



(11) **EP 2 878 657 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
13.06.2018 Bulletin 2018/24

(51) Int Cl.:
C10M 145/14 (2006.01) C10N 30/02 (2006.01)

(21) Application number: **13823599.9**

(86) International application number:
PCT/JP2013/070100

(22) Date of filing: **24.07.2013**

(87) International publication number:
WO 2014/017558 (30.01.2014 Gazette 2014/05)

(54) **POLY(METH)ACRYLATE VISCOSITY INDEX IMPROVER, AND LUBRICATING OIL COMPOSITION AND LUBRICATING OIL ADDITIVE CONTAINING SAID VISCOSITY INDEX IMPROVER**

POLY(METH)ACRYLAT VISKOSITÄTSINDEXVERBESSERER UND SCHMIERÖLZUSAMMENSETZUNG SOWIE SCHMIERÖLADDITIV MIT DIESEM VISKOSITÄTSINDEXVERBESSERER

AMÉLIORANT D'INDICE DE VISCOSITÉ À BASE DE POLY(MÉTH)ACRYLATE, ET COMPOSITION D'HUILE LUBRIFIANTE ET ADDITIF POUR HUILE LUBRIFIANTE LE CONTENANT

(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

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(30) Priority: **24.07.2012 JP 2012163619**
24.07.2012 JP 2012163624
24.07.2012 JP 2012163622
05.04.2013 JP 2013079828
05.04.2013 JP 2013079816
05.04.2013 JP 2013079829
05.04.2013 JP 2013079830
05.04.2013 JP 2013079832
05.07.2013 JP 2013142014
05.07.2013 JP 2013142036

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(43) Date of publication of application:
03.06.2015 Bulletin 2015/23

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Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

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Description**Technical Field**

5 [0001] The present invention relates to a poly(meth)acrylate-based viscosity index improver, a lubricating oil additive and a lubricating composition containing the viscosity index improver.

Background Art

10 [0002] Conventionally, in the field of lubricating oils, improvement of lubricating oils has been studied from the viewpoint of an energy saving property. Especially in recent years, a trend toward the global environmental protection has increased, and a need for an energy saving property improving effect for lubricating oils has been further strengthened.

[0003] For example, in the case of lubricating oils used for internal combustion engines such as a vehicle engine (also referred to as "lubricating oils for an internal combustion engine" or "engine oils"), as one means of improving a fuel saving property, a method of increasing a viscosity index of a lubricating oil by adding a viscosity index improver to a lubricating base oil has been known.

15 [0004] Moreover, for example, in the case of lubricating oils used for transmissions of vehicles, such as ATF, MTF, and CVTF (also referred to as "lubricating oils for a transmission" or "drive system oils"), as one means of improving a fuel saving property, there is a method of decreasing viscosity resistance by lowering the viscosity of a lubricating oil for a transmission. However, when the viscosity of a lubricating oil for a transmission is lowered, other problems such as oil leak and seizure may arise.

[0005] Therefore, as another method for improving a fuel saving property, there is a method involving use of a viscosity index improver. This method increases the viscosity index of a lubricating oil for a transmission by using a viscosity index improver, and suppresses the viscosity increase in a low-temperature region while maintaining the viscosity in a high-temperature region.

20 [0006] Regarding a viscosity index improver, the use of various viscosity index improvers has been proposed, and in particular, the use of poly(meth)acrylate-based viscosity index improvers has been often proposed (for example, refer to Patent Literatures 1 to 7).

Citation List**Patent Literature****[0007]**

35 Patent Literature 1: Japanese Patent Application Laid-Open No. 7-48421
 Patent Literature 2: Japanese Patent Application Laid-Open No. 7-62372
 Patent Literature 3: Japanese Patent Application Laid-Open No. 6-145258
 Patent Literature 4: Japanese Patent Application Laid-Open No. 3-100099
 40 Patent Literature 5: Japanese Patent Application Laid-Open No. 2002-302687
 Patent Literature 6: Japanese Patent Application Laid-Open No. 2004-124080
 Patent Literature 7: Japanese Patent Application Laid-Open No. 2005-187736

[0008] WO 2007/127660 A1 relates to a lubricating composition comprising (a) a polymer derived from greater than 50 wt % or more of a non-diene monomer, wherein the polymer has a weight-average molecular weight of about 2000 to about 200,000, and wherein the polymer has a shear stability index of about 0 to about 25; (b) a phosphorus-containing acid, salt, or ester; (c) an extreme pressure agent, other than a phosphorus-containing acid, salt, or ester; and (d) an oil of lubricating viscosity.

[0009] WO 2007/127615 A2 discloses a lubricating composition comprising (a) about 0.1 to about 15 wt % of a polymer with (i) a weight-average molecular weight of about 100,000 to about 500,000; and (ii) a shear stability index of about 10 to about 60; (b) a phosphorus-containing acid, salt, or ester; (c) a dispersant; and (d) an oil of lubricating viscosity.

[0010] US 2012/046207 A1 relates to a poly(meth)acrylate-based viscosity index improver and lubricating oil compositions comprising same. In the Working Examples, the index improver comprises structural units of formula 1 with R¹ being methyl and R² being a C12-C15 alkyl, having an average molecular weight of 69,000-82,700 g/mol.

55 [0011] WO 2012/076676 A1 discloses a viscosity index improver comprising a polyalkyl(meth)acrylate polymer characterized in that the polyalkyl(meth)acrylate polymer comprises a polydispersity Mw/Mn in the range of 1.05 to 2.0.

[0012] US 2009/221461 A1 relates to a polymer according to Formula (I) with specific pendant groups, further to a lubricating composition containing said polymer, and to a method and use of controlling viscosity index by supplying to

an oil of lubricating viscosity the polymer with pendant groups.

[0013] US 2011/237477 A1 relates to a hydrocarbon-based lubricating base oil comprising as an additive a viscosity index improver. Said index improver is a poly(meth)acrylate-based viscosity index improver wherein the molecular weight is more than 100000 and wherein the polymer chain contains 10 mol% of units with an alkyl group of 22 carbon atoms.

Summary of Invention

Technical Problem

[0014] However, for example, in lubricating oils for an internal combustion engine, in the case where the above-described conventional poly(meth)acrylate-based viscosity index improvers are used, there is a room for improvement in a high shear viscosity so as to achieve a practically sufficient fuel saving property. Especially, in 0W-20 whose requirement for fuel saving property is high, there is a need to maintain the high shear viscosity at a high level to some extent at 150°C, and on the other hand, to lower the high shear viscosity at 100°C. In contrast, in the conventional poly(meth)acrylate-based viscosity index improvers, it is difficult to lower the high shear viscosity at 100°C while maintaining the high shear viscosity at 150°C.

[0015] Moreover, for example, for lubricating oils for a transmission, as one cause of deterioration in a fuel saving property, there is friction loss of a gear in a driving device during power transmission. Therefore, if a lubricating oil whose viscosity resistance is low in a high shear condition can be achieved, friction loss can be decreased and a fuel saving property can be further improved.

[0016] However, the above-described conventional viscosity index improvers attempt to improve a viscosity property in a high-temperature region and a low-temperature region by improving the viscosity index, and they are not considered to be sufficient in terms of a friction loss decreasing effect.

[0017] Therefore, an object of the present invention is to provide a viscosity index improver capable of achieving a fuel saving property, a lubricating oil additive and a lubricating composition containing the viscosity index improver.

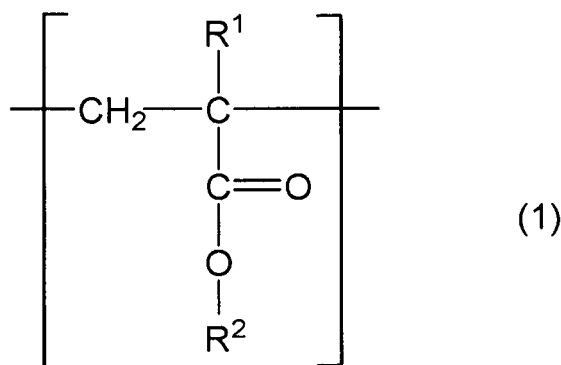
[0018] Moreover, another object of the present invention is to provide a viscosity index improver capable of sufficiently lowering a high shear viscosity at 100°C while maintaining a high shear viscosity at 150°C, a lubricating oil additive and a lubricating composition containing the viscosity index improver.

Solution to Problem

[0019] The present inventors made extensive research and found that a poly(meth)acrylate-based viscosity index improver which has a specific structure and in which the weight-average molecular weight, and the ratio of the weight-average molecular weight M_w to the number average molecular weight M_n , M_w/M_n satisfy specific conditions can sufficiently lower a high shear viscosity at 100°C while maintaining a high shear viscosity at 150°C, which leads to accomplish the present invention.

[0020] That is, the present invention provides a poly(meth)acrylate-based viscosity index improver consisting of a polymer chain comprising a structural unit represented by the following formula (1), wherein the weight-average molecular weight M_w is 100000 or more and 500000 or less, and the ratio of the weight-average molecular weight M_w to the number average molecular weight M_n , M_w/M_n , is 1.6 or less

[Chemical Formula 1]



wherein R^1 represents hydrogen or a methyl group, and R^2 represents a C1 to C36 alkyl group, and wherein the polymer chain contains 20 to 45 mass% or more of the structural unit in which R^2 is a methyl group, and

wherein the polymer chain contains 20 mass% or more of the structural unit in which R² is an alkyl group having 18 or more carbon atoms, based on the total amount of the structural units contained in the polymer chain.

[0021] Moreover, the present invention provides a lubricating oil additive comprising the above-described poly(meth)acrylate-based viscosity index improver.

[0022] Furthermore, the present invention provides a lubricating composition comprising a lubricating base oil, and the above-described poly(meth)acrylate-based viscosity index improver.

Advantageous Effects of Invention

[0023] According to the present invention, a viscosity index improver capable of achieving a fuel saving property, a lubricating oil additive and a lubricating composition containing the viscosity index improver are provided.

[0024] Moreover, according to the present invention, a viscosity index improver capable of sufficiently lowering a high shear viscosity at 100°C while maintaining a high shear viscosity at 150°C, a lubricating oil additive and a lubricating composition containing the viscosity index improver can be provided.

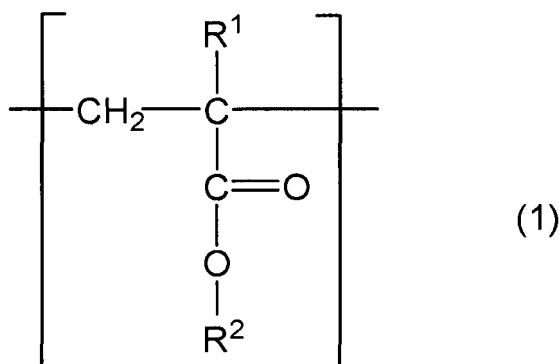
Description of Embodiments

[0025] Hereinafter, preferred embodiments of the present invention will be described in detail, but the present invention is not limited to the following embodiments.

[First Embodiment: Poly(meth)acrylate-based Viscosity Index Improver]

[0026] A poly(meth)acrylate-based viscosity index improver comprises a polymer chain containing a structural unit represented by the following formula (1). The weight-average molecular weight Mw (hereinafter, just referred to as "Mw" in some cases) of the poly(meth)acrylate-based viscosity index improver is 100000 or more, and the ratio of the weight-average molecular weight Mw to the number average molecular weight Mn (hereinafter, just referred to as "Mn" in some cases), Mw/Mn (hereinafter, just referred to as "Mw/Mn" in some cases), is 1.6 or less.

[Chemical Formula 3]



wherein in the formula (1), R¹ represents hydrogen or a methyl group, and R² represents a C1 to C36 alkyl group.

[0027] R¹ may be either hydrogen or a methyl group, and is preferably a methyl group.

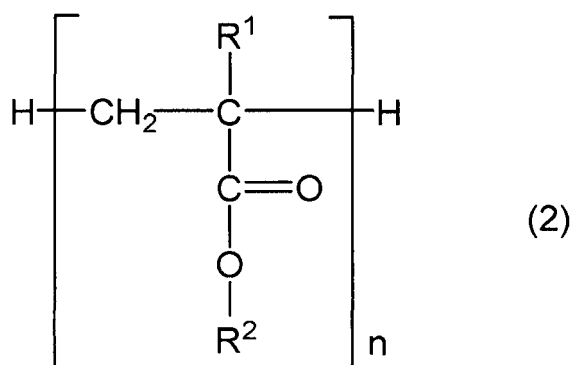
[0028] The number of carbon atoms of the alkyl group represented by R² is 1 to 36 as described above, preferably 1 to 30, more preferably 1 to 26, and further preferably 1 to 22 from the viewpoint of handleability and ease of manufacture. Moreover, the alkyl group represented by R² may be straight-chain or branched.

[0029] In the case where two or more structural units represented by the above formula (1) are contained in the polymer chain, R¹s and R²s may be the same or different between the respective structural units. From the viewpoint of a fuel saving property and solubility, the polymer chain contains 20 to 45 mass% of the structural unit in which R² is a methyl group, based on the total amount of the structural units contained in the polymer chain. Moreover, from the viewpoint of a fuel saving property, the polymer chain contains 20 mass% or more of the structural unit in which R² is an alkyl group having 18 or more carbon atoms, based on the total amount of the structural units contained in the polymer chain.

[0030] The polymer chain may contain only the structural unit represented by the above formula (1), or may further contain a structural unit other than the structural unit represented by the above formula (1) in addition to the structural unit represented by the above formula (1). Moreover, terminals of the polymer chain are not particularly limited. Among

these polymer chains, a polymer chain containing only the structural unit represented by the above formula (1), whose terminals are hydrogen atoms, that is, a polymer chain represented by the following formula (2) is preferable.

[Chemical Formula 4]



[0031] In the formula (2), R¹ represents hydrogen or a methyl group, R² represents a C1 to C36 alkyl group, and n represents an integer selected such that the Mw and the Mw/Mn satisfy the above-described conditions. For example, n is an integer of 400 to 2000.

[0032] The weight-average molecular weight Mw is 100000 or more, and it is preferably 125000 or more, more preferably 150000 or more, and further preferably 175000 or more from the viewpoint of a fuel saving property. The upper limit of Mw is 500000 or less.

[0033] The number average molecular weight Mn is arbitrarily selected such that the Mw/Mn satisfies the above-described condition. The Mn is preferably 75000 or more, more preferably 94000 or more, and further preferably 110000 or more from the viewpoint of lowering the HTHS viscosity at 100°C. The upper limit of Mn is not particularly limited, and the Mn is, for example, 300000 or less.

[0034] The Mw/Mn is 1.6 or less, and it is preferably 1.5 or less, more preferably 1.4 or less, and further preferably 1.2 or less from the viewpoint of a fuel saving property. Moreover, from the viewpoint of the yield of poly(meth)acrylate, the Mw/Mn is preferably 1.0 or more, more preferably 1.01 or more, and further preferably 1.02 or more.

[0035] It is to be noted that "the weight-average molecular weight Mw", "the number average molecular weight Mn", and "the ratio Mw/Mn of the weight-average molecular weight Mw to the number average molecular weight Mn" in the present invention mean Mw, Mn, and Mw/Mn (converted values with polystyrene (standard sample)) obtained by GPC analysis. Specifically, they are measured as follows, for example.

[0036] A solution whose sample concentration is 2 mass% is prepared by dilution using tetrahydrofuran as a solvent. The sample solution is analyzed using GPC equipment (Waters Alliance2695). The analysis is carried out at the flow rate of the solvent of 1 ml/min, by using a column whose analyzable molecular weight is 10000 to 256000, and a refractive index as a detector. It is to be noted that the relationship between the column retention time and the molecular weight is determined using a polystyrene standard whose molecular weight is clear and a calibration curve is separately made, and after that, the molecular weight is determined from the obtained retention time.

[0037] Although the manufacturing method of the poly(meth)acrylate-based viscosity index improver according to the present embodiment is not particularly limited, examples thereof include a method in which an initiator is added to a mixed solution containing an alkyl(meth)acrylate, a polymerization reagent, and a solvent to polymerize the alkyl(meth)acrylate at predetermined temperature.

[0038] As the alkyl(meth)acrylate, an alkyl(meth)acrylate represented by the following formula (3) can be used.

[0051] Examples of the viscosity index improvers other than the above-described poly(meth)acrylate-based viscosity index improver include poly(meth)acrylate-based viscosity index improvers other than the above-described poly(meth)acrylate-based viscosity index improver, polyisobutene-based viscosity index improvers, ethylene-propylene copolymer-based viscosity index improvers, and styrene-butadiene hydrogenated copolymer-based viscosity index improvers.

[0052] Examples of the antioxidants include ashless antioxidants such as phenolic or amine antioxidants, and metallic antioxidants such as zinc, copper, or molybdenum antioxidants.

[0053] Examples of the phenolic antioxidants include 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylenebis(4-ethyl-6-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-nonyl phenol), 2,2'-isobutylidenebis(4,6-dimethylphenol), 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butylphenol, 2,6-di-tert- α -dimethylamino-p-cresol, 2,6-di-tert-butyl-4-(N,N-dimethylaminomethylphenol), 4,4'-thiobis(2-methyl-6-tert-butylphenol), 4,4'-thiobis(3-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), bis(3-methyl-4-hydroxy-5-tert-butylbenzyl)sulfide, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, 2,2'-thio-diethylenebis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], tridecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, pentaerythrityl-tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], octyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, stearyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, and octyl-3-(3-methyl-5-di-tert-butyl-4-hydroxyphenyl)propionate. Two or more thereof may be mixed to be used.

[0054] Examples of the amine antioxidants include known amine antioxidants generally used for lubricating oils, such as aromatic amine compounds, alkyldiphenylamines, alkylnaphthylamines, phenyl- α -naphthylamine, and alkylphenyl- α -naphthylamines.

[0055] Examples of the corrosion inhibitors include benzotriazole, tolyltriazole, thiadiazole, and imidazole compounds.

[0056] Examples of the rust-preventive agents include petroleum sulfonates, alkylbenzene sulfonates, dinonylnaphthalene sulfonates, alkenylsuccinic acid esters, and polyhydric alcohol esters.

[0057] Examples of the metal deactivators include imidazoline, pyrimidine derivatives, alkylthiadiazoles, mercaptobenzothiazole, benzotriazole or derivatives thereof, 1,3,4-thiadiazole polysulfide, 1,3,4-thiadiazolyl-2,5-bisdialkylthiocarbamate, 2-(alkylthio)benzimidazole, and β -(o-carboxybenzylthio)propionitrile.

[0058] Examples of the antifoamers include silicone oil whose kinematic viscosity at 25°C is 1000 to 100000 mm²/s, alkenylsuccinic acid derivatives, esters of polyhydroxy aliphatic alcohols and long-chain fatty acids, methylsalicylate, and o-hydroxybenzyl alcohol.

[0059] As the ashless friction modifiers, arbitrary compounds generally used as ashless friction modifiers for lubricating oils can be used, and examples thereof include ashless friction modifiers such as amine compounds, fatty acid esters, fatty acid amides, fatty acids, aliphatic alcohols, and aliphatic ethers, each of which has at least one alkyl group or alkenyl group having 6 to 30 carbon atoms, in particular straight-chain alkyl group or straight-chain alkenyl group having 6 to 30 carbon atoms in a molecule. Moreover, nitrogen-containing compounds and acid-modified derivatives thereof and the like described in Japanese Patent Application Laid-Open No. 2009-286831 and various ashless friction modifiers exemplified in International Publication No. WO 2005/037967 Pamphlet can also be used.

[0060] Furthermore, the lubricating oil additive according to the present embodiment may further contain a solvent. As the solvent, highly-refined mineral oils, anisole, and toluene can be used. Among them, it is preferable to use highly-refined mineral oils. In the case where the lubricating oil additive contains the solvent, the content of the solvent is preferably 5 to 75 mass%, and more preferably 30 to 60 mass% based on the total amount of the lubricating oil additive from the viewpoint of handling as an additive.

[Third Embodiment: Lubricating composition]

[0061] A lubricating composition according to the third embodiment contains a lubricating base oil, and the above poly(meth)acrylate-based viscosity index improver comprising a polymer chain containing a structural unit represented by the above formula (1), wherein the weight-average molecular weight Mw is 100000 or more and 500000 or less, and the ratio of the weight-average molecular weight Mw to the number average molecular weight Mn, Mw/Mn, is 1.6 or less. The lubricating composition according to the present embodiment includes an aspect containing a lubricating base oil and the lubricating oil additive according to the above-described second embodiment. The poly(meth)acrylate-based viscosity index improver in the present embodiment is the same as the poly(meth)acrylate-based viscosity index improvers in the above-described first embodiment and second embodiment, and furthermore, other additives and a solvent which can be contained in the lubricating composition are the same as the other additives and the solvent in the second embodiment, and an overlapping explanation is omitted here.

[0062] The lubricating base oil is not particularly limited, and lubricating base oils used for general lubricating oils can be used. Specifically, mineral lubricating base oils, synthetic lubricating base oils, a mixture in which two or more

lubricating base oils selected therefrom are mixed at an arbitrary ratio and the like can be used.

[0063] Examples of the mineral lubricating base oils include those obtained by refining a lubricating oil fraction obtained by reduced-pressure distillation of an atmospheric residue obtained by atmospheric distillation of a crude oil by carrying out one or more treatment, such as solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, and hydrotreating, and base oils manufactured by a method of isomerizing wax-isomerized mineral oils and GTL waxes (gas-to-liquid waxes).

[0064] Examples of the synthetic lubricating oils include polybutene or hydrides thereof; poly- α -olefins such as 1-octene oligomer and 1-decene oligomer, or hydrides thereof; diesters such as ditridecyl glutarate, di-2-ethylhexyl adipate, diisodecyl adipate, ditridecyl adipate, and di-2-ethylhexyl sebacate; polyol esters such as trimethylolpropane caprylate, trimethylolpropane pelargonate, pentaerythritol-2-ethylhexanoate, and pentaerythritol pelargonate; aromatic synthetic oils such as alkylnaphthalenes and alkylbenzenes, and mixtures thereof.

[0065] The kinematic viscosity at 100°C of the lubricating base oil is preferably 2.5 to 10.0 mm²/s, more preferably 3.0 to 8.0 mm²/s, and further preferably 3.5 to 6.0 mm²/s. Moreover, the viscosity index of the lubricating base oil is preferably 90 to 165, more preferably 100 to 155, and further preferably 120 to 150.

[0066] The saturated component of the lubricating base oil by chromatography analysis is preferably 80% or more, more preferably 85% or more, further preferably 90% or more, and most preferably 95% or more so as to make it easy to exert an effect of additives such as the poly(meth)acrylate-based viscosity index improver according to the first embodiment.

[0067] The content of the poly(meth)acrylate-based viscosity index improver according to the first embodiment is preferably 0.1 to 20.0 mass%, more preferably 0.5 to 15.0 mass%, and further preferably 1.0 to 10.0 mass% based on the total amount of the lubricating composition. When the content is the above-described lower limit or more, a sufficient effect of addition becomes easy to be obtained, and on the other hand, when the content is the above-described upper limit or less, shear stability increases and fuel consumption sustainability is improved.

[0068] The kinematic viscosity at 100°C of the lubricating composition is preferably 3.0 to 16.3 mm²/s, more preferably 3.5 to 12.5 mm²/s, and further preferably 4.0 to 9.3 mm²/s. When the kinematic viscosity at 100°C is the above-described lower limit or more, a lubricating property becomes easy to be ensured, and on the other hand, when the kinematic viscosity at 100°C is the above-described upper limit or less, a fuel saving property is further improved. It is to be noted that the kinematic viscosity at 100°C in the present invention means a kinematic viscosity at 100°C defined by JIS K-2283-1993.

[0069] The viscosity index of the lubricating composition is preferably 150 to 250, more preferably 160 to 240, and further preferably 170 to 230. When the viscosity index is the above-described lower limit or more, a fuel saving property can be further improved, and moreover, the low-temperature viscosity becomes easy to be lowered while maintaining the HTHS viscosity. On the other hand, when the viscosity index is the above-described upper limit or less, low-temperature fluidity, solubility of additives, and compatibility with a sealing material can be ensured. It is to be noted that the viscosity index in the present invention means a viscosity index defined by JIS K 2283-1993.

[0070] The HTHS viscosity at 150°C of the lubricating composition is preferably 1.7 mPa·s or more, more preferably 2.0 mPa·s or more, further preferably 2.3 mPa·s or more, and most preferably 2.6 mPa·s or more. When the HTHS viscosity at 150°C is the above-described lower limit or more, evaporation of the lubricating composition can be suppressed, and a lubricating property can be ensured. Moreover, the HTHS viscosity at 100°C of the lubricating composition is preferably 5.2 mPa·s or less, more preferably 5.1 mPa·s or less, and further preferably 5.0 mPa·s or less. When the HTHS viscosity at 100°C is the above-described upper limit or less, a higher fuel saving property can be obtained. It is to be noted that the HTHS viscosity at 150°C or 100°C in the present invention means a high temperature high shear viscosity at 150°C or 100°C defined by ASTM D-4683.

[0071] The viscosity index improver according to the first embodiment, the lubricating oil additive according to the second embodiment, and the lubricating composition according to the third embodiment, which are described above, can be used in a wide range of fields such as lubricating oils for an internal combustion engine and drive system lubricating oils, and in particular, are useful in the field of lubricating oils for an internal combustion engine. Fuel of the internal combustion engine in this case may be either gasoline or diesel fuel.

Examples

[0072] Hereinafter, the present invention will be described in further detail with reference to Examples.

[Example 1-1]

[0073] A poly(meth)acrylate-based viscosity index improver was synthesized in the following condition (designated as "Synthesis Condition 1-1").

[0074] 12 g of methyl methacrylate (compound in which both R¹ and R² in the formula (3) are methyl groups, and

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hereinafter, designated as "C1-MA"), 18 g of stearyl methacrylate (compound in which R¹ and R² in the formula (3) are a methyl group and a stearyl group (straight-chain alkyl group having 18 carbon atoms), respectively, and hereinafter, designated as "C18-MA"), 0.030 g of cumyl dithiobenzoic acid (CDTBA), and 30 g of a highly-refined mineral oil as a solvent were charged into a 300 ml five-neck separable flask fitted with an anchor-type metal stirring blade (with vacuum seal), a Dimroth condenser, a three-way cock for introducing nitrogen, and a sample inlet, and a homogeneous solution was obtained under stirring. The solution was cooled to 0°C on an ice bath, and vacuum deaeration/nitrogen purge of a reaction system was carried out 5 times using a diaphragm pump. Furthermore, from the sample inlet, as a radical initiator, 0.052 g of azobisisobutyronitrile (AIBN) was charged under nitrogen flow, and then, polymerization was carried out for 12 hours at the solution temperature of 110°C under a nitrogen atmosphere to obtain a solution containing a poly(meth)acrylate-based viscosity index improver.

[0075] For the obtained poly(meth)acrylate-based viscosity index improver, the weight-average molecular weight Mw and the number average molecular weight Mn were measured by GPC analysis. As a result, the weight-average molecular weight Mw was 230000, the number average molecular weight Mn was 152000, and the Mw/Mn was 1.51. The procedure of the GPC analysis is as follows.

[0076] A solution whose sample concentration is 2 mass% was prepared by dilution using tetrahydrofuran as a solvent. The sample solution was analyzed using GPC equipment (Waters Alliance2695). The analysis was carried out at the flow rate of the solvent of 1 ml/min, by using a column whose analyzable molecular weight is 10000 to 256000, and a refractive index as a detector. It is to be noted that the relationship between the column retention time and the molecular weight was determined using a polystyrene standard whose molecular weight is definite and the molecular weight was determined from the obtained retention time based on the calibration curve which was separately made.

[Example 1-2]

[0077] A poly(meth)acrylate-based viscosity index improver was synthesized in the following condition (designated as "Synthesis Condition 1-2").

[0078] 12 g of methyl methacrylate (C1-MA), 18 g of stearyl methacrylate (C18-MA), 0.031 g of cumyl dithiobenzoic acid (CDTBA), and 30 g of a highly-refined mineral oil as a solvent were charged into a 300 ml five-neck separable flask fitted with an anchor-type metal stirring blade (with vacuum seal), a Dimroth condenser, a three-way cock for introducing nitrogen, and a sample inlet, and a homogeneous solution was obtained under stirring. The solution was cooled to 0°C with an ice bath, and vacuum deaeration/nitrogen purge of a reaction system was carried out 5 times using a diaphragm pump. Furthermore, from the sample inlet, as a radical initiator, 0.051 g of azobisisobutyronitrile (AIBN) was charged under nitrogen flow, and then, polymerization was carried out for 12 hours at the solution temperature of 100°C under a nitrogen atmosphere to obtain a solution containing a poly(meth)acrylate-based viscosity index improver.

[0079] For the obtained poly(meth)acrylate-based viscosity index improver, GPC analysis was carried out in the same manner as Example 1-1, and as a result, the weight-average molecular weight Mw was 220000, the number average molecular weight Mn was 167000, and the Mw/Mn was 1.32.

[Example 1-3]

[0080] A poly(meth)acrylate-based viscosity index improver was synthesized in the following condition (designated as "Synthesis Condition 1-3").

[0081] 12 g of methyl methacrylate (C1-MA), 18 g of stearyl methacrylate (C18-MA), 0.033 g of cumyl dithiobenzoic acid (CDTBA), and 30 g of a highly-refined mineral oil as a solvent were charged into a 300 ml five-neck separable flask fitted with an anchor-type metal stirring blade (with vacuum seal), a Dimroth condenser, a three-way cock for introducing nitrogen, and a sample inlet, and a homogeneous solution was obtained under stirring. The solution was cooled to 0°C on an ice bath, and vacuum deaeration/nitrogen purge of a reaction system was carried out 5 times using a diaphragm pump. Furthermore, from the sample inlet, as a radical initiator, 0.055 g of azobisisobutyronitrile (AIBN) was charged under nitrogen flow, and then, polymerization was carried out for 12 hours at the solution temperature of 90°C under a nitrogen atmosphere to obtain a solution containing a poly(meth)acrylate-based viscosity index improver.

[0082] For the obtained poly(meth)acrylate-based viscosity index improver, GPC analysis was carried out in the same manner as Example 1-1, and as a result, the weight-average molecular weight Mw was 210000, the number average molecular weight Mn was 186000, and the Mw/Mn was 1.13.

[Comparative Example 1-1]

[0083] A poly(meth)acrylate-based viscosity index improver was synthesized in the following condition (designated as "Synthesis Condition 1-4").

[0084] 30 g of a highly-refined mineral oil as a solvent was charged into a 300 ml four-neck reaction flask fitted with

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a stirring blade (with vacuum seal), a Dimroth condenser, a three-way cock for introducing nitrogen, and a dropping funnel for introducing a sample, and it was stirred for 1 hour in an oil bath at 85°C while carrying out nitrogen purge. A raw material in which 12 g of methyl methacrylate (C1-MA) and 18 g of stearyl methacrylate (C18-MA) as raw material monomers, and 0.12 g of azobisisobutyronitrile (AIBN) as a radical initiator are mixed was charged into the dropping

funnel for introducing a sample, and the raw material was dropped in the reaction flask for 70 minutes. After that, polymerization was carried out for 8 hours at 85°C under nitrogen flow while maintaining stirring to obtain a solution containing a poly(meth)acrylate-based viscosity index improver. After that, unreacted monomers were removed from the above-described solution by carrying out vacuum distillation for 3 hours at 130°C and 1 mmHg.

[0085] For the obtained poly(meth)acrylate-based viscosity index improver, GPC analysis was carried out in the same manner as Example 1-1, and as a result, the weight-average molecular weight Mw was 260000, the number average molecular weight Mn was 158000, and the Mw/Mn was 1.65.

[Examples 1-4 to 1-15, Comparative Examples 1-2 to 1-4]

[0086] A poly(meth)acrylate-based viscosity index improver was synthesized in the same manner as any of the above-described Synthesis Conditions 1-1 to 1-4 other than changing the amount of the raw material blended as shown in Tables 1, 3, 5, and 7. It is to be noted that, in Tables, C12-MA represents a compound in which R¹ and R² in the formula (3) are a methyl group and a dodecyl group (straight-chain alkyl group having 12 carbon atoms), respectively, and moreover, C22-MA represents a compound in which R¹ and R² in the formula (3) are a methyl group and a docosanyl group (straight-chain alkyl group having 22 carbon atoms), respectively. Mw, Mn, and Mw/Mn of the obtained poly(meth)acrylate-based viscosity index improver are shown in Tables 2, 4, 6, and 8.

<Preparation of Lubricating composition>

[0087] The poly(meth)acrylate-based viscosity index improver obtained in each of Examples 1-1 to 1-15 and Comparative Examples 1-1 to 1-4, performance additives including a metallic (calcium sulfonate) cleaner, an ashless dispersant (succinimide), a friction modifier (glycerin monooleate), and a wear inhibitor (zinc dithiophosphate), and a highly-refined mineral oil (Group III base oil, kinematic viscosity at 100°C: 4.2 mm²/s, VI: 125) were blended at a ratio shown in Tables 2, 4, 6, and 8 to prepare a lubricating composition.

<Evaluation of Lubricating composition>

[0088] For each lubricating composition of Examples 1-1 to 1-15 and Comparative Examples 1-1 to 1-4, the kinematic viscosity at 100°C, the viscosity index, and the HTHS viscosities at 100°C and 150°C were respectively measured by methods in conformity with the following. The results are shown in Tables 2, 4, 6, and 8.

kinematic viscosity: JIS K-2283-1993

viscosity index: JIS K-2283-1993

HTHS viscosity: ASTM D-4683

[Table 1]

	Example 1-1	Example 1-2	Example 1-3	Example 1-4	Example 1-5
Amount Blended (g)					
C1-MA	12.0	12.0	12.0	12.0	12.0
C18-MA	18.0	18.0	18.0	18.0	18.0
C12-MA	-	-	-	-	-
C22-MA	-	-	-	-	-
CDTBA	0.030	0.031	0.033	0.078	0.077
AIBN	0.052	0.051	0.055	0.013	0.013
Synthesis Condition	1-1	1-2	1-3	1-3	1-1
Yield (%)	95.2	94.3	94.5	90.8	98.8

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[Table 2]

	Example 1-1	Example 1-2	Example 1-3	Example 1-4	Example 1-5
Alkyl(meth)acrylate Blending Ratio (mass%)					
C1-MA	40	40	40	40	40
C18-MA	60	60	60	60	60
C12-MA	-	-	-	-	-
C22-MA	-	-	-	-	-
Mw	230,000	220,000	210,000	110,000	108,000
Mn	152,000	167,000	186,000	102,000	70,000
Mw/Mn	1.51	1.32	1.13	1.03	1.55
Blending Proportion in Lubricating composition (mass%)					
Base Oil	Balance	Balance	Balance	Balance	Balance
Performance Additive	9.5	9.5	9.5	9.5	9.5
Viscosity Index Improver	2.8	2.	2.7	2.8	3.3
Kinematic Viscosity (mm ² /s)/ 100°C	7.29	7.21	7.18	7.85	7.53
Viscosity Index	197	195	194	198	199
HTHS VISCOSITY (mPa·s)					
150°C	2.60	2.60	2.60	2.60	2.60
100°C	4.98	4.89	4.80	4.88	4.96

[Table 3]

	Example 1-6	Example 1-7	Example 1-8	Example 1-9	Example 1-10
Amount Blended (g)					
C1-MA	9.0	13.5	9.0	6.0	13.5
C18-MA	21.0	16.5	9.0	9.0	9.0
C12-MA	-	-	15.0	15.0	7.5
C22-MA	-	-	-	-	-
CDTBA	0.079	0.028	0.079	0.078	0.021
AIBN	0.014	0.005	0.013	0.012	0.003
Synthesis Condition	1-3	1-1	1-1	1-3	1-1
Yield (%)	95.3	95.0	93.8	94.8	95.2

[Table 4]

	Example 1-6	Example 1-7	Example 1-8	Example 1-9	Example 1-10
Alkyl(meth)acrylate Blending Ratio (mass%)					
C1-MA	20	45	20	20	45
C18-MA	80	55	30	30	30
C12-MA	-	-	50	50	25
C22-MA	-	-	-	-	-
Mw	105,000	250,000	106,000	110,000	280,000
Mn	94,000	185,000	69,000	100,000	190,000
Mw/Mn	1.12	1.04	1.54	1.10	1.46

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(continued)

	Example 1-6	Example 1-7	Example 1-8	Example 1-9	Example 1-10
5	Blending Proportion in Lubricating composition (mass%)				
	Balance	Balance	Balance	Balance	Balance
	9.5	9.5	9.5	9.5	9.5
10	3.2	2.5	2.4	2.9	2.7
	Kinematic Viscosity (mm ² /s)/100°C				
	7.62	7.14	7.62	7.53	7.47
	Viscosity Index				
	198	194	191	198	205
15	HTHS VISCOSITY (mPa·s)				
	150°C				
	2.60	2.60	2.60	2.60	2.60
	100°C				
	4.96	4.76	5.04	4.99	4.86

[Table 5]

	Example 1-11	Example 1-12	Example 1-13	Example 1-14	Example 1-15
20	Amount Blended (g)				
	12.0	12.0	12.0	13.5	13.5
25	9.0	9.0	9.0	16.5	7.5
	-	4.5	9.0	-	4.5
	9.0	4.5	-	-	4.5
	0.031	0.039	0.031	0.029	0.042
30	0.005	0.007	0.005	0.005	0.007
	Synthesis Condition				
	1-2	1-3	1-3	1-3	1-3
	Yield (%)				
	95.2	94.3	94.5	90.8	97.2

[Table 6]

	Example 1-11	Example 1-12	Example 1-13	Example 1-14	Example 1-15
40	Alkyl(meth)acrylate Blending Ratio (mass%)				
	40	40	40	45	45
	30	30	30	55	25
	-	15	30	-	15
45	30	15	-	-	15
	Mw				
	230,000	198,000	228,000	250,000	198,000
	Mn				
	174,000	175,000	211,000	247,000	187,000
	Mw/Mn				
	1.32	1.13	1.08	1.01	1.06
50	Blending Proportion in Lubricating composition (mass%)				
	Balance	Balance	Balance	Balance	Balance
	9.5	9.5	9.5	9.5	9.5
55	2.8	3.3	3.2	2.5	2.9
	Kinematic Viscosity (mm ² /s)/100°C				
	7.35	7.53	7.62	7.14	7.41
	Viscosity Index				
	198	199	198	194	194

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(continued)

	Example 1-11	Example 1-12	Example 1-13	Example 1-14	Example 1-15
HTHS VISCOSITY (mPa·s)					
150°C	2.60	2.60	2.60	2.60	2.60
100°C	4.92	4.89	4.82	4.80	5.18

[Table 7]

	Comparative Example 1-1	Comparative Example 1-2	Comparative Example 1-3	Comparative Example 1-4
Amount Blended (g)				
C1-MA	12.0	12.0	9.0	9.0
C18-MA	18.0	18.0	9.0	9.0
C12-MA	-		12.0	12.0
C22-MA	-		-	-
CDTBA	-	0.085	0.029	-
AIBN	0.010	0.013	0.010	0.091
Synthesis Condition	1-4	1-1	1-1	1-4
Yield (%)	95.1	98.9	96.2	99.5

[Table 8]

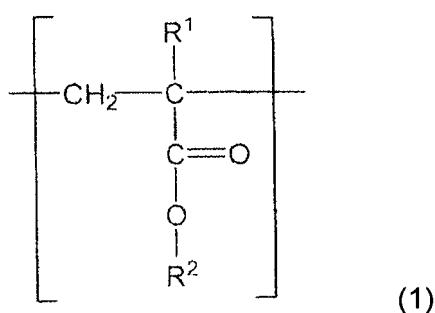
	Comparative Example 1-1	Comparative Example 1-2	Comparative Example 1-3	Comparative Example 1-4
Alkyl(meth)acrylate Blending Ratio (mass%)				
C1-MA	45	45	30	30
C18-MA	55	55	30	30
C12-MA	-	-	40	40
C22-MA	-	-	-	-
Mw	260,000	98,000	240,000	240,000
Mn	158,000	90,000	148,000	148,000
Mw/Mn	1.65	1.09	1.62	1.62
Blending Proportion in Lubricating composition (mass%)				
Base Oil	Balance	Balance	Balance	Balance
Performance Additive	9.5	9.5	9.5	9.5
Viscosity Index Improver	2.2	3.8	2.9	2.9
Kinematic Viscosity (mm ² /s)/100°C	7.28	7.13	7.39	7.39
Viscosity Index	195	189	215	215
HTHS VISCOSITY (mPa·s)				
150°C	2.60	2.60	2.60	2.60

(continued)

	Comparative Example 1-1	Comparative Example 1-2	Comparative Example 1-3	Comparative Example 1-4
100°C	5.28	5.45	5.48	5.45

Claims

1. A poly(meth)acrylate-based viscosity index improver consisting of a polymer chain comprising a structural unit represented by the following formula (1), wherein a weight-average molecular weight M_w is 100000 or more and 500000 or less, and a ratio of the weight-average molecular weight M_w to a number average molecular weight M_n , M_w/M_n , is 1.6 or less

[Chemical Formula 1]

wherein R^1 represents hydrogen or a methyl group, and R^2 represents a C1 to C36 alkyl group, and wherein the polymer chain contains 20 to 45 mass% or more of the structural unit in which R^2 is a methyl group, and wherein the polymer chain contains 20 mass% or more of the structural unit in which R^2 is an alkyl group having 18 or more carbon atoms, based on the total amount of the structural units contained in the polymer chain.

2. A lubricating oil additive comprising the poly(meth)acrylate-based viscosity index improver according to claim 1.
3. A lubricating composition comprising:
- a lubricating base oil; and
 - the poly(meth)acrylate-based viscosity index improver according to claim 1.

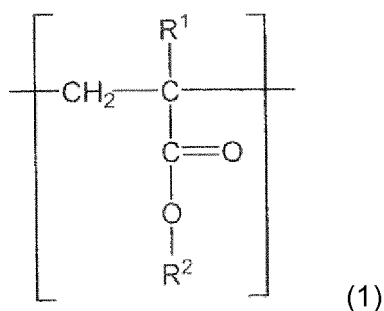
Patentansprüche

1. Viskositätsindexverbesserer auf Poly(meth)acrylat-Basis, bestehend aus einer Polymerkette, die eine Struktureinheit umfasst, die durch die folgende Formel (1) wiedergegeben ist, wobei ein Gewichtsmittel des Molekulargewichts M_w 100.000 oder mehr und 500.000 oder weniger beträgt, und ein Verhältnis des Gewichtsmittels des Molekulargewichts M_w zu einem Zahlenmittel des Molekulargewichts M_n , M_w/M_n , 1,6 oder weniger beträgt

[Chemische Formel 1]

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15 wobei R¹ Wasserstoff oder eine Methylgruppe bedeutet, und R² eine C₁- bis C₃₆-Alkylgruppe bedeutet, und wobei die Polymerkette 20 bis 45 Masse-% oder mehr der Struktureinheit enthält, in welcher R² eine Methylgruppe ist, und wobei die Polymerkette 20 Masse-% oder mehr der Struktureinheit enthält, in welcher R² eine Alkylgruppe mit 18 oder mehr Kohlenstoffatomen ist, bezogen auf die Gesamtmenge der Struktureinheiten, die in der Polymerkette enthalten sind.

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2. Schmieröladditiv, umfassend den Viskositätsindexverbesserer auf Poly(meth)acrylat-Basis gemäß Anspruch 1.

3. Schmiermittelzusammensetzung, umfassend:

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ein Schmierbasisöl; und
den Viskositätsindexverbesserer auf Poly(meth)acrylat-Basis gemäß Anspruch 1.

Revendications

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1. Agent améliorant l'indice de viscosité à base de poly(méth)acrylate constitué d'une chaîne polymère comprenant un motif structural représenté par la formule (1) suivante, où une masse moléculaire moyenne en poids Mw est de 100 000 ou plus et 500 000 ou moins, et un rapport de la masse moléculaire moyenne en poids Mw sur une masse moléculaire moyenne en nombre Mn, Mw/Mn, est de 1,6 ou moins

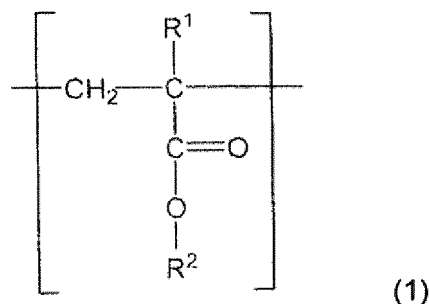
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[Formule chimique 1]

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où R¹ représente l'hydrogène ou un groupe méthyle et R² représente un groupe alkyle en C1 à C36, et où la chaîne polymère contient de 20 à 45 % en masse ou plus du motif structural dans lequel R² est un groupe méthyle, et où la chaîne polymère contient 20 % en masse ou plus du motif structural dans lequel R² est un groupe alkyle ayant 18 atomes de carbone ou plus, sur la base de la quantité totale des motifs structuraux présents dans la chaîne polymère.

2. Additif pour huile lubrifiante comprenant l'agent améliorant l'indice de viscosité à base de poly(méth)acrylate selon

la revendication 1.

3. Composition lubrifiante comprenant :

- 5 une huile de base lubrifiante ; et
 l'agent améliorant l'indice de viscosité à base de poly(méth)acrylate selon la revendication 1.

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REFERENCES CITED IN THE DESCRIPTION

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