, 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 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% by weight, preferably at least 50% by weight, and more preferably at least 55% by weight 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 to 59 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.

[0014] The Fischer-Tropsch derived product 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.

[0015] 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-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.

[0016] 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 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 boiling range product corresponding with the desired viscosity. Distillation may be suitably a vacuum distillation step.

[0017] The hydroconversion/hydroisomerisation reaction of step (a) is preferably performed in the presence of 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 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 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 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.

[0018] 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% by weight, preferably 2 to 15% by weight, 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.

[0019] 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.

[0020] 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% by weight, preferably between 20 and 85% by weight. The silica content as SiO₂ is preferably between 15 and 80% by weight. Also, the support may contain small amounts, e.g., 20-30% by weight, of a binder, e.g., alumina, silica, Group IVA metal oxides, and various types of clays, magnesia, etc., preferably alumina or silica.

[0021] 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.

[0022] 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% by weight or less, preferably 1-12% by weight, 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.

[0023] A typical catalyst is shown below:

Ni, % by weight	2.5-3.5
Cu, % by weight	0.25-0.35
Al ₂ O ₃ -SiO ₂ % by weight	65- 75
Al ₂ O ₃ (binder) % byweight	25-30
Surface Area	290-325 m ² /g
Pore Volume (Hg)	0.35-0.45 ml/g
Bulk Density	0.58-0.68 g/ml

[0024] 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 Y, Ultra Stable Y, ZSM-5, ZSM-12, ZSM-22, ZSM-23, ZSM-48, MCM-68, ZSM-35, SSZ-32, ferrierite, mordenite and silica-aluminophosphates, 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 hydrocon-

version/ 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 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.

[0025] 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.

[0026] 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 NI//hr, preferably from 500 to 5000 NI//hr. The hydrocarbon feed may be provided at a weight hourly space velocity of from 0.1 to 5 kg//hr, preferably higher than 0.5 kg//hr and more preferably lower than 2 kg//hr. The ratio of hydrogen to hydrocarbon feed may range from 100 to 5000 NI/kg and is preferably from 250 to 2500 NI/kg.

[0027] The conversion in step (a) as defined as the weight percentage of the feed boiling above 370 °C which reacts per pass to a fraction boiling below 370 °C, is at least 20% by weight, preferably at least 25% by weight, but preferably not more than 80% by weight, more preferably not more than 65% by weight. 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).

[0028] 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.

[0029] Applicants found that for the low viscosity base oil, having a kinematic viscosity at 100 °C of between 1 and 5.5 mm²/sec, the biodegradability of the oil is qualified as readily biodegradable according to ISO 14593, entitled "Evaluation of ultimate aerobic biodegradability of organic compounds in aqueous medium". It is known that Fischer-Tropsch derived base oils may have good biodegradability properties as described in for example EP A-876446 or WO-A-01/57166. However in said publication the biodegradability was measured using the CEC-L-33-T-82 and OECD 310B tests, which are much less stringent. Applicants have now found that base oils derived from a Fischer-Tropsch product and having the properties of the base oils as disclosed in EP A-876446 are not always readily biodegradable according to the more accurate testing method as laid down in ISO 14593. It is widely known that the CEC-L-32-T-82 test and the more recent version of this test, known as the CEC L-33-A-93, can overestimate the biodegradability when compared to the ultimate biodegradability as measured by ISO 14593.

[0030] It has further been found with increasing average molecular weight that the biodegradability is strongly reduced. Accordingly, the base oil component (i) has a kinematic viscosity at 100 °C of at most 3 mm²/s. Fluids based on these base oil components were found particularly useful as hydraulic oils.

[0031] It has furthermore been found that the specific requirements for shock absorbers and for hydraulic fluids in terms of viscosity and compatibility with additives and viscosity improvers at low temperatures can be obtained by either basing the fluid composition on paraffinic base oils, or on a combination thereof with readily biologically degradable ester base oils.

[0032] Accordingly, the ester component (ii) is an ester of a polyhydroxy compound. Such esters may be beneficial in order to improve the solvency of the oil formulation. Suitable ester compounds are ester compounds (ii) derivable by the reaction of an aliphatic mono, di and/or poly carboxylic acid with iso-tridecyl alcohol under esterification conditions. Examples of said ester compounds are isotridecyl ester of octane-1,8-dioic acid, 2-ethylhexane-1,6 dioic acid and dodecane-1,12-dioic acid. Preferably the ester compound is a so-called pentaerythritol tetrafattyacid ester (PET ester) as made by esterification of pentaerythritol (=PET) with branched or linear fatty acids, preferably up to C10 acids. The ester may contain di-PET as alcohol component as an impurity. Preferably, the ester component (ii) of the fluid composition according to the invention is a pentaerythritol ester of pentaerythritol with from 1 to 4 branched or linear fatty acids having up to 10 carbon atoms. The ester component (ii) is preferably present in an amount of from 0 to 15% by weight, more

preferably in an amount of from 0 to 10% by weight, based on the base oil composition.

[0033] The fluid composition according to the invention may comprise as the base oil component (a) 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% by weight, more preferably less than 10% by weight, again more preferably less than 5% by weight 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 biodegradability that is to be attained. Preferably, the fluid composition further comprises saturated cyclic hydrocarbons in an amount of from 5 to 10% by weight, based on the total fluid composition since this improves the low temperature compatibility of the different components in the fluid composition.

[0034] The fluid composition according to the invention further comprises a viscosity improver (b) in an amount of from 0.01 to 30% by weight.

[0035] 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 viscosity at low temperatures. As disclosed herein, viscosity index improvers include both low molecular weight and high molecular weight hydrocarbons, polyesters and viscosity index improver dispersants that function as both a viscosity index improver and a dispersant. Typical molecular weights of these polymers are between about 10,000 to 1,000,000, more typically about 20,000 to 500,00, and even more typically between about 50,000 and 200,000. Examples of viscosity index improvers are polymers and copolymers of methacrylate, butadiene, olefins, or alkylated styrenes. The viscosity index improvers may be used in an amount of 0.01 to 30% by weight, preferably 0.01 to 25% by weight, yet more preferably from 0.01 to 20% by weight, again more preferably from 0.1 to 18% by weight, and most preferably from 5 to 15% by weight, based on the total fluid composition.

[0036] The viscosity index improver is poly methyl methacrylate (further referred to as PMMA), i.e. a copolymer of various chain length methyl and alkyl methacrylates. Accordingly, the fluid composition according to the invention comprises a viscosity improver comprising a polymethylmethacrylate polymer. Particularly preferred PMMA viscosity index improvers are those commercially available Viscoplex viscosity improvers (Viscoplex is a tradename of the Röhm GmbH & CO. KG, Darmstadt, Germany), in particular Viscoplex 7-310. PMMA viscosity index improvers were surprisingly found to be highly compatible with the base oil compositions according to the invention, while at the same time providing an outstanding performance at low temperatures as compared to other viscosity improvers. Furthermore, it was found that the PMMA viscosity improvers do not influence the biodegradability of the overall fluid composition in a negative way. The compatibility increased with the presence of polyhydroxy component esters, as well as with base oils having a viscosity below 3.5 mm²/s at 100 °C. Such compositions gave a very high overall performance and high biodegradability.

[0037] The fluid composition further preferably comprises at least one other additional lubricant component in effective amounts, such as for instance polar and/or nonpolar lubricant base oils, and 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, 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 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 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. Ranney, published by Noyes Data Corporation of Parkridge, N.J. (1973).

[0038] Preferable additional antiwear additives to be used with the composition according to the invention include metal alkylthiophosphates, more particularly zinc dialkyldithiophosphates, typically used in amounts of from about 0.4% by weight to about 1.4% by weight of the total fluid composition. Other preferred antiwear additives include phosphorus-free antiwear additives such as sulphur-containing aliphatic, arylaliphatic or alicyclic olefinic hydrocarbons containing from about 3 to 30 carbon atoms, more preferably 3 to 20 carbon atoms. Again more preferred hydrocarbon radicals are alkyl or alkenyl radicals, as for instance disclosed in US-A-4,941,984.

[0039] Other preferred antiwear additives include polysulfides of thiophosphorus acids and thiophosphorus acid esters, and phosphorothionyl disulfides as disclosed in US-A-2,443,264; US-A-2,471,115; US-A-2,526,497; US-A-2,591,577; and US-A-3,770,854. Use of alkyl-thiocarbamoyl compounds, such as bis(dibutyl)thiocarbamoyl in combination with a molybdenum compounds such as oxymolybdenum diisopropylphosphorodithioate sulfide and a phosphorus ester such as dibutyl hydrogen phosphite as antiwear additive disclosed in US-A-4,501,678. US-A-4,758,362 discloses use of a carbamate additive to provide improved antiwear and extreme pressure properties. The use of thiocarbamate as an antiwear additive is disclosed in US-A-5,693,598. Esters of glycerol may be used as antiwear agents. For example, mono-, di, and tri-oleates, mono-palmitates and mono-myristates may preferably be used. US-A-5,034,141 discloses a combination of a zinc dialkyldithiophosphate, a thiodioxanthogen compound and a metal thiophosphate that result in

improved antiwear properties. US-A-5,034,142 discloses that use of a metal alkoxyalkylxanthate and a dixanthogen in combination with zinc dialkyldithiophosphate may improve antiwear properties. Generally, antiwear additives may be used in an amount of about 0.01 to 6% by weight, preferably about 0.01 to 4% by weight, based on the total weight of the fluid composition.

[0040] Suitable antioxidants retard the oxidative degradation of the fluid composition during service. Such degradation may result in deposits on metal surfaces, the presence of sludge, or a viscosity increase in the fluid. A wide variety of suitable oxidation inhibitors are known, as for instance those described in Klamann in Lubricants, and for example US-A-4,798,684 and US-A-5,084,197. Useful antioxidants include hindered phenols. These phenolic antioxidants may be ashless (metal-free) phenolic compounds or neutral or basic metal salts of certain phenolic compounds. Typical phenolic antioxidant compounds are the hindered phenolics which are the ones which contain a sterically hindered hydroxyl group, and these include those derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or p-position to each other. Examples of phenolic materials of this type 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-t-butyl-4-heptyl phenol; and 2-methyl-6-t-butyl-4-dodecyl phenol. Other useful hindered mono-phenolic antioxidants may include for example hindered 2,6-di-alkyl-phenolic propionic ester derivatives.

[0041] Bis-phenolic antioxidants may also be advantageously used in the fluid composition. Non-phenolic oxidation inhibitors which may be used include aromatic amine antioxidants and these may be used either as such or in combination with phenolics. Typical examples of non-phenolic antioxidants include alkylated and non-alkylated aromatic amines such as aromatic monoamines with aliphatic, aromatic or substituted aromatic group substituents at the nitrogen atom. Typical aromatic amines antioxidants have alkyl substituent groups of at least about 6 carbon atoms. Examples of aliphatic groups include hesyl, heptyl, octyl, nonyl, and decyl. Generally, the aliphatic groups will not contain more than about 14 carbon atoms. The general types of amine antioxidants useful in the present compositions include diphenylamines, phenyl naphthylamines, phenothiazines, imidodibenzyls and diphenyl phenylene diamines. Mixtures of two or more aromatic amines are also useful. Polymeric amine antioxidants may also be used. Particular examples of aromatic amine antioxidants useful in the present invention include: p,p'-diocetyl diphenylamine; t-octylphenyl-alpha-naphthylamine; phenyl-lphanaphthylamine; and p-octylphenyl-alpha-naphthylamine. Sulphurized alkyl phenols and alkali or alkaline earth metal salts thereof also are useful antioxidants. Low sulfur peroxide decomposers are useful as antioxidants. Another class of suitable antioxidants are oil soluble copper compounds. Examples of suitable copper antioxidants include copper dihydrocarbyl-thio or dithio- phosphates and copper salts of carboxylic acids. Other suitable copper salts include copper dithiacarbamates, sulphonates, phenates, and acetylacetonates. Basic, neutral, or acidic copper Cu(I) and/or Cu(II) salts derived from alkenyl succinic acids or anhydrides are known to be particularly useful. Preferred antioxidants include hindered phenols, arylamines, low sulfur peroxide decomposers and other related components. These antioxidants may be used individually by type or in combination with one another. Such additives may be used in an amount of about 0.01 to 5% by weight, preferably about 0.01 to 2% by weight.

[0042] Detergents useful as additives may be simple detergents or hybrid or complex detergents. The latter can provide the properties of two detergents without the need to blend separate materials, as for instance described in US-A-6,034,039. Suitable detergents include anionic compounds that contains a long chain oleophilic portion of the molecule and a smaller anionic or oleophobic portion of the molecule. The anionic portion of the detergent is typically derived from an organic acid such as a sulphuric acid, carboxylic acid, phosphorus acid, phenol, or mixtures thereof. The counter ion is typically an alkaline earth or alkali metal. Salts that contain a substantially stoichiometric amount of the metal are described as neutral salts and have a total base number (TBN, as measured by ASTM D2896) of from 0 to 80. Preferred detergents include the alkali or alkaline earth metal salts of sulfates, sulofantes, phenates, carboxylates, phosphates, and salicylates. Suitable alkaryl sulfonates typically contain about 9 to about 80 carbon or more carbon atoms, more typically from about 16 to 60 carbon atoms. Preferred are those disclosed in Klamann in Lubricants and Related Products, and in "Lubricant Additives" cited above, and C. V. Smallheer and R. K. Smith, published by the Lezius-Hiles Co. of Cleveland, Ohio (1967). Alkaline earth phenolates represent another useful class of detergent. These detergents are the products of reacting alkaline earth metal hydroxides or oxides with an alkyl phenol or sulphurized alkylphenol. Useful alkyl groups include straight chain or branched C1-C30 alkyl groups, preferably, C4-C20. Examples of suitable phenols include isobutylphenol, 2-ethylhexylphenol, nonylphenol, 1-ethyldecylphenol, and the like. Metal salts of carboxylic acids are also useful as detergents. Another preferred class of detergents are alkaline earth metal salicylates, including monoalkyl to tetraalkyl salicylates, wherein the alkyl groups have from 1 to 30 carbon atoms. Preferably, the alkaline earth metal is calcium, magnesium, or barium; calcium being the most preferred. Another useful class of detergents encompasses alkaline earth metal phosphates. Typically, the total detergent concentration is about 0.01 to about 6% by weight, preferably, about 0.1 to 4% by weight, calculated on the total fluid composition. In addition, non-ionic detergents may be preferably used in lubricating compositions. Such non-ionic detergents may be ashless or low-ash compounds, and may include discrete molecular compounds, as well as oligomeric and/or polymeric compounds.

[0043] The additives may further comprise dispersants. Suitable dispersants typically contain a polar group attached to a relatively high molecular weight hydrocarbon chain. The polar group typically contains at least one element of

nitrogen, oxygen, or phosphorous. Typical hydrocarbon chains contain about 50 to 400 carbon atoms. Suitable dispersants include phenolates, sulfonates, sulphurized phenolates, salicylates, naphthenates, stearates, carbamates and thiocarbamates. A particularly useful class of dispersants are alkenylsuccinic derivatives, in which the alkenyl chain constitutes the oleophilic portion of the molecule which confers solubility in the oil. The alkenyl chain may be a polyisobutylene group, such as those described in US-A-3,172,892; US-A-3,214,707; US-A-3,219,666; US-A-3,316,177; US-A-3,341,542; US-A-3,454,607; US-A-3,541,012; US-A-3,630,904; US-A-3,632,511; US-A-3,787,374 and US-A-4,234,435.

[0044] Other types of suitable dispersants are described in US-A-3,036,003; US-A-3,200,107; US-A-3,254,025; US-A-3,275,554; US-A-3,438,757; US-A-3,454,555; US-A-3,565,804; US-A-3,413,347; US-A-3,697,574; US-A-3,725,277; US-A-3,725,480; US-A-3,726,882; US-A-4,454,059; US-A-3,329,658; US-A-3,449,250; US-A-3,519,565; US-A-3,666,730; US-A-3,687,849; US-A-3,702,300; US-A-4,100,082; US-A-5,705,458; and EP-A-471071.

[0045] Other suitable dispersants include hydrocarbyl-substituted succinic acid compounds, such as succinimides, succinate esters, or succinate ester amides prepared by the reaction of hydrocarbon-substituted succinic acid preferably having at least 50 carbon atoms in the hydrocarbon substituent, with at least one equivalent of an alkylene amine, are particularly useful.

[0046] More preferred succinic dispersants include borated and non-borated succinimides, including those derivatives from mono-succinimides, bis-succinimides, and/or mixtures of mono- and bis-succinimides, wherein the hydrocarbyl succinimide is derived from an alkylene group such as polyisobutylene having a Mn of from about 500 to about 5000. Other preferred dispersants include succinic acid-esters and amides, alkylphenolpolyamine Mannich adducts, their capped derivatives, and other related components. Such additives may be used in an amount of about 0.1 to 20% by weight preferably about 0.1 to 8% by weight.

[0047] Other useful dispersants include oxygen-containing compounds, such as polyether compounds, polycarbonate compounds, and/or polycarbonyl compounds, as oligomers or polymers, ranging from low molecular weight to high molecular weight.

[0048] Friction modifier i.e. a material or compound that can alter the coefficient of friction of the fluid may be effectively used in combination with the base oil components. Suitable friction modifiers may include metal salts or metal-ligand complexes where the metals may include alkali, alkaline earth, or transition group metals, as those described in WO2004/053030.

[0049] Other useful additives include pour point depressants to lower the minimum temperature at which the fluid will flow or can be poured. Examples of suitable pour point depressants include polymethacrylates, polyacrylates, polyarylamides, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, and terpolymers of dialkylfumarates, vinyl esters of fatty acids and allyl vinyl ethers, such as those referred to in WO2004/053030.

[0050] Suitable corrosion inhibitors include thiadizoles. See, for example, US-A-2,719,125; US-A-2,719,126; and US-A-3,087,932, and may be used in an amount of about 0.01 to 5% by weight, preferably about 0.01 to 1.5% by weight. Suitable seal compatibility agents include organic phosphates, aromatic esters, aromatic hydrocarbons, esters (butylbenzyl phthalate, for example), and polybutenyl succinic anhydride.

[0051] Such additives may be used in an amount of about 0.01 to 3% by weight, and is limited by the biodegradability of the fluid.

[0052] Anti-foaming agents may advantageously be added to fluid compositions. These agents retard the formation of stable foams. Silicones and organic polymers are typical anti-foam agents, such as for example polysiloxanes. Anti-foam agents are commercially available and may be used in conventional minor amounts along with other additives such as demulsifiers; usually the amount of these additives combined is less than 1% by weight.

[0053] Suitable corrosion inhibitors are those referred to in Klamann, as cited above. Examples of suitable corrosion inhibitors include zinc dithiophosphates, metal phenolates, basic metal sulfonates, fatty acids and amines. Such additives may be used in an amount of about 0.01 to 5% by weight, preferably about 0.01 to 1.0% by weight. Additional types of additives may be further incorporated into the fluid compositions of this invention may include one or more additives such as, for example, demulsifiers, solubilizers, fluidity agents, colouring agents, chromophoric agents, and the like. Each additive may include individual additives or mixtures thereof.

[0054] The present invention further relates to shock absorbers and hydraulic systems comprising the fluid according to the invention, as well as to a vehicle comprising a shock absorber and/or a hydraulic system, and to the use of a hydraulic fluid according to the claims as biodegradable fluid for shock absorbers or hydraulic systems. Shock absorbers are expected to have high response values already at low temperatures, while both applications show the high biodegradability and the superior low temperature performance.

[0055] A shock absorber (sometimes referred to as a damper) is a mechanical device designed to smooth out or damp a sudden shock impulse and dissipate kinetic energy. Shock absorbers are an important part of automobile or bicycle suspensions, aircraft landing gear, and the supports for many industrial machines. Large shock absorbers are also used in architecture and civil engineering to reduce the susceptibility of structures to earthquake damage and resonance. Applied to a structure such as a building or bridge it may be part of a seismic retrofit or as part of new, earthquake resistant construction. In this application it allows yet restrains motion and absorbs resonant energy, which could otherwise

cause excessive motion and eventual structural failure.

[0056] Shock absorbers generally have the task of converting kinetic energy to heat energy, which can then be dissipated. Hydraulic shock absorbers usually are composed of a cylinder with a sliding piston inside. The cylinder is filled with a fluid. This fluid filled piston/cylinder combination is also referred to as a dashpot. In a transport vehicle such as a bicycle fork, as described for instance in JP-A-2004-44643, or bicycle rear wheel suspension, passenger car or heavy duty transport vehicles or air craft landing gear, the wheel suspension usually contains several shock absorbers, mostly in combination with a pressure resilient means such as coil springs, leaf springs, or torsion bars. These springs are not shock absorbers as springs only store and do not dissipate or absorb energy. If a wheel is put into a horizontal motion, the spring will absorb the up-and downward force, and convert this into heat. The shock absorber, along with hysteresis in for instance the tires of the wheel, dampens the motion of the unsprung weight up and down, thereby effectively damping the wheel bounce.

[0057] This is achieved by converting the kinetic energy into heat through fluid friction due to the flow of the shock absorber fluid through a narrow orifice, such as an internal valve. The fluids according to the invention were found to improve the low temperature handling, i.e. directly after start at low temperatures, when used as shock absorber fluids.

[0058] In hydraulic systems, the fluid has the role of transferring kinetic energy from one location to another within a closed system, for instance in the control of airplane steering and landing gears. It has been found that the compositions according to the invention are particularly useful as hydraulic fluids due to the high compatibility with viscosity improvers even at low temperatures, as well as low shear loss. Shear loss is a measure that shows the loss of effective viscosity index improver over time through shearing. A higher shear loss indicates a shorter lifetime of the fluid, and hence of the shock absorber.

[0059] The invention will be further illustrated by the following, non-limiting examples:

Example 1

[0060] Blends were prepared of mineral oil derived base oils and of a Fischer-Tropsch derived base oil according to the invention having a similar viscosity index(see Table 1).

Table 1: Properties of employed base oils

			Fischer-Tropsch derived base oil	Mineral Base Oil Blend
Vk @ 100°C	D445	mm ² /s	2,4	2,0
Vk @ 40°C	D445	mm ² /s	7,9	7,1
density @ 15°C	D4052	kg/m ³	803	870
VI	D2270		126	62
Pour Point	D5950	°C	-51	-50

[0061] The obtained blends were formulated into shock absorber fluids (see Table 2), which were in turn subjected to a number of tests (see Table 3).

[0062] The amount of viscosity improve required to achieve the same viscosity index was higher for the mineral oil based comparative example (see Table 2).

Table 2: Shock absorber fluids

	Example 1 [% by weight]	Comparative example [% by weight]
Formulation		
Fischer Tropsch base oil	96,83	-
Mineral base oil blend	-	94,43
Antioxidant	0,20	0,20
Viscosity improver	2,30	4,70
Corrosion inhibitor	0,37	0,37
Colouring agent	0,3	0,3

Table 3: Results

Properties	Method		Example 1	Comparative Example
DENSITY @ 15 °C	DIN 51757		807	874,8
FLASH POINT COC	DIN ISO 2592	°C	192	143
POUR POINT	DIN ISO 3016	°C	-60	-63
KINEMATIC VISCOSITY @ -30 °C	DIN 51562	°C	274,4	684,9
KINEMATIC VISCOSITY @ 20 °C	DIN 51562	mm ² /s	17,2	22,9
KINEMATIC VISCOSITY @ 40 °C	DIN 51562	mm ² /s	9,1	11,5
KINEMATIC VISCOSITY @ 100 °C	DIN 51562	mm ² /s	2,82	3,32
DYNAMIC VISCOSITY @ 20 °C	calculated	mm ² /s	13,9	19,9
VISCOSITY INDEX VI	DIN ISO 2909		171	175
NOACK EVAPORATION LOSS -1h / 120 °C	DIN 51581	%m	0,6	0,4
KINEMATIC VISCOSITY @ 100 °C after test	DIN 51562	mm ² /s	2,75	2,82
SHEAR LOSS (VKA/KRL 20 h/5000 N @ 60 °C)	DIN 51350-6	%	2,3	15,2

[0063] It is clear from the results, that a Fischer-Tropsch based shock absorber formulation according to the invention has improved low temperature performance, and a higher flash point, and overall lower shear loss as compared to a mineral oil derived shock absorber fluid. Furthermore, less viscosity improver is required.

[0064] Similar results are obtained with blends of polyhydroxy ester compounds, in particular esters of pentaerythritol and Fischer-Tropsch derived base oils.

[0065] Furthermore, the shear loss over time is strongly reduced leading to an increased lifetime of the blend, and the shock absorber.

Example 2: Biodegradability of base oil compositions

[0066] Base oil compositions comprising components (i) and (ii) were subjected to biodegradability tests.

Table 4: Biodegradability

F-T derived base oil	100	80
Pentaerythrol tetra fatty acid ester (C6-C10)	-	20
Biodegradation after 28 d ([%], measured by ISO 14593)	60	63

[0067] From Table 4, it is clear that component (i), or a mixture of components (i) and (ii) are readily biodegradable, as determined by ISO 14593.

Claims

1. A hydraulic fluid composition comprising

(a) from 70 to 99.99% by weight, based on the total hydraulic fluid composition, of a base oil composition qualified as readily biodegradable according to ISO 14593, the base oil composition comprising

(i) from 80 to 100% by weight of a base oil or base stock having a paraffin content of greater than 80% by weight paraffins and a saturates content of greater than 98% by weight and comprising a series of iso-paraffins having n, n+1, n+2, n+3 and n+4 carbon atoms and wherein n is between 15 and 35, and having a kinematic viscosity at 100 °C of at most 3 mm²/s; and

(ii) of from 0 to 20% by weight of an ester of a polyhydroxy compound, calculated on the base oil composition;

and

(b) a viscosity index improver that is a polymethylmethacrylate polymer in an amount of from 0.01 to 30% by weight, based on the total hydraulic fluid composition,

wherein the hydraulic fluid composition has a viscosity index in the range of from 50 to 1000, a kinematic viscosity at 40°C of at least 7 mm²/s and a pour point of below or at -30°C.

2. A fluid composition according to claim 1, wherein viscosity index is in the range of from 100 to 600.
3. A fluid composition according to claim 1 or claim 2, having a flashpoint of at least 80 °C according to ISO 2592.
4. A fluid composition according to any one of claims 1 to 3, wherein the viscosity improver is present in an amount of from 5 to 15% by weight, based on the total fluid composition.
5. A fluid composition according to any one of claims 1 to 4, further comprising saturated cyclic hydrocarbons in an amount of from 5 to 10% by weight, based on the total fluid composition.
6. A fluid composition according to any one of claims 1 to 5, wherein the ester component is a pentaerythritol ester of pentaerythritol with from 1 to 4 branched or linear fatty acids having up to 10 carbon atoms.
7. A shock absorber comprising the fluid according to any one of claims 1 to 6.
8. A hydraulic system comprising the fluid according to any one of claims 1 to 7.
9. A vehicle comprising a shock absorber and/or a hydraulic system according to claims 7 or 8.

Patentansprüche

1. Hydraulikfluidzusammensetzung, umfassend

(a) 70 bis 99,99 Gew.-%, bezogen auf die gesamte Hydraulikfluidzusammensetzung, einer Basisölszusammensetzung, die gemäß ISO 14593 als ohne weiteres biologisch abbaubar qualifiziert ist, wobei die Basisölszusammensetzung Folgendes umfasst:

- (i) 80 bis 100 Gew.-% eines Basisöls oder Basismaterials mit einem Paraffingehalt von mehr als 80 Gew.-% Paraffinen und einem Gehalt an gesättigten Verbindungen von mehr als 98 Gew.-% und umfassend eine Reihe von Isoparaffinen mit n, n + 1, n + 2, n + 3 und n + 4 Kohlenstoffatomen und worin n zwischen 15 und 35 liegt und mit einer kinematischen Viskosität bei 100 °C von höchstens 3 mm²/s; und
- (ii) 0 bis 20 Gew.-% eines Esters einer Polyhydroxyverbindung, berechnet in Bezug auf die Basisölszusammensetzung; und

(b) einen Viskositätsindexverbesserer, bei dem es sich um ein Polymethylmethacrylatpolymer handelt, in einer Menge von 0,01 bis 30 Gew.-%, bezogen auf die gesamte Hydraulikfluidzusammensetzung,

wobei die Hydraulikfluidzusammensetzung einen Viskositätsindex im Bereich von 50 bis 1000, eine kinematische Viskosität bei 40 °C von mindestens 7 mm²/s und einen Fließpunkt von -30 °C oder darunter aufweist.

2. Fluidzusammensetzung nach Anspruch 1, wobei der Viskositätsindex im Bereich von 100 bis 600 liegt.
3. Fluidzusammensetzung nach Anspruch 1 oder Anspruch 2 mit einem Flammpunkt von mindestens 80 °C gemäß ISO 2592.
4. Fluidzusammensetzung nach einem der Ansprüche 1 bis 3, wobei der Viskositätsverbesserer in einer Menge von 5 bis 15 Gew.-% vorliegt, bezogen auf die gesamte Fluidzusammensetzung.
5. Fluidzusammensetzung nach einem der Ansprüche 1 bis 4, ferner umfassend gesättigte cyclische Kohlenwasser-

stoffe in einer Menge von 5 bis 10 Gew.-%, bezogen auf die gesamte Fluidzusammensetzung.

6. Fluidzusammensetzung nach einem der Ansprüche 1 bis 5, wobei die Esterkomponente ein Pentaerythritolester von Pentaerythritol mit 1 bis 4 verzweigten oder linearen Fettsäuren mit bis zu 10 Kohlenstoffatomen ist.

7. Stoßdämpfer, umfassend das Fluid nach einem der Ansprüche 1 bis 6.

8. Hydrauliksystem, umfassend das Fluid nach einem der Ansprüche 1 bis 7.

9. Fahrzeug umfassend einen Stoßdämpfer und/oder ein Hydrauliksystem nach den Ansprüchen 7 oder 8.

Revendications

1. Composition de fluide hydraulique comprenant

(a) de 70 à 99,99 % en poids, sur la base de la composition de fluide hydraulique totale, d'une composition d'huile de base considérée comme facilement biodégradable conformément à la norme ISO 14593, la composition d'huile de base comprenant

(i) de 80 à 100 % en poids d'une huile de base ayant une teneur en paraffine supérieure à 80 % en poids de paraffines et une teneur en hydrocarbures saturés supérieure à 98 % en poids et comprenant une série d'iso-paraffines ayant n, n+1, n+2, n+3 et n+4 atomes de carbone et dans laquelle n est compris entre 15 et 35, et ayant une viscosité cinématique à 100°C d'au maximum 3 mm²/s ; et

(ii) de 0 à 20 % en poids d'un ester d'un composé polyhydroxy, calculé à partir de la composition d'huile de base ; et

(b) un améliorant d'indice de viscosité qui est un polymère polyméthacrylate de méthyle dans une quantité de 0,01 à 30 % en poids, sur la base de la composition de fluide hydraulique totale,

dans laquelle la composition de fluide hydraulique a un indice de viscosité dans la plage de 50 à 1 000, une viscosité cinématique à 40°C d'au moins 7 mm²/s et un point d'écoulement inférieur ou égal à -30°C.

2. Composition de fluide selon la revendication 1, dans laquelle l'indice de viscosité est dans la plage de 100 à 600.

3. Composition de fluide selon la revendication 1 ou la revendication 2, ayant un point d'éclair d'au moins 80°C conformément à la norme ISO 2592.

4. Composition de fluide selon l'une quelconque des revendications 1 à 3, dans laquelle l'améliorant de viscosité est présent dans une quantité de 5 à 15 % en poids, sur la base de la composition de fluide totale.

5. Composition de fluide selon l'une quelconque des revendications 1 à 4, comprenant en outre des hydrocarbures cycliques saturés dans une quantité de 5 à 10 % en poids, sur la base de la composition de fluide totale.

6. Composition de fluide selon l'une quelconque des revendications 1 à 5, dans laquelle le constituant ester est un ester pentaérythritol de pentaérythritol avec de 1 à 4 acides gras ramifiés ou linéaires ayant jusqu'à 10 atomes de carbone.

7. Amortisseur de chocs comprenant le fluide selon l'une quelconque des revendications 1 à 6.

8. Système hydraulique comprenant le fluide selon l'une quelconque des revendications 1 à 7.

9. Véhicule comprenant un amortisseur de chocs et/ou un système hydraulique selon les revendications 7 ou 8.

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