(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 855 645 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
14.08.2019 Bulletin 2019/33

(21) Application number: **13728157.2**

(22) Date of filing: **04.06.2013**

(51) Int Cl.:
C10M 145/14 $^{(2006.01)}$
C10M 169/04 $^{(2006.01)}$
C10N 20/04 $^{(2006.01)}$
C10N 30/02 $^{(2006.01)}$
C10N 30/04 $^{(2006.01)}$
C10N 30/06 $^{(2006.01)}$
C10N 40/02 $^{(2006.01)}$
C10N 40/04 $^{(2006.01)}$
C10N 40/06 $^{(2006.01)}$
C10N 40/08 $^{(2006.01)}$
C10N 40/30 $^{(2006.01)}$

(86) International application number:
PCT/EP2013/061497

(87) International publication number:
WO 2013/182565 (12.12.2013 Gazette 2013/50)

---

(54) **LUBRICATING OIL COMPOSITION**
SCHMIERÖLZUSAMMENSETZUNG
COMPOSITION D'HUILE DE GRAISSAGE

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **04.06.2012 JP 2012127557**

(43) Date of publication of application:
08.04.2015 Bulletin 2015/15

(73) Proprietor: **Shell Internationale Research Maatschappij B.V.**
2596 HR The Hague (NL)

(72) Inventors:
- **NAGAKARI, Mitsuhiro**
  Tokyo 135-8074 (JP)
- **OTSUKA, Ayano**
  Aikou-Gun
  Kanagawa 243-0303 (JP)

(74) Representative: **Shell Legal Services IP**
p/a Carel van Bylandtlaan 16
2596 HR Den Haag (NL)

(56) References cited:
EP-A1- 0 566 048
EP-A1- 2 395 068
EP-A1- 2 439 258
WO-A1-00/55222
SU-A1- 1 348 347
US-A1- 2012 115 763

EP 2 855 645 B1

Printed by Jouve, 75001 PARIS (FR)

Description

Technical Field of the Invention

[0001] The present invention relates to a lubricating oil composition, and specifically relates to a lubricating oil composition which has superior extreme pressure properties, which generates a small amount of sludge and which also has a high viscosity index.

Background of the Invention

[0002] Attention is being paid to the generation of electricity by wind power as a renewable energy source. In apparatus for wind-power generation of electricity the slow rotation of blades is speeded up by means of step-up gears, so that an electricity generator can be rotated by means of their power. But there are many gear wheels in the step-up gear box and a gear oil is required to lubricate these wheels (Gekkan Tribology, No. 273, pages 50-51, May 2010).

[0003] In particular, the scale of the apparatus for wind-power generation of electricity has increased in recent years, and since it is necessary to convert large slow forces to high speed by means of step-up gearing, the burden on the gear wheels within the gearing has increased, with the result that there has been a demand for greater ability in the gear oils that lubricate them to resist welding (extreme pressure properties). However, the extreme pressure agents which are capable of resisting welding when blended in gear oils are prone to turn into sludge through ageing and oxidation, and the sludge so produced may cause wear and welding by biting into the wheels as foreign matter, and may also end up causing problems by clogging filters and blocking oil pipes. Maintenance such as carrying out oil changes early before too large amounts of sludge are generated in the oil is therefore important.

[0004] At the same time, apparatus for wind-power generation of electricity is often located in remote areas such as mountainous regions or sea shores, so that frequent maintenance is difficult. Also, greater costs are required for maintenance in out-of-the-way areas, so that, to reduce operating costs, there is demand to extend maintenance intervals and oil-change intervals. In order, therefore, to reduce costs for protection and operation of the gear wheels, there has been demand to improve the oxidative stability performance of gear oils and to minimise the amount of sludge created.

[0005] Also, apparatus for wind-power generation of electricity is run continuously under a wide range of temperature conditions in response to fluctuations between day and night and weather conditions, and so there has likewise been demand for the gear oil used to have small fluctuations in viscosity due to temperature change, that is to have a high viscosity index.

[0006] EP0566048 relates to a method for lubrication of machine components using synthetic oils containing co-oligomers built up from 1-alkenes and (meth)acrylate esters.

[0007] Given the above, there has been demand for an industrial-level lubricating oil which has superior extreme pressure properties (ability to prevent welding), which generates a small amount of sludge and which also has a high viscosity index.

[0008] The problem to be addressed by the present invention is to offer a lubricating oil composition which has superior extreme pressure properties (ability to prevent

Summary of the Invention

[0009] By dint of various and repeated investigations and research to reduce the amount of sludge generated in an industrial-level lubricating oil, the inventors arrived at this invention after discovering that when a copolymer of a specified olefin and an alkyl methacrylate is added in a given fixed range of molecular weights, the amount of sludge generated is reduced, and in addition the viscosity index improves.

[0010] In general, copolymers of olefins and alkyl methacrylates are used in lubricating oil compositions as viscosity index improvers, but nothing has been known about reducing the amount of sludge generated. This invention is an attempt to reduce the amount of sludge by adding a copolymer of an olefin and an alkyl methacrylate as an effective constituent to a lubricating oil base oil which contains an extreme pressure agent.

[0011] Accordingly the present invention provides a lubricating oil composition comprising (A) 50 to 90% by mass of at least one kind of lubricating oil base oil selected from mineral oils and synthetic oils and (B) 10 to 50% by mass of a copolymer, being of weight average molecular weight 5000 to 20,000, of an olefin and an alkyl methacrylate, wherein the lubricating base oil comprises 5 to 14% by mass relative to the total amount of the lubricating oil composition of (C) a carboxylic acid ester compound, wherein the carboxylic acid ester (c) is a polyol ester.

[0012] According to this invention, a lubricating oil composition which has superior extreme pressure properties (ability to prevent welding), which generates a small amount of sludge and which also has a high viscosity index is obtained. By reducing the amount of sludge generated by oxidative ageing, wear and welding due to foreign matter becoming embedded are inhibited, and the service life of the machinery (for example, gears) is extended. Also, the fact that the viscosity index is higher means that low temperature flow characteristics are superior and an oil film can be maintained at higher temperatures.

Brief Description of the Drawings

[0013] Figure 1 shows the molecular weight distribution curves for Additive A1 and Additive A2.

Detailed Description of the Invention

[0014] This invention relates to a lubricating oil composition characterised in that it comprises (A) at least one kind of lubricating oil base oil selected from mineral oils and synthetic oils; (B) a copolymer of an olefin and an alkyl methacrylate of molecular weight within a specified range; and wherein the lubricating base oil comprises 5 to 14% by mass relative to the total amount of the lubricating oil composition of (C) a carboxylic acid ester compound, wherein the carboxylic acid ester (c) is a polyol ester.

[0015] For the base oil of the present lubricating oil composition it is possible to use the mineral oils and synthetic oils known as highly refined base oils, and in particular it is possible to use, singly or as mixtures, base oils which belong to Group II, Group III and Group IV of the API (American Petroleum Institute) base oil categories. For the base oils used here, the sulphur content is not more than 300 ppm, but preferably not more than 200 ppm, more preferably not more than 100 ppm, and most preferably not more than 50 ppm. Also, the density is 0.8 to 0.9 g/cm^3, but preferably 0.8 to 0.865 g/cm^3, and more preferably 0.81 to 0.83 g/cm^3. The aromatic content (aromatic contents in this invention are determined by n-d-M analysis in accordance with ASTM D3238) is less than 3%, but preferably less than 2% and more preferably less than 0.1%.

[0016] As examples of Group II base oils, mention may be made of paraffinic mineral oils obtained by appropriate use of a suitable combination of refining processes such as hydrorefining and dewaxing in respect of lubricating oil fractions obtained by atmospheric distillation of crude oil. Group II base oils refined by hydrorefining methods such as the Gulf Company method have a total sulphur content of less than 10 ppm and an aromatic content of not more than 5% and so are suitable for this invention. The viscosity of these base oils is not specially limited, but the viscosity index (viscosity indexes in this invention are determined in accordance with ASTM D2270 and JIS K2283) should be 80 to 120 and preferably 100 to 120. The kinematic viscosity at 40°C (kinematic viscosities in this invention are determined in accordance with ASTM D445 and JIS K2283) should preferably be 2 to 680 mm^2/s and even more preferably 8 to 220 mm^2/s. Also, the total sulphur content should be less than 300 ppm, preferably less than 200 ppm and even more preferably less than 10 ppm. The total nitrogen content should be less than 10 ppm and preferably less than 1 ppm. In addition, oils with an aniline point (aniline points in this invention are determined in accordance with ASTM D611 and JIS K2256) of 80 to 150°C and preferably 100 to 135°C should be used.

[0017] Suitable Group III and Group II+ base oils include paraffinic mineral oils manufactured by a high degree of hydrorefining in respect of lubricating oil fractions obtained by atmospheric distillation of crude oil, base oils refined by the Isodewaxing process which dewaxes and substitutes the wax produced by the dewaxing process with isoparaffins, and base oils refined by the Mobil wax isomerisation process. The viscosity of these base oils is not specially limited, but the viscosity index should be 95 to 145 and preferably 100 to 140. The kinematic viscosity at 40°C should preferably be 2 to 680 mm^2/s and even more preferably 8 to 220 mm^2/s. Also, the total sulphur content should be 0 to 100 ppm and preferably less than 10 ppm. The total nitrogen content should be less than 10 ppm and preferably less than 1 ppm. In addition, oils with an aniline point of 80 to 150°C and preferably 110 to 135°C should be used.

[0018] GTLs (gas to liquid) synthesised by the Fischer-Tropsch method of converting natural gas to liquid fuel have a very low sulphur content and aromatic content compared with mineral oil base oils refined from crude oil and have a very high paraffin constituent ratio, and so have excellent oxidative stability, and because they also have extremely small evaporation losses, they are suitable as base oils for this invention. The viscosity characteristics of GTL base oils are not specially limited, but normally the viscosity index should be 130 to 180 and preferably 140 to 175. Also, the kinematic viscosity at 40°C should be 2 to 680 mm2/s and preferably 5 to 120 mm2/s.

[0019] Normally the total sulphur content should also be less than 10 ppm and the total nitrogen content less than 1 ppm. A commercial example of such a GTL base oil is Shell XHVI (registered trademark).

[0020] As examples of synthetic oils mention may be made of polyolefins, alkylbenzenes, alkylnaphthalenes, esters, polyoxyalkylene glycols, polyphenyl ethers, dialkyldiphenyl ethers, fluorine-containing compounds (perfluoropolyethers, fluorinated polyolefins) and silicone oils, or mixtures thereof.

[0021] The aforementioned polyolefins include polymers of various olefins or hydrides thereof. Any olefin may be used, and as examples mention may be made of ethylene, propylene, butene and α-olefins with five or more carbons. In the manufacture of the polyolefins, one kind of the aforementioned olefins may be used singly or two or more kinds may be used in combination.

[0022] Particularly suitable are the polyolefins called polyalphaolefins (PAO). These are base oils of Group IV. The polyalphaolefins may also be mixtures of two or more kinds of synthetic oil.

[0023] The viscosity of these synthetic oils is not specially limited, but the kinematic viscosity at 40°C should be 2 to 680 mm^2/s, but preferably 20 to 500 mm^2/s and more preferably 30 to 450 mm^2/s. The kinematic viscosity at 100°C of said synthetic base oils should be 2 to 100 mm^2/s, but preferably 4 to 70 mm^2/s and more preferably 6 to 50 mm^2/s. The viscosity index of said synthetic base oils should be 110 to 170, but preferably 120 to 160 and more preferably 130 to 155. The 15°C density of said synthetic base oils should be 0.8000 to 0.8600 g/cm^3, but preferably 0.8100 to 0.8550 g/cm^3 and more preferably 0.8250 to 0.8550 g/cm^3. The aniline point of said synthetic base oils should be 110 to 180°C, but preferably 120 to 170°C and more preferably 130 to 165°C.

[0024] The amount of the aforementioned base oil to be incorporated in the lubricating oil composition of this invention is not specially limited, but, taking as a basis the total amount of the lubricating oil composition, a typical range can be given as 50 to 90 wt%, but preferably 50 to 80 wt% and more preferably 50 to 70 wt%. The lower limit of the amount incorporated in the base oil, on the basis of the total amount of the lubricating oil composition, should be selected from any of not less than 50, 51, 52, 53, 54, 55, 56, 57, 58 or 59 wt%, and the upper limit of the amount incorporated in the base oil, on the basis of the total amount of the lubricating oil composition, should be selected from any of not more than 67, 68, 69 or 70 wt%.

[0025] Apart from what is stated above, said base oils may also include carboxylic acid ester compounds. These are discussed below.

[0026] As examples of the copolymers of olefins and alkyl methacrylates of the present lubricating oil composition, mention may be made of copolymers in which the essential constituent monomers are at least one kind of olefin having 2 to 20 carbons and at least one kind of alkyl methacrylate having alkyl groups with 1 to 20 carbons.

[0027] The aforementioned olefins include various kinds of olefin polymers or hydrides thereof. Any olefin may be used, but as examples mention may be made of ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, tridecene, tetradecene, pentadecene, hexadecene, heptadecene, octadecene, nonadecene and eicosene. It is also possible to use a single kind of the aforementioned olefins or combinations of two or more kinds for the olefins comprised in the constituent monomers.

[0028] As specific examples of the aforementioned alkyl methacrylates having alkyl groups with 1 to 20 carbons, mention may be made of:

(1) alkyl methacrylates having alkyl groups with 1 to 4 carbons: for example, methyl methacrylate, ethyl methacrylate, n- or iso-propyl methacrylate, n-, iso- or sec-butyl methacrylate;

(2) alkyl methacrylates having alkyl groups with 8 to 20 carbons: for example, n-octyl methacrylate, 2-ethylhexyl methacrylate, n-decyl methacrylate, n-isodecyl methacrylate, n-undecyl methacrylate, n-dodecyl methacrylate, 2-methylundecyl methacrylate, n-tridecyl methacrylate, 2-methyldodecyl methacrylate, n-tetradecyl methacrylate, 2-methyltridecyl methacrylate, n-pentadecyl methacrylate, 2-methyltetradecyl methacrylate, n-hexadecyl methacrylate, and n-octadecyl methacrylate, n-eicosyl methacrylate, n-docosyl methacrylate, methacrylate of Dobanol 23 [mixture of C-12/C-13 oxoalcohols made by Mitsubishi Chemical (Ltd.)] and methacrylate of Dobanol 45 [mixture of C-13/C-14 oxoalcohols made by Mitsubishi Chemical Company Ltd.];

(3) alkyl methacrylates having alkyl groups with 5 to 7 carbons: for example, n-pentyl methacrylate and n-hexyl methacrylate.

[0029] Of the aforementioned monomers (1) ~ (3), the preferred ones are those belonging to (1) and (2), and the monomers of (2) are further preferred. Also, the preferred monomers of the aforementioned (1), from the standpoint of the viscosity index, are those with 1 to 2 carbons in the alkyl groups. The preferred monomers of the aforementioned (2), from the standpoint of solubility in the base oil and low-temperature characteristics, are those with 10 to 20 carbons in the alkyl groups, and further preferred are those with 12 to 14 carbons.

[0030] The molecular weight of the aforementioned olefin and alkyl methacrylate copolymers is 1,200 to 80,000, but preferably 1,200 to 50,000 and more preferably 2,000 to 50,000. The weight average molecular weight is 5,000 to 20,000, but preferably 7,000 to 20,000 and more preferably 9,000 to 16,000. The number average molecular weight is 2,000 to 12,000, but preferably 4,000 to 10,000 and more preferably 5,000 to 9,000. In the case of these molecular weights, the weight average molecular weight (Mw) and number average molecular weight (Mn) are those determined by means of gel permeation chromatography (GPC), and are those obtained by conversion, taking polystyrene as the standard.

[0031] The aforementioned weight average molecular weight can be regulated by means of the temperature during polymerisation, the monomer concentration (solvent concentration), the amount of catalyst or the amount of chain transfer agent.

[0032] The dispersion (Mw/Mn) of the aforementioned olefin and alkyl methacrylate copolymers is 1 to 2.5, but preferably 1.3 to 2.2 and especially 1.7 to 1.9.

[0033] The viscosity of the aforementioned olefin and alkyl methacrylate copolymers is not specially limited, but the viscosity index should be 100 to 250, but preferably 130 to 220 and more preferably 160 to 200. The kinematic viscosity at 40°C of said copolymers should be 1,000 to 12,000 mm^2/s, but preferably 2,000 to 10,000 mm^2/s and more preferably 2,500 to 9,000 mm^2/s. The kinematic viscosity at 100°C of said copolymers should be 50 to 600 mm^2/s, but preferably 100 to 500 mm^2/s and more preferably 150 to 450 mm^2/s. The 15°C density of said copolymers should be 0.900 to 0.950 g/cm^3, but preferably 0.910 to 0.940 g/cm^3 and more preferably 0.925 to 0.935 g/cm^3.

[0034] The copolymers of this invention can be readily obtained by any of the usual methods, and the method of manufacture is not limited. For example, they can be obtained by radical polymerisation using a diluent, olefins and alkyl methacrylates of selected kinds and amounts, a copolymerisation initiator and a chain transfer agent. They can also be obtained by thermal polymerisation of olefins and alkyl methacrylates of selected kinds and amounts with a diluent. The use of a diluent is optional, but the use of a diluent makes it easier to control the molecular weight of the copolymer. It is also thus often possible to resolve problems to do with handling, because copolymers have viscous properties. Any diluent may be used so long as it an inert hydrocarbon, but it must have solubility properties for the copolymer and lubricating oil. As examples of suitable copolymerisation initiators, mention may be made of initiators which break down through application of heat and produce free radicals, for instance peroxide compounds such as benzoyl peroxide, t-butyl peroctoate and cumene hydroperoxide, and azo compounds such as azobisisobutyronitrile and 2,2'-azobis(2-methylbutanenitrile). As examples of suitable chain transfer agents mention may be made of those normally used in the art, for instance α-styrene dimers, dodecylmercaptan and ethylmercaptan. The use of a chain transfer agent is optional, but the use of a chain transfer agent makes it easier to control the molecular weight of the copolymer.

[0035] The amount of the aforementioned olefin and alkyl methacrylate copolymer in the lubricating oil composition of this invention (the amount of the aforementioned olefin and alkyl methacrylate copolymer within the aforementioned molecular weight range) is not specially limited, but, taking as a basis the total amount of the lubricating oil composition, a typical range can be given as 10 to 50 wt%, but preferably 10 to 45 wt% and more preferably 15 to 40 wt%. The lower limit of the amount of olefin and alkyl methacrylate copolymer, on the basis of the total amount of the lubricating oil composition, should be selected from any of not less than 10, 11, 12, 13, 14 or 15 wt%, and the upper limit of the amount incorporated in the base oil, on the basis of the total amount of the lubricating oil composition, should be selected from any of not more than 40, 41, 42, 43, 44, 45, 46, 47, 48, 49 or 50 wt%. The method of determining the amount of said copolymer within a certain molecular weight range in this case is not specially limited, and can be a value converted theoretically from molecular weight distribution curves. For example, when using additives containing said copolymers as raw material {containing olefin and alkyl methacrylate copolymers within the aforementioned specified range (a suitable range or especially suitable range appertaining thereto), olefin and alkyl methacrylate copolymers divergent from said specified range and diluents}, molecular weight distribution curves may be produced by analysing said additives (see, for example, Figure 1). The molecular weight component of a specified range (say, 1200 to 50000) in said molecular weight distribution curves is inferred to be an "olefin and alkyl methacrylate copolymer within said specified range" and the amount of the component within said specified range in the total additive is calculated on the basis of said molecular weight distribution curves.

[0036] In the case of the present lubricating oil composition, the aforementioned lubricating oil base oil comprises carboxylic acid ester compounds.

[0037] As examples of carboxylic acid ester compounds, mention may be made of polyol esters. As examples of polyol esters mention may be made of trihydroxymethylpropyl trioleate (CAS No. 11138-60-6), esters of TMP (trimethylolpropane) and carboxylic acids, esters of PE (pentaerythritol) and carboxylic acids, dicarboxylic acid esters and trimellitic acid esters. The number of carbons in the carboxylic acid residual groups of the ester molecules should also preferably be from 4 to 20 but more preferably from 6 to 18.

[0038] The amount of the aforementioned carboxylic acid ester incorporated in the lubricating oil composition of this invention is, taking as a basis the total amount of the lubricating oil composition, in the range of from 5 to 14 wt%, but preferably 7 to 13 wt% and more preferably 8 to 12 wt%. The amount of carboxylic acid ester incorporated, on the basis of the total amount of the lubricating oil composition, should be selected from any of 5, 6, 7, 8, 9, 10, 11, 12, 13 or 14 wt%.

[0039] In order to improve performance further, it is possible where necessary to make appropriate use of various kinds of additives other than the aforementioned constituents. As examples of these, mention may be made of anti-oxidants, metal deactivators, extreme pressure agents, oiliness improvers, defoaming agents, viscosity index improvers, pour-point depressants, detergent-dispersants, rust preventatives, demulsifying agents, and other lubricating oil additives of the known art.

[0040] For the anti-oxidants used in this invention, those used in lubricating oils are preferred for practical use, and mention may be made of amine-based anti-oxidants, sulphur-based anti-oxidants, phenol-based anti-oxidants and phosphorus-based anti-oxidants. These anti-oxidants may be used singly or in plural combinations within the range of 0.01 to 5 parts by weight relative to 100 parts by weight of the base oil.

[0041] As examples of the aforementioned amine-based anti-oxidants, mention may be made of dialkyl-diphenylamines such as p,p'-dioctyl-diphenylamine (Nonflex OD-3, made by Seiko Chemical Ltd), p,p'-di-α-methylbenzyl-diphenylamine and N-p-butylphenyl-N-p'-octylphenylamine, monoalkyldiphenylamines such as mono-t-butyldiphenylamine and monooctyldiphenylamine, bis(dialkylphenyl)amines such as di(2,4-diethylphenyl)amine and di(2-ethyl-4-nonylphenyl)amine, alkylphenyl-1-naphthylamines such as octyl-phenyl-1-naphthylamine and N-t-dodecylphenyl-1-naphthylamine, 1-naphthylamine, aryl-naphthylamines such as phenyl-1-naphthylamine, phenyl-2-naphthylamine, N-hexylphenyl-2-naphthylamine and N-octylphenyl-2-naphthylamine, phenylenediamines such as N,N'-diisopropyl-p-phenylenediamine and N,N'-diphenyl-p-phenylenediamine, and phenothiazines such as Phenothiazine (made by Hodogaya Chemical Ltd.) and 3,7-dioctylphenothiazine.

[0042] As examples of sulphur-based anti-oxidants, mention may be made of dialkyl sulphides such as didodecyl sulphide and dioctadecyl sulphide, thiodipropionate esters such as didodecyl thiodipropionate, dioctadecyl thiodipropionate, dimyristyl thiodipropionate and dodecyloctadecyl thiodipropionate, and 2-mercaptobenzoimidazole.

[0043] Phenol-based anti-oxidants include 2-t-butylphenol, 2-t-butyl-4-methylphenol, 2-t-butyl-5-methylphenol, 2,4-di-t-butylphenol, 2,4-dimethyl-6-t-butylphenol, 2-t-butyl-4-methoxyphenol, 3-t-butyl-4-methoxyphenol, 2,5-dit-butylhydroquinone (Antage DBH, made by Kawaguchi Chemical Industry Co. Ltd.), 2,6-di-t-butylphenol, 2,6-di-t-butyl-4-alkylphenols such as 2,6-di-t-butyl-4-methylphenol and 2,6-di-t-butyl-4-ethylphenol, and 2,6-di-t-butyl-4-alkoxyphenols such as 2,6-di-t-butyl-4-methoxyphenol and 2,6-di-t-butyl-4-ethoxyphenol.

[0044] Also, there are 3,5-di-t-butyl-4-hydroxybenzylmercapto-octylacetate, alklyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionates such as n-octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate (Yoshinox SS, made by Yoshitomi Fine Chemicals Ltd.), n-dodecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate and 2'-ethylhexyl-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate, and benzenepropanoic acid 3,5-bis(1,1-dimethyl-ethyl)-4-hydroxy-C7~C9 side-chain alkyl esters (Irganox L135, made by Ciba Specialty Chemicals Ltd.), 2,6-di-t-butyl-α-dimethylamino-p-cresol, and 2,2'-methylenebis(4-alkyl-6-t-butylphenol)s such as 2,2'-methylenebis(4-methyl-6-t-butylphenol) (Antage W-400, made by Kawaguchi Chemical Industry Ltd.) and 2,2'-methylenebis(4-ethyl-6-t-butylphenol) (Antage W-500, made by Kawaguchi Chemical Industry Ltd).

[0045] Furthermore, there are bisphenols such as 4,4'-butylidenebis(3-methyl-6-t-butylphenol) (Antage W-300, made by Kawaguchi Chemical Industry Ltd.), 4,4'-methylenebis(2,6-di-t-butylphenol) (Ionox 220AH, made by Shell Japan Ltd.), 4,4'-bis(2,6-di-t-butylphenol), 2,2-(di-p-hydroxyphenyl)propane (Bisphenol A, made by Shell Japan Ltd.), 2,2-bis(3,5-di-t-butyl-4-hydroxyphenyl)propane, 4,4'-cyclohexylidenebis(2,6-t-butylphenol), hexamethylene glycol bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] (Irganox L109, made by Ciba Specialty Chemicals Ltd.), triethylene glycol bis[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionate] (Tominox 917, made by Yoshitomi Fine Chemicals Ltd.), 2,2'-thio-[diethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate (Irganox L115, made by Ciba Specialty Chemicals Ltd.), 3,9-bis{1,1-dimethyl-2-[3-(3-t-butyl-4-hydroxy-5-methylphenyl) propionyloxy]ethyl} 2,4,8,10-tetraoxaspiro[5,5]undecane (Sumilizer GA80, made by Sumitomo Chemicals), 4,4'-thiobis(3-methyl-6-t-butylphenol) (Antage RC, made by Kawaguchi Chemical Industry Ltd.) and 2,2'-thiobis(4,6-di-t-butyl-resorcinol).

[0046] Mention may also be made of polyphenols such as tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate]methane (Irganox L101, made by Ciba Specialty Chemicals Ltd.), 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane (Yoshinox 930, made by Yoshitomi Fine Chemicals Ltd.), 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene (Ionox 330, made by Shell Japan Ltd.), bis-[3,3'-bis-(4'-hydroxy-3'-t-butylphenyl) butyric acid] glycol ester, 2-(3',5'-di-t-butyl-4-hydroxyphenyl) methyl-4-(2",4"-di-t-butyl-3"-hydroxyphenyl)methyl-6-t-butylphenol and 2,6,-bis(2'-hydroxy-3'-t-butyl-5'-methyl-benzyl)-4-methylphenol, and phenol-aldehyde condensates such as condensates of p-t-butylphenol and formaldehyde and condensates of p-t-butylphenol and acetaldehyde.

[0047] As examples of phosphorus-based anti-oxidants mention may be made of triarylphosphites such as triphenylphosphite and tricresylphosphite, trialkylphosphites such as trioctadecylphosphite and tridecylphosphite, and tridodecyltrithiophosphite.

[0048] Metal deactivators that can be used together with the composition of this invention include benzotriazole and benzotriazole derivatives which are 4-alkyl-benzotriazoles such as 4-methyl-benzotriazole and 4-ethyl-benzotriazole, 5-alkyl-benzotriazoles such as 5-methyl-benzotriazole and 5-ethyl-benzotriazole, 1-alkyl-benzotriazoles such as 1-dioctylaminomethyl-2,3-benzotriazole and 1-alkyl-tolutriazoles such as 1-dioctylaminomethyl-2,3-tolutriazole, and benzoimidazole and benzoimidazole derivatives which are 2-(alkyldithio)-benzoimidazoles such as 2-(octyldithio)-benzoimidazole, 2-(decyldithio)-benzoimidazole and 2-(dodecyldithio)-benzoimidazole and 2-(alkyldithio)toluimidazoles such as 2-(octyldithio)-toluimidazole, 2-(decyldithio)-toluimidazole and 2-(dodecyldithio)toluimidazole.

[0049] Also, mention may be made of indazole, indazole derivatives which are toluindazoles such as 4-alkyl-indazoles and 5-alkyl-indazoles, benzothiazole, and benzothiazole derivatives which are 2-mercaptobenzothiazole derivatives (Thiolite B-3100, made by Chiyoda Chemical Industries Ltd.), 2-(alkyldithio)benzothiazoles such as 2-(hexyldithio)benzothiazole and 2-(octyldithio)benzothiazole, 2-(alkyldithio)toluthiazoles such as 2-(hexyldithio)toluthiazole and 2-(octyldithio)toluthiazole, 2-(N,N-dialkylydithiocarbamyl)-benzothiazoles such as 2-(N,N-diethyldithiocarbamyl)-benzothiazole, 2-(N,N-dibutyldithiocarbamyl)-benzothiazole and 2-(N,N-dihexyldithiocarbamyl)-benzothiazole, and 2-(N,N-dialkylydithiocarbamyl)-benzothiazoles such as 2-(N,N-diethyldithiocarbamyl)-toluthiazole, 2-(N,N-dibutyldithiocarbamyl)-toluthiazole and 2-(N,N-dihexyldithiocarbamyl)-toluthiazole.

[0050] Further, mention may be made of benzooxazole derivatives which are 2-(alkyldithio)benzooxazoles such as 2-(octyldithio)benzooxazole, 2-(decyldithio)benzooxazole and 2-(dodecyldithio)benzooxazole or which are

2-(alkyldithio)toluoxazoles such as 2-(octyldithio)toluoxazole, 2-(decyldithio)toluoxazole and 2-(dodecyldithio)toluoxazole, thiadiazole derivatives which are 2,5-bis(alkyldithio)-1,3,4-thiadiazoles such as 2,5-bis(heptyldithio)-1,3,4-thiadiazole, 2,5-bis(nonyldithio)-1,3,4-thiadiazole, 2,5-bis(dodecyldithio)-1,3,4-thiadiazole and 2,5-bis(octadecyldithio)-1,3,4-thiadiazole, 2,5-bis(N,N-dialkyldithiocarbamyl)-1,3,4-thiadiazoles such as 2,5-bis(N,N-diethyldithiocarbamyl)-1,3,4-thiadiazole, 2,5-bis(N,N-dibutyldithiocarbamyl)-1,3,4-thiadiazole and 2,5-bis(N,N-dioctyldithiocarbamyl)-1,3,4-thiadiazole and 2-N,N-dialkyldithiocarbamyl-5-mercapto-1,3,4-thiadiazoles such as 2-N,N-dibutyldithiocarbamyl-5-mercapto-1,3,4-thiadiazole and 2-N,N-dioctyldithiocarbamyl-5-mercapto-1,3,4-thiadiazole, and triazole derivates which are, for example, 1-alkyl-2,4-triazoles such as 1-di-octylaminomethyl-2,4-triazole. These metal deactivators may be used singly or in plural combinations within the range of 0.01 to 0.5 part by weight relative to 100 parts by weight of the base oil.

[0051] It is possible also to add phosphorus compounds to the lubricating oil composition of this invention in order to impart anti-wear properties and extreme-pressure properties. As examples of phosphorus compounds suitable for this invention, mention may be made of phosphate esters, acidic phosphate esters, amine salts of acidic phosphate esters, basic phosphate esters, phosphite esters, phosphorothionates, zinc dithiophosphates, esters of dithiophosphoric acid and alkanols or polyether-type alcohols, and derivatives thereof, phosphorus-containing carboxylic acids and phosphorus-containing carboxylic acid esters. These phosphorus compounds may be used singly or in plural combinations within the range of 0.01 to 2 parts by weight relative to 100 parts by weight of the base oil.

[0052] As examples of the aforementioned phosphate esters, mention may be made of tributyl phosphate, tripentyl phosphate, trihexyl phosphate, triheptyl phosphate, trioctyl phosphate, trinonyl phosphate, tridecyl phosphate, triundecyl phosphate, tridodecyl phosphate, tritridecyl phosphate, tritetradecyl phosphate, tripentadecyl phosphate, trihexadecyl phosphate, triheptadecyl phosphate, trioctadecyl phosphate, trioleyl phosphate, triphenyl phosphate, tris(isopropylphenyl)phosphate, triallyl phosphate, tricresyl phosphpate, trixylenyl phosphate, cresyldiphenyl phosphate and xylenyldiphenyl phosphate.

[0053] As specific examples of the aforementioned acidic phosphate esters, mention may be made of monobutyl acid phosphate, monopentyl acid phosphate, monohexyl acid phosphate, monoheptyl acid phosphate, monooctyl acid phosphate, mononoyl acid phosphate, monodecyl acid phosphate, monoundecyl acid phosphate, monododecyl acid phosphate, monotridecyl acid phosphate, monotetradecyl acid phosphate, monopentadecyl acid phosphate, monohexadecyl acid phosphate, monoheptadecyl acid phosphate, monooctadecyl acid phosphate, monooleyl acid phosphate, dibutyl acid phosphate, dipentyl acid phosphate, dihexyl acid phosphate, diheptyl acid phosphate, dioctyl acid phosphate, dinonyl acid phosphate, didecyl acid phosphate, diundecyl acid phosphate, didodecyl acid phosphate, ditridecyl acid phosphate, ditetradecyl acid phosphate, dipentadecyl acid phosphate, dihexadecyl acid phosphate, diheptadecyl acid phosphate, dioctadecyl acid phosphate and dioleyl acid phosphate.

[0054] As examples of the aforementioned amine salts of acidic phosphate esters, mention may be made of the methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, heptylamine, octylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, dipentylamine, dihexylamine, diheptylamine, dioctylamine, trimethylamine, triethylamine, tripropylamine, tributylamine, tripentylamine, trihexylamine, triheptylamine and trioctylamine salts of the previously mentioned acidic phosphate esters.

[0055] As examples of the aforementioned phosphite esters, mention may be made of dibutyl phosphite, dipentyl phosphite, dihexyl phosphite, diheptyl phosphite, dioctyl phosphite, dinonyl phosphite, didecyl phosphite, diundecyl phosphite, didodecyl phosphite, dioleyl phosphite, diphenyl phosphite, dicresyl phosphite, tributyl phosphite, tripentyl phosphite, trihexyl phosphite, triheptyl phosphite, trioctyl phosphite, trinonyl phosphite, tridecyl phosphite, triundecyl phosphite, tridodecyl phosphite, trioleyl phosphite, triphenyl phosphite and tricresyl phosphite.

[0056] As examples of the aforementioned phosphorothionates, mention may be made specifically of tributyl phosphorothionate, tripentyl phosphorothionate, trihexyl phosphorothionate, triheptyl phosphorothionate, trioctyl phosphorothionate, trinonyl phosphorothionate, tridecyl phosphorothionate, triundecyl phosphorothionate, tridodecyl phosphorothionate, tritridecyl phosphorothionate, tritetradecyl phosphorothionate, tripentadecyl phosphorothionate, trihexadecyl phosphorothionate, triheptadecyl phosphorothionate, trioctadecyl phosphorothionate, trioleyl phosphorothionate, triphenyl phosphorothionate, tricresyl phosphorothionate, trixylenyl phosphorothionate, cresyldiphenyl phosphorothionate, xylenyldiphenyl phosphorothionate, tris(n-propylphenyl) phosphorothionate, tris(isopropylphenyl) phosphorothionate, tris(n-butylphenyl) phosphorothionate, tris(isobutylphenyl) phosphorothionate, tris(s-butylphenyl) phosphorothionate and tris(t-butylphenyl) phosphorothionate. Mixtures of these may also be used.

[0057] As examples of the aforementioned zinc dithiophosphates, mention may be made in general of zinc dialkyl dithiophosphates, zinc diaryl dithiophosphates and zinc arylalkyl dithiophosphates. For example, zinc dialkyl dithiophosphates where the alkyl groups of the zinc dialkyl dithiophosphates have primary or secondary alkyl groups of 3 ~ 22 carbons or alkylaryl groups substituted with alkyl groups of 3 ~ 18 carbons may be used. As specific examples of zinc dialkyl dithiophosphates, mention may be made of zinc dipropyl dithiophosphate, zinc dibutyl dithiophosphate, zinc dipentyl dithiophosphate, zinc dihexyl dithiophosphate, zinc diisopentyl dithiophosphate, zinc diethylhexyl dithiophosphate, zinc dioctyl dithiophosphate, zinc dinonyl dithiophosphate, zinc didecyl dithiophosphate, zinc didodecyl dithiophosphate, zinc dipropylphenyl dithiophosphate, zinc dipentylphenyl dithiophosphate, zinc dipropylmethylphenyl dithiophosphate, zinc dinonylphenyl dithiophosphate, zinc didodecylphenyl dithiophosphate and zinc didodecylphenyl dithiophosphate.

[0058] It is possible to incorporate fatty acid esters of polyhydric alcohols in the lubricating oil composition of this invention with a view to improving oiliness. For example, it is possible to use partial or complete esters of saturated or unsaturated fatty acids having 1 ~ 24 carbons of polyhydric alcohols such as glycerol, sorbitol, alkylene glycol, neopentyl glycol, trimethylolpropane, pentaerythritol and xylidol, and further it is also possible to incorporate those made with kinds different from the aforementioned carboxylic acid ester compounds.

[0059] Examples of glycerol esters include glycerol monolaurylate, glycerol monostearate, glycerol monopalmitate, glycerol monooleate, glycerol dilaurylate, glycerol distearate, glycerol dipalmitate and glycerol dioleate. For sorbitol esters mention may be made of sorbitol monolaurylate, sorbitol monopalmitate, sorbitol monostearate, sorbitol monooleate, sorbitol dilaurylate, sorbitol dipalmitate, sorbitol distearate, sorbitol dioleate, sorbitol tristearate, sorbitol trilaurylate, sorbitol trioleate, and sorbitol tetraoleate.

[0060] Alkylene glycol esters include ethylene glycol monolaurylate, ethylene glycol monostearate, ethylene glycol monooleate, ethylene glycol dilaurylate, ethylene glycol distearate, ethylene glycol dioleate, propylene glycol monolaurylate, propylene glycol monostearate, propylene glycol monooleate, propylene glycol dilaurylate, propylene glycol distearate and propylene glycol dioleate. For neopentyl glycol esters mention may be made of neopentyl glycol monolaurylate, neopentyl glycol monostearate, neopentyl glycol monooleate, neopentyl glycol dilaurylate, neopentyl glycol distearate and neopentyl glycol dioleate.

[0061] Trimethylolpropane esters include trimethylolpropane monolaurylate, trimethylolpropane monostearate, trimethylolpropane monooleate, trimethylolpropane dilaurylate, trimethylolpropane distearate, and trimethylolpropane dioleate. Pentaerythritol esters include pentaerythritol monostearate, pentaerythritol monooleate, pentaerythritol dilaurylate, pentaerythritol distearate, pentaerythritol dioleate and dipentaerythritol monooleate. For such fatty acid esters of polyhydric alcohols it is preferable to use partial esters of polyhydric alcohols and unsaturated fatty acids.

[0062] In order to improve the low-temperature flow characteristics and viscosity characteristics, pour-point depressants and viscosity-index improvers may also be added to the lubricating oil composition of this invention. As examples of viscosity-index improvers mention may be made of non-dispersant type viscosity-index improvers such as polymethacrylates and olefin polymers such as ethylene-propylene copolymers, styrene-diene copolymers, polyisobutylene and polystyrene, and dispersant type viscosity-index improvers where nitrogen-containing monomers have been copolymerised with these, and they may be made with kinds different from the aforementioned copolymers of olefins and alkyl methacrylates. As regards the amount to be added, they may be used within the range of 0.05 ~ 20 parts by weight relative to 100 parts by weight of the base oil.

[0063] As examples of pour-point depressants mention may be made of polymethacrylate-based polymers. As regards the amount to be added, they may be used within the range of approximately 0.01 ~ 5 parts by weight relative to 100 parts by weight of the base oil.

[0064] Defoaming agents may also be added in order to impart defoaming characteristics to the lubricating oil composition of this invention. As examples of such defoaming agents suitable for this invention, mention may be made of organosilicates such as dimethylpolysiloxane, diethylsilicate and fluorosilicone, and non-silicone type defoaming agents such as polyalkylacrylates. As regards the amount to be added, they may be used singly or in plural combinations within the range of 0.0001 to 0.1 part by weight relative to 100 parts by weight of the base oil.

[0065] As examples of demulsifiers suitable for this invention, mention may be made of those in the known art normally used as additives for lubricating oils. As regards the amount to be added, they may be used within the range of 0.0005 to 0.5 part by weight relative to 100 parts by weight of the base oil.

[0066] The viscosity of the lubricating oil composition of this invention is not specially limited, but the viscosity index should be not less than 130, preferably not less than 140 and more preferably not less than 150. The kinematic viscosity at 40°C of said lubricating oil composition should be 140 to 320 mm^2/s, but preferably 140 to 200 mm^2/s and more preferably 140 to 160 mm^2/s. The amount of sludge in a Dry TOST test of said lubricating oil composition should be not more than 1500 mg/kg, but preferably not more than 1300 mg/kg and more preferably not more than 1200 mg/kg. The RPVOT remainder rate in RPVOT tests on a fresh oil of said lubricating oil composition and the test oil after a Dry TOST test should be not less than 40% but preferably not less than 50% and more preferably not less than 60%.

[0067] The lubricating oil composition of this invention is used as a machine oil, a hydraulic oil, a turbine oil, a compressor oil, a gear-tooth oil, an oil for sliding surfaces, a bearing oil or a calibration oil. The lubricating oil composition of this invention is ideally used as a long drain gear oil. What is meant by "long drain gear oil" in this invention is an industrial-level gear oil with long intervals between changes of the lubricating oil. The intervals between lubricating oil changes are not specially limited, but typical examples would be not less than one year and preferably not less than 2 years or more preferably not less than 3 years. In particular the lubricating oil composition of this invention is ideally used for the wheels of step-up gearing in apparatus for wind-power generation of electricity.

Examples

[0068] A more specific explanation of the lubricating oil composition of this invention which has superior extreme pressure properties (ability to prevent welding), which generates a small amount of sludge and which also has a high viscosity index is given below by using examples of embodiment and comparative examples, but the invention is not in any way limited by these.

[0069] The following constituent materials were used for the preparation of the examples of embodiment and comparative examples.

1. Base oils

[0070] Polyalphaolefin (PAO) synthetic oils classified as Group IV according to the API (American Petroleum Institute) base oil categories.

(1-1) Base oil 1: Polyalphaolefin (ordinary name: PAO6, characteristics being kinematic viscosity at 40°C: 35.4 mm^2/s; kinematic viscosity at 100°C: 6.44 mm^2/s; viscosity index 136; 15°C density: 0.8291 g/cm^3; aniline point: 130°C)

(1-2) Base oil 2: Polyalphaolefin (ordinary name: PAO40, characteristics being kinematic viscosity at 40°C: 401 mm^2/s; kinematic viscosity at 100°C: 40.3 mm^2/s; viscosity index 151; 15°C density: 0.8491 g/cm^3; aniline point: 161°C)

2. Additives

[0071]

(2-1) Additive A1: Copolymer of olefin and alkyl methacrylate (ordinary name: Viscobase 11-570, made by Evonik Ltd.)

- Molecular weight: 1200 to 25,000 (Figure 1)
- Number average molecular weight: 5400
- Weight average molecular weight: 9400
- Molecular weight distribution: 1.7
- Kinematic viscosity at 40°C: 2,500 mm^2/s
- Kinematic viscosity at 100°C: 150 mm^2/s
- Viscosity index: 160
- 15°C Density: 0.926 g/cm^3

(2-2) Additive A2: Copolymer of olefin and alkyl methacrylate (ordinary name: Viscobase 11-574, made by Evonik Ltd.)

- Molecular weight: 1200 to 50,000 (Figure 1)
- Number average molecular weight: 8000
- Weight average molecular weight: 15000
- Molecular weight distribution: 1.9
- Kinematic viscosity at 40°C: 9,000 mm^2/s
- Kinematic viscosity at 100°C: 450 mm^2/s
- Viscosity index: 200
- 15°C Density: 0.934 g/cm^3

(2-3) Additive A3: Olefin copolymer (ordinary name: Lucant HC-1100, made by Mitsui Chemicals Ltd.)

- Number average molecular weight: 6,000
- Kinematic viscosity at 40°C: 18,900 mm^2/s
- Kinematic viscosity at 100°C: 1,100 mm^2/s
- Viscosity index: 270
- 15°C Density: 0.850 g/cm^3

(2-4) Additive A4: Polyisoolefin (ordinary name: Nisseki Polybutene HV300, made by JX Nippon Oil & Energy Corp.)

- Number average molecular weight: 1,400

- Kinematic viscosity at 40°C: 26,000 mm^2/s
- Kinematic viscosity at 100°C: 590 mm^2/s
- Viscosity index: 155
- 15°C Density: 0.898 g/cm^3

(2-5) Additive B: Gear-oil additives package (ordinary name: Anglamo 199, made by Lubrizol Corp.)

- Kinematic viscosity at 40°C: 68 mm^2/s
- Kinematic viscosity at 100°C: 8.2 mm^2/s
- 15°C Density: 1.07 g/cm^3
- Sulphur content: 29.8 to 33.8 wt%
- Phosphorus content: 1.55 to 1.89 wt%
- Nitrogen content: 0.85 to 1.03 wt%

Additive B: Anglamo is a known gear-oil additives package and it is stated in the Lubrizol catalogue that if 3.25 to 3.9% of this package is blended into the lubricating oil, it will satisfy the API GL-4 standard. The API GL-4 standard is divided into six categories, and the proportion of additives is larger as the number increases, thus increasing the extreme pressure properties. In the examples of embodiment, the amount of this Additive B in the formulation was made 2.0% to meet the API GL-3 standard (having extreme pressure properties of at least a medium level), but the amount of Additive B in the formulation is not specially limited.
(2-6) Additive C: Trihydroxymethylpropyl trioleate (ordinary name: Unister H327R, made by NOF Corp.)

[0072] The lubricating oil compositions of the Examples of Embodiment and Comparative Examples were prepared using the aforementioned constituent materials and using the compositions shown in the Tables.

[0073] Dry TOST and RPVOT tests as shown below were carried out on the lubricating oil compositions of the Examples of Embodiment and the Comparative Examples to observe their performance.

Dry TOST

[0074] Following the test method for the oxidative stability of turbine oils in JIS K2514, 360 ml of test oil was poured into a container and, without adding any water or catalyst, it was heated for 336 hours by blowing in 3 litres of oxygen every hour in a 120°C constant-temperature tank. 24 hours after completion of the test, the test oil was filtered by means of a membrane filter of 1 μm pore diameter, and the amount of sludge produced was measured.

RPVOT

[0075] In accordance with the test method for the rotating bomb oxidative stability test in JIS K2514, 50 g of test oil was drawn off into a container, and in the co-presence of 5 ml of distilled water and a copper catalyst it was placed in a bomb pressurised with oxygen at 6.3 kgf/cm^2 at a room temperature of 25°C. The bomb was rotated 100 times a minute inside a 150°C constant-temperature tank. The pressure inside the bomb was recorded, and the time from the maximum pressure reached after introducing the bomb into the constant-temperature tank until a pressure drop of 1.75 kgf/cm^2 was observed was measured, and this value was taken as the RPVOT value. The RPVOT was carried out on fresh oil and on test oil (before filtering) after completion of the TOST.

[0076] As shown in Table 1 below, Comparative Examples 1A and 2A in which an olefin and alkyl methacrylate copolymer has been used as a viscosity index improver exhibit a high viscosity index of more than 150, and the amount of sludge after the Dry TOST test is less than 1,100 mg/kg. In contrast, Comparative Example 1, which uses an olefin copolymer, has a high viscosity index but a large amount of sludge. Comparative Example 2, which uses polyisobutylene, has little sludge but a low value for the viscosity index.

[0077] Table 2 shows the results when trihydroxymethylpropyl trioleate (Additive C) was added to Comparative Examples 1A and 2A and Comparative Examples 1 and 2. Example of Embodiment 3 and Example of Embodiment 4, which used an olefin and alkyl methacrylate copolymer as a viscosity index improver showed greater improvement of viscosity index and greater reduction in the amount of sludge than Comparative Example 1A or Comparative Example 2A through the addition of the trihydroxymethylpropyl trioleate. This effect due to the addition of the trihydroxymethylpropyl trioleate is also clear from the difference in the results between Comparative Example 3 and Comparative Example 1, and Comparative Example 4 and Comparative Example 2, but compared to Examples of Embodiment 3 and 4, Comparative Example 3 still has a greater amount of sludge, and Comparative Example 4 can be seen to have a lower viscosity index.

[0078] For the RPVOT remainder rate, a value of not less than 40% is preferable, but a value of not less than 50% is more preferable.

Table 1

		Comparative Example 1A	Comparative Example 2A	Comparative Example 1	Comparative Example 2
Composition	Base oil 1, wt%	44.79	48.79	56.58	50.46
	Base oil 2, wt%	33.21	33.21	33.21	33.21
	Additive A1, wt%	20.0			
	Additive A2, wt%		16.0		
	Additive A3, wt%			8.21	
	Additive A4, wt%				14.33
	Additive B, wt%	2.0	2.0	2.0	2.0
Test results	Kinematic viscosity 40°C, mm^2/s	149	154	150	149
	Kinematic viscosity 100°C, mm^2/s	19.6	20.7	20.3	18.4
	Viscosity index	151	157	157	138
	Amount of sludge, mg/kg	1,065	796	1,640	574

Table 2

		Example of Embodiment 3	Example of Embodiment 4	Comparative Example 3	Comparative Example 4
Composition	Base oil 1, wt%	34.79	38.79	46.58	40.46
	Base oil 2, wt%	33.21	33.21	33.21	33.21
	Additive A1, wt%	20.0			
	Additive A2, wt%		16.0		
	Additive A3, wt%			8.21	
	Additive A4, wt%				14.33
	Additive B, wt%	2.0	2.0	2.0	2.0
	Additive C, wt%	10.0	10.0	10.0	10.0

(continued)

		Example of Embodiment 3	Example of Embodiment 4	Comparative Example 3	Comparative Example 4
Test results	Kinematic viscosity 40°C, mm^2/s	140	148	139	137
	Kinematic viscosity 100°C, mm^2 /s	18.9	20.3	19.4	17.5
	Viscosity index	154	160	159	140
	Amount of sludge, mg/kg	837	796	1,500	502
	RPVOT value of fresh oil, min	200	220	220	230
	RPVOT value after test, min	130	140	110	140
	RPVOT remainder rate, %	65	64	50	61

Claims

1. Lubricating oil composition comprising:

   (A) 50 to 90% by mass of at least one kind of lubricating oil base oil selected from mineral oils and synthetic oils; and
   (B) 10 to 50% by mass of a copolymer, being of weight average molecular weight 5,000 to 20,000, of an olefin and an alkyl methacrylate;

   wherein the lubricating base oil comprises 5 to 14% by mass relative to the total amount of the lubricating oil composition of (C) a carboxylic acid ester compound, wherein the carboxylic acid ester (c) is a polyol ester.

2. Lubricating oil composition according to claim 1, wherein the lubricating oil base oil is a polyalphaolefin or a GTL (gas-to-liquid) oil.

3. Lubricating oil composition according to claim 1 or claim 2, wherein the weight average molecular weight of the copolymer is from 7000 to 20000.

4. Lubricating oil composition according to any one of claims 1 to 3, wherein the 40°C kinematic viscosity of the lubricating oil composition is 140 to 320 mm^2/s, the viscosity index is not less than 150 and the amount of sludge in a Dry TOST test is not more than 1200 mg/kg.

5. Use of a lubricating oil composition according to any one of claims 1 to 4, as a machine oil, a hydraulic oil, a turbine oil, a compressor oil, a gear-tooth oil, an oil for sliding surfaces, a bearing oil or a calibration oil.

6. Use of a lubricating oil composition according to any one of claims 1 to 4, as a long drain gear oil.

Patentansprüche

1. Schmierölzusammensetzung, Folgendes umfassend:

   (A) 50 bis 90 Masse-% wenigstens einer Art von Schmierölgrundöl, das ausgewählt ist aus Mineralölen und

Synthetikölen; und
(B) 10 bis 50 Masse-% eines Copolymers, wobei das Massenmittel 5.000 bis 20.000 beträgt, eines Olefins und eines Alkylmethacrylats;

wobei das Schmiergrundöl 5 bis 14 Masse-% relativ zu der Gesamtmenge der Schmierölzusammensetzung von (C) einer Carbonsäureesterverbindung umfasst, wobei der Carbonsäureester (c) ein Polyolester ist.

2. Schmierölzusammensetzung nach Anspruch 1, wobei das Schmierölgrundöl ein Polyalphaolefin oder ein GTL (Gas-zu-Flüssigkeit - *gas-to-liquid*)-Öl ist.

3. Schmierölzusammensetzung nach Anspruch 1 oder 2, wobei das Massenmittel des Copolymers von 7000 bis 20000 beträgt.

4. Schmierölzusammensetzung nach einem der Ansprüche 1 bis 3, wobei die 40 °C kinematische Viskosität der Schmierölzusammensetzung 140 bis 320 mm^2/s ist, der Viskositätsindex wenigstens 150 ist, und die Menge an Schlamm in einem trockenen TOST-Test höchstens 1200 mg/kg ist.

5. Verwenden einer Schmierölzusammensetzung nach einem der Ansprüche 1 bis 4 als ein Maschinenöl, ein Hydrauliköl, ein Turbinenöl, ein Kompressorenöl, ein Zahnradöl, ein Öl für Gleitoberflächen, ein Lageröl oder ein Kalibrierungsöl.

6. Verwenden einer Schmierölzusammensetzung nach einem der Ansprüche 1 bis 4 als ein Getriebeöl mit langem Ablauf.

Revendications

1. Composition d’huile lubrifiante comprenant :

(A) 50 à 90 % en masse d’au moins un type d’huile de base pour huile lubrifiante choisie parmi des huiles minérales et des huiles synthétiques ; et
(B) 10 à 50 % en masse d’un copolymère, ayant un poids moléculaire moyen en poids de 5 000 à 20 000, d’une oléfine et d’un méthacrylate d’alkyle ;

dans laquelle l’huile de base lubrifiante comprend 5 à 14 % en masse par rapport à la quantité totale de la composition d’huile lubrifiante de (C) un composé ester d’acide carboxylique, dans laquelle l’ester d’acide carboxylique (c) est un ester de polyol.

2. Composition d’huile lubrifiante selon la revendication 1, dans laquelle l’huile de base pour huile lubrifiante est une polyalphaoléfine ou une huile GTL (transformation de gaz en liquide).

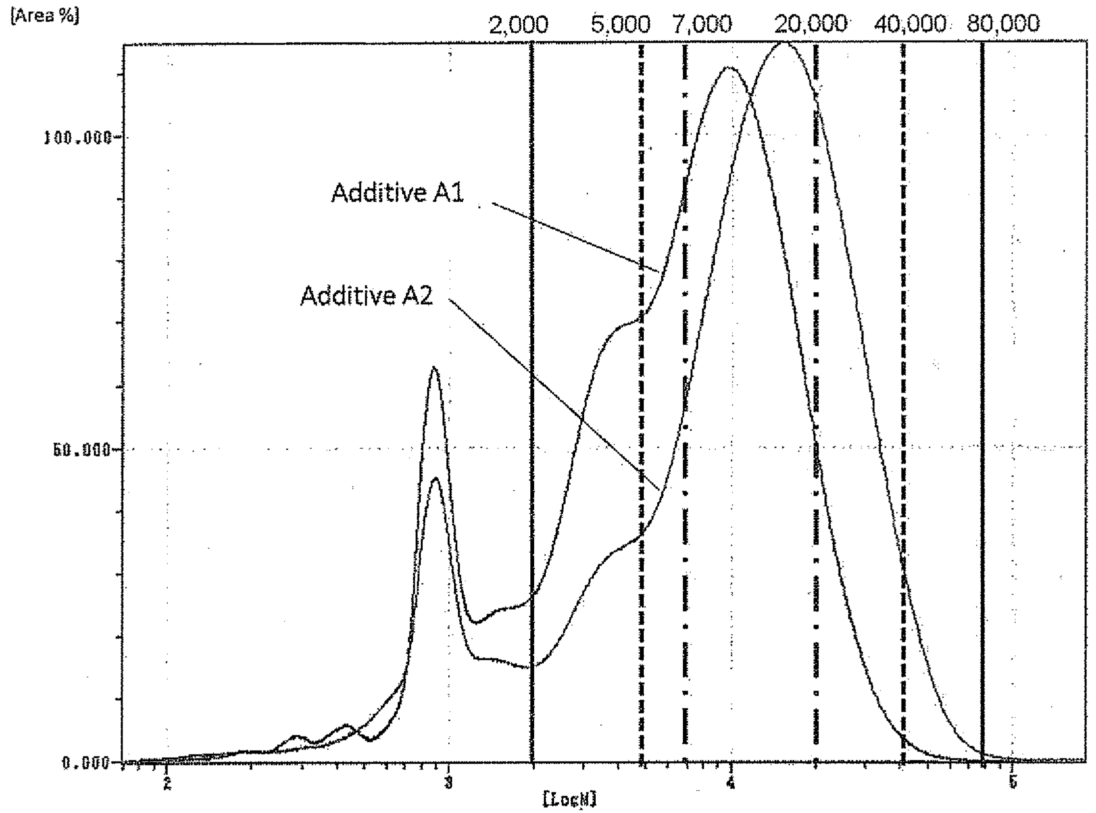
3. Composition d’huile lubrifiante selon la revendication 1 ou la revendication 2, dans laquelle le poids moléculaire moyen en poids du copolymère est compris entre 7 000 et 20 000.

4. Composition d’huile lubrifiante selon l’une quelconque des revendications 1 à 3, dans laquelle la viscosité cinématique à 40°C de la composition d’huile lubrifiante est de 140 à 320 mm^2/s, l’indice de viscosité n’est pas inférieur à 150 et la quantité de boue dans un essai d’oxydation des huiles inhibées pour turbines TOST sec n’est pas supérieure à 1 200 mg/kg.

5. Utilisation d’une composition d’huile lubrifiante selon l’une quelconque des revendications 1 à 4, en tant qu’huile de machine, huile hydraulique, huile de turbine, huile de compresseur, huile pour engrenages, huile pour surfaces glissantes, huile à palier ou huile d’étalonnage.

6. Utilisation d’une composition d’huile lubrifiante selon l’une quelconque des revendications 1 à 4, en tant qu’huile pour engrenages à intervalle de vidange long.

Figure 1


[Area %]
100.000
50.000
0.000
2,000
5,000
7,000
20,000
40,000
80,000
Additive A1
Additive A2
2
3
4
5
[LogM]

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- EP 0566048 A **[0006]**

Non-patent literature cited in the description

- *Gekkan Tribology,* May 2010, 50-51 **[0002]**
- *CHEMICAL ABSTRACTS,* 11138-60-6 **[0037]**