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(54) LONG-LIFE FUEL-SAVING ENGINE OIL COMPOSITION

LANGLEBIGE KRAFTSTOFFSPARENDE MOTORENÖLZUSAMMENSETZUNG

COMPOSITION D'HUILE POUR MOTEUR A LONGUE DUREE DE VIE ET PERMETTANT
D'ECONOMISER DU CARBURANT

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EP 1 878 784 B1

Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a long-life fuel-saving engine oil composition which exhibits excellent high-temperature oxidation stability and maintain low friction property for a long time.

BACKGROUND ART

10 **[0002]** In recent years, there has been an increasing demand for improving the fuel mileage of automobiles and suppressing emission of CO₂ in order to prevent global warming. It is important to improve the efficiency of engines in order to improve the fuel efficiency of automobiles. Therefore, lean-burn technology and direct-injection technology have been employed for gasoline engines. On the other hand, since a reduction in friction of engines can contribute to a reduction in fuel consumption, use of a low-friction material for sliding parts and use of a fuel-saving engine oil have been attempted.

15 **[0003]** In order to prepare a fuel-saving engine oil, it is known that it is effective to reduce the viscosity of engine oil to low viscosity of 5W-20 or 0W-20 specified in the Society of Automotive Engineers (SAE) J300 viscosity classification and to simultaneously blend an organomolybdenum friction modifier such as molybdenum dithiocarbamate (MoDTC) as an additive (friction modifier, hereinafter may be abbreviated as "FM") which reduces friction (see Non-patent Document 1).

20 **[0004]** Since a lean-burn engine or a direct-injection engine exhibits high efficiency as compared with conventional engines, the combustion temperature tends to increase and the piston and the like are exposed to a higher temperature. Therefore, it is necessary to improve the high-temperature oxidation stability of engine oil. Specifically, a fuel-saving engine oil in the future will be required to exhibit more excellent high-temperature oxidation stability as compared with conventional engine oil.

25 On the other hand, MoDTC deteriorates during use and disappears in the oil. As a result, the fuel-saving effect of MoDTC also deteriorates together with duration of use. Therefore, it is an important subject to improve the sustainability of the fuel-saving effect.

30 [Patent Document 1] JP-A-10-17883

[Non-patent Document 1] K. Hoshino et al., Fuel Efficiency of SAE 5W-20 Friction Modified Gasoline Engine Oil, SAE Technical Paper 982506 (1998)

DISCLOSURE OF THE INVENTION

35 [Problems to be Solved by the Invention]

[0005] In view of the above situation, an object of the present invention is to provide an engine oil which exhibits excellent high-temperature oxidation stability and excellent fuel-saving sustainability.

40 [Means for Solving the Problems]

[0006] The inventors of the present invention have conducted extensive studies in order to achieve the above object. As a result, the inventors have found that a composition containing a mineral oil and/or a synthetic base oil and a specific antioxidant in a specific ratio and containing MoDTC in a certain amount or more is useful as a long-life fuel-saving engine oil which exhibits an excellent high-temperature oxidation stability. This finding has led to the completion of the present invention.

45 **[0007]** Specifically, the present invention provides an engine oil composition comprising: a mineral oil and/or a synthetic base oil; an amine antioxidant and a phenolic antioxidant in an amount of 1.2 mass % or more in total and in the ratio (mass: N/O) of the nitrogen content (N) of the amine antioxidant to the oxygen content (O) of the phenolic antioxidant being 0.20 to 0.50; and molybdenum dithiocarbamate (MoDTC) in an amount of 0.055 mass % or more as molybdenum element (Mo).

50 Particularly, it is preferable that the composition comprises the amine antioxidant and the phenolic antioxidant in an amount of 1.5 mass % or more in total and in the ratio (mass: N/O) of the nitrogen content (N) of the amine antioxidant to the oxygen content (O) of the phenolic antioxidant being 0.20 to 0.35, and the molybdenum dithiocarbamate (MoDTC) in an amount of 0.055 mass % or more as molybdenum element (Mo).

The specific choices of amine antioxidant and phenolic antioxidant are set out in the claims and discussed below.

[Effect of the Invention]

[0008] The long-life fuel-saving engine oil composition according to the present invention having the above-described configuration exhibits excellent high-temperature oxidation stability, shows a small increase in viscosity even if after long period use, and maintains low friction for a long time. Therefore, the composition can be utilized for internal combustion engines such as a lean-burn gasoline engine and a direct-injection gasoline engine in particular. It exhibits a particular effect that the composition thus reduces fuel consumption and maintains this good mileage for a long time.

[Best Mode for Carrying out the Invention]

[0009] As the base oil used in the engine oil composition according to the present invention having the above-described configuration, the kinematic viscosity of the base oil at 100°C is preferably 3.5 to 5.0 mm²/s, and more preferably 4.0 to 4.5 mm²/s. The viscosity index of the base oil is preferably 110 to 160, and more preferably 120 to 140. As the mineral oil, a high-viscosity-index lubricant base oil having a viscosity index of 120 or more is desirable. A high-viscosity-index lubricant base oil having a viscosity index of 120 or more may be obtained by subjecting an oil produced by hydroisomerization of wax or hydrocracking of heavy oil to solvent dewaxing or hydrodewaxing. An example of these production methods is concretely described in detail below.

[0010] Hydroisomerization of wax may be carried out by causing wax having a boiling point of 300 to 600°C and containing 20 to 70 carbon atoms (e.g., slack wax obtained during solvent dewaxing of a mineral oil lubricant, or wax obtained by Fischer-Tropsch synthesis which synthesizes a liquid fuel from a hydrocarbon gas or the like) as a raw material to come in contact with a hydroisomerization catalyst (e.g., a catalyst in which at least one of the group 8 metals such as nickel and cobalt and the group 6A metals such as molybdenum and tungsten is supported on an alumina or silica-alumina support, a zeolite catalyst, or a catalyst in which platinum or the like is supported on a zeolite-containing support) under the hydrogen atmosphere of a hydrogen partial pressure of 5 to 14 MPa, at a temperature of 300 to 450°C, and a liquid hourly space velocity (LHSV) of 0.1 to 2 hr⁻¹. It is preferable that the conversion rate of the linear paraffin be 80% or more and the conversion rate to the light fraction be 40% or less.

[0011] Meanwhile, hydrocracking may be carried out by causing an atmospheric distillate, vacuum distillate, or bright stock having a boiling point of 300 to 600°C and optionally obtained through hydrodesulfurization and hydrodedenitrication to come in contact with a hydrocracking catalyst (e.g., catalyst in which at least one of the group 8 metals such as nickel and cobalt and the group 6A metals such as molybdenum and tungsten is supported on a silica-alumina carrier) under the hydrogen atmosphere of a hydrogen partial pressure of 7 to 14 MPa, at a temperature of 350 to 450°C, and a liquid hourly space velocity (LHSV) of 0.1 to 2 hr⁻¹. It is preferable that the decomposition rate (reduction rate (mass %) of fractions having a boiling point of 360°C or more in the product) be 40 to 90%.

[0012] A lubricant fraction is obtained by distilling off the light fraction from the oil obtained by the above hydroisomerization or hydrocracking. Since this fraction generally has a high pour point and high viscosity and does not have a sufficiently high viscosity index, wax is removed by dewaxing to obtain a lubricant base oil having a %Cp according to n-d-M analysis of 80% or more, a pour point of -10°C or less, and a viscosity index of 120 or more.

[0013] When removing the wax by solvent dewaxing, it is preferable to separate the light fraction by distillation using a precision distillation device so that the content of the fraction having a boiling point, determined by gas chromatography distillation, of 371°C or more and less than 491°C is 70 mass % or more in order to efficiently perform solvent dewaxing. The solvent dewaxing may be performed at a temperature of -15 to -40°C and a solvent/oil ratio of 2/1 to 4/1 using methyl ethyl ketone/toluene (volume ratio: 1/1) as a dewaxing solvent.

[0014] When removing the wax by hydrodewaxing, it is preferable that the light fraction is distilled off to such an extent that hydrodewaxing is not disturbed, and the light fraction is separated by distillation using a precision distillation device so that the content of the fraction having a boiling point, determined by gas chromatography distillation, of 371°C or more and less than 491°C is 70 mass % or more after hydrodewaxing from the viewpoint of efficiency. Hydrodewaxing may be carried out by causing the fraction to come in contact with a zeolite catalyst under the hydrogen atmosphere of a hydrogen partial pressure of 3 to 15 MPa, at a temperature of 320 to 430°C, and a liquid hourly space velocity (LHSV) of 0.2 to 4 hr⁻¹ so that the pour point of the resulting lubricant base oil is -10°C or less.

[0015] A lubricant base oil having a viscosity index of 120 or more can be obtained using the above method. The lubricant base oil may be optionally subjected to solvent refining or hydro treating.

[0016] As the synthetic oil, an alpha-olefin oligomer, a diester synthesized from a dibasic acid such as adipic acid and a monohydric alcohol, a polyol ester synthesized from a polyhydric alcohol such as neopentyl glycol, trimethylolpropane, or pentaerythritol and a monobasic acid, a mixture thereof, and the like can be given.

Furthermore, a mixed oil obtained by blending an appropriate mineral oil with a synthetic oil may also be used as the base oil for the engine oil of the present invention.

[0017] MoDTC used in the engine oil according to the present invention is shown by the following general formula (1).



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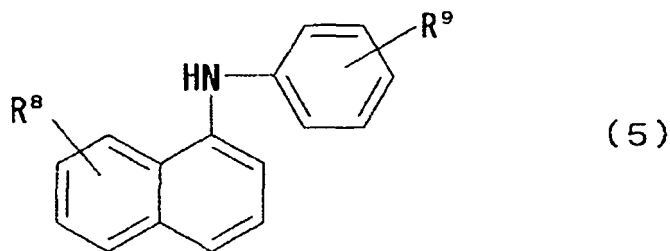
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group may be the same or different. A linear or branched alkyl group ranging from a butyl group to a nonyl group is more preferable.

[0021]



wherein R^8 and R^9 represent hydrocarbon groups having 3 to 20 carbon atoms. Although the formula (5) shows that the naphthyl group and the phenyl group are replaced with a substituent, at least one of these groups may be replaced with one or more substituents, or each group may be replaced with one or more substituents. When two or more R^8 s and R^9 s exist, the R^8 s and R^9 s may be the same or different each other. R^8 and R^9 are preferably alkyl groups having 6 to 12 carbon atoms, and particularly preferably the compound has either the naphthyl group or the phenyl group replaced with a substituent of a linear or branched octyl group to nonyl group.

As the amine antioxidant, the compounds shown by the general formulas (4) and (5) may be used in combination.

[0022] The phenolic antioxidant and the amine antioxidant are preferably blended so that the total content is 1.5 mass % or more and the mass ratio (N/O) of the nitrogen content (N) of the amine antioxidant and the oxygen content (O) of the phenolic antioxidant is 0.20 to 0.35, and particularly preferably 0.25 to 0.30. The total content of the antioxidant is preferably 1.5 mass % or more, and particularly preferably 1.5 to 3 mass %. If the total content of the antioxidant is less than 1.5 mass %, the desired high-temperature oxidation stability (e.g., a viscosity increase rate in Sequence III G test of 150% or less, and particularly preferably 0 to 100%) may not be obtained. If the ratio of the nitrogen content of the amine antioxidant and the oxygen content of the phenolic antioxidant is less than 0.20, the desired high-temperature oxidation stability may not be obtained. If the ratio of the nitrogen content of the amine antioxidant and the oxygen content of the phenolic antioxidant exceeds 0.35, the desired low-friction life due to MoDTC may not be obtained.

[0023] The engine oil according to the present invention may be optionally added with additives such as detergents such as zinc alkyldithiophosphate (ZnDTP), sulfonates, phenates, and salicylates of metals such as Ca, Mg, Ba, and Na, ashless dispersants such as alkenylsuccinimide, viscosity index improvers, pour-point depressants, metal deactivators, rust preventives, and anti-foaming agents.

[Examples]

[0024] The present invention will be described below in more detail by way of examples.

As the base oil, a mineral base oil (kinematic viscosity: 20.3 mm²/s (40°C), 4.34 mm²/s (100°C); viscosity index: 124) obtained by subjecting an oil produced by hydrocracking heavy oil to hydrodewaxing was used.

[0025] A phenolic antioxidant A, an amine antioxidant B, MoDTC, and another additive described below were blended to the base oil in a ratio shown in Table 1 to prepare engine oils of Example 1 and Comparative Examples 1 to 3. Table 1 also shows the ratio (mass: N/O) of the nitrogen content (N) of the amine antioxidant to the oxygen content (O) of the phenolic antioxidant and the Mo content. The other additive was an additive mixture containing zinc alkyldithiophosphate (ZnDTP), calcium sulfonate, alkenylsuccinimide, a viscosity index improver, a pour-point depressant, and an anti-foaming agent. The additive was added in an equal amount in the example and the comparative examples.

[0026] As the phenolic antioxidant A, a phenolic antioxidant (oxygen content: 12.3 mass %) shown by the general formula (2) in which the substituent R^5 was an octyl group was used.

As the amine oxidant B, an amine antioxidant (nitrogen content: 4.5 mass %) which is a reaction product of N-phenylbenzencamine and 2,4,4-trimethylpentene was used.

As the MoDTC, a compound shown by the general formula (1) in which R^1 to R^4 were a mixture of a 2-ethylhexyl group and an isotridecyl group and the oxygen atom/sulfur atom ratio was 1/1 was used.

[0027]

EP 1 878 784 B1

[Table 1]

				Example	Comparative example			
				1	1	2	3	
Base oil				Mass %	84.06	84.71	83.76	84.45
Additive				Mass %	15.94	15.29	16.24	15.55
	Antioxidant			Mass %	1.75	1.1	2.05	1.75
		(A)phenolic		Mass %	1.0	1.1	0.8	1.0
		(B)amine		Mass %	0.75	-	1.25	0.75
	MoDTC			Mass %	1.44	1.44	1.44	1.05
			Molybdenum (Mo)	Mass %	0.065	0.065	0.065	0.047
	Other additives			Mass %	12.75	12.75	12.75	12.75
Ratio (N/O) of N-content in amine antioxidant to O-content in phenol antioxidant				(Mass)	0.27	0	0.58	0.27

[0028] The engine oils of the example and the comparative examples shown in Table 1 were subjected to a Sequence III G test to evaluate the engine oil performance. The test includes an item of evaluating high-temperature oxidation stability by means of the viscosity increase rate. A viscosity increase rate of 150% or less is defined as an acceptable level (see Suzuki, Latest Trend of Gasoline Engine Oil Standard, Monthly Tribology, 2003. 5, page 17). Each engine oil subjected to the Sequence III G test for 100 hours was compared with the corresponding engine oil at the time of starting the engine test (0 hours) to determine the viscosity increase rate. The results are shown in Table 2.

[0029] The engine oils shown in Table 1 were subjected to an engine test (a bench durability test on chassis dynamometer) and an SRV friction test under the following conditions to determine the test time at which the friction coefficient of the engine oil became 0.070. Fuel-saving efficiency sustainability was evaluated in comparison with a standard oil (test time at which the friction coefficient became 0.070: 165 hours, driving distance corresponding to this time: 10,000 km). The results are shown in the bottom of Table 2 as low friction sustainable life (km).

Engine test conditions

[0030]

Engine: 2 liter straight six-cylinder gasoline engine
Oil pan capacity: 3.4 liter was reduced to 2 liter (the severity of the test was accelerated)
Oil temperature in the oil pan: 100°C
Test mode: AMA travel mode (repetition)
Oil sampling: every 24 hours (SRV friction test sample)

SRV friction test conditions

[0031]

Contact conditions: cylinder on block
Sliding conditions: load: 400N; frequency: 50 Hz; amplitude: 1.5 mm; and
temperature: 120°C

[0032] The test time at which the friction coefficient of the engine oil became 0.070 was determined by interpolating the sampling times of two samples sandwiched the friction coefficient of 0.070 of the sample (engine oil) sampled every 24 hours. The low friction sustainable life (driving distance, km) was determined based on the resulting test time at which the friction coefficient of the engine oil became 0.070, the test time (165 hours) at which the friction coefficient of the standard oil became 0.070, and the driving distance (10,000 km).

[0033]

[Table 2]

		Example	Comparative example		
		1	1	2	3
Viscosity increase rate in Sequence .. test	%	83	270	88	120
MoDTC Low-friction sustainable life	km	10000	11000	8000	7000

[0034] As is clear from the above results, the engine oil composition shown as an example blending the mineral oil and/or the synthetic base oil, the amine antioxidant and the phenolic antioxidant in an amount of 1.5 mass % or more in total and in the mass ratio (N/O) of the nitrogen content (N) of the amine antioxidant to the oxygen content (O) of the phenolic antioxidant being 0.20 to 0.35, and MoDTC in an amount of 0.055 mass % or more as Mo element content exhibited a low viscosity increase rate of the Sequence III G test of 83% to be anticipated excellent high-temperature oxidation stability. Further, since the MoDTC low friction sustainable life calculated from the SRV friction test of the oil used in the engine durability test was as large as 9000 km or more, it is known that the engine oil composition exhibited excellent fuel-saving sustainability.

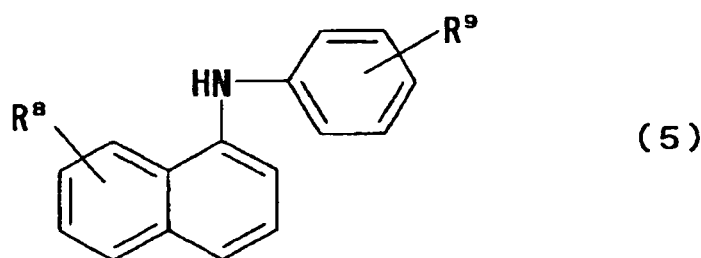
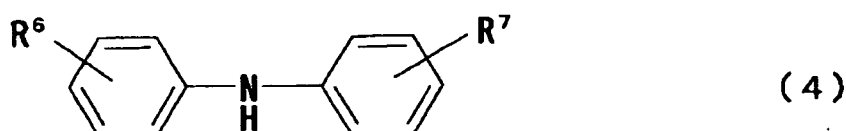
[0035] The engine oil composition of Comparative Example 1 to which only the phenolic antioxidant was added exhibited a long low friction sustainable life, but showed a very high viscosity increase rate and thus may exhibit inferior high-temperature oxidation stability. The engine oil composition of Comparative Example 2 in which the mass ratio of the nitrogen content of the amine antioxidant to the oxygen content of the phenolic antioxidant was high exhibited excellent high-temperature oxidation stability, but showed an inferior low friction life. The engine oil composition of Comparative Example 3 in which the amount of MoDTC was reduced showed a high viscosity increase rate and inferior high-temperature oxidation stability as compared with Example 1 and exhibited an inferior low friction life.

Claims

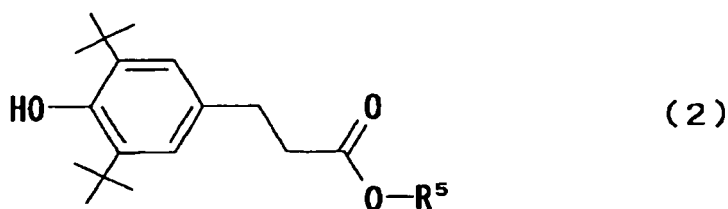
1. A long-life fuel-saving engine oil composition comprising:

a mineral oil and/or a synthetic base oil;

an amine antioxidant consisting of diphenylamine and/or phenyl-naphthylamine, as shown by the following general formula (4) or (5), wherein each of R⁶, R⁷, R⁸ and R⁹ may be hydrocarbon group having 3 to 20 carbon atoms



and a phenolic antioxidant shown by the following general formula (2):



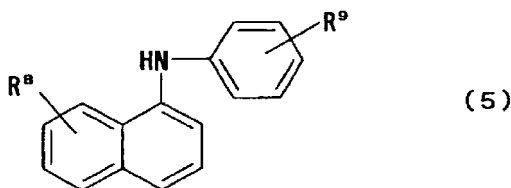
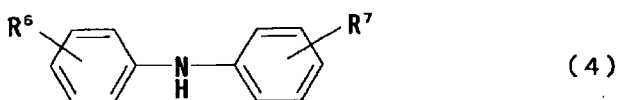
10 wherein R^5 is a hydrocarbon group having 3-20 carbon atoms,
in an amount of 1.2 mass % or more in total and in the ratio (mass: N/O) of the nitrogen content (N) of the amine
antioxidant to the oxygen content (O) of the phenolic antioxidant being 0.20 to 0.50; and
molybdenum dithiocarbamate (MoDTC) in an amount of 0.055 mass % or more as molybdenum element (Mo).

- 15 2. The composition according to claim 1, wherein the ratio (mass: N/O) of the nitrogen content (N) of the amine
antioxidant to the oxygen content (O) of the phenolic antioxidant is 0.20 to 0.35.
- 20 3. The composition according to claim 1, wherein the total content of the amine antioxidant and the phenolic antioxidant
is 1.5 mass % or more, the ratio (mass: N/O) of the nitrogen content (N) of the amine antioxidant to the oxygen
content (O) of the phenolic antioxidant is 0.20 to 0.35, and the content of molybdenum dithiocarbamate (MoDTC) is
0.055 mass % or more as molybdenum element (Mo).

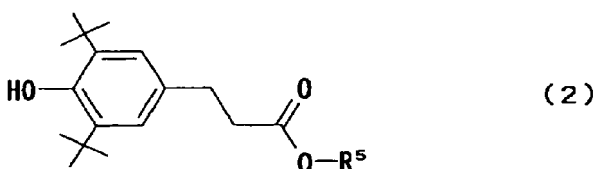
Patentansprüche

- 25 1. Langlebige, kraftstoffsparende Motorölzusammensetzung, die Folgendes umfasst:

ein Mineralöl und/oder ein synthetisches Basisöl;
ein Amin-Antioxidationsmittel, das aus Diphenylamin und/oder Phenyl-naphthylamin besteht, wie durch die fol-
gende allgemeine Formel (4) oder (5) dargestellt, wobei R^6 , R^7 , R^8 und R^9 jeweils eine Kohlenwasserstoffgruppe
30 mit 3 bis 20 Kohlenstoffatomen sein können



45 und ein phenolisches Antioxidationsmittel, dargestellt durch die folgende allgemeine Formel (2):



55 wobei R^5 eine Kohlenwasserstoffgruppe mit 3-20 Kohlenstoffatomen ist,
in einer Menge von insgesamt 1,2 Masse-% oder mehr und in einem Verhältnis (Masse: N/O) zwischen Stick-
stoffgehalt (N) des Amin-Antioxidationsmittels und Sauerstoffgehalt (O) des phenolischen Antioxidationsmittels
von 0,20 bis 0,50; und
Molybdändithiocarbamat (MoDTC) in einer Menge von 0,055 Masse-% oder mehr als Molybdänelement (Mo).

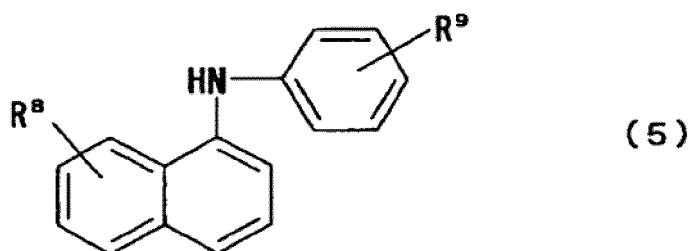
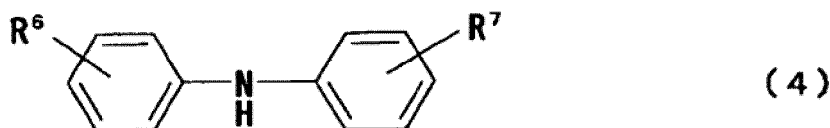
2. Zusammensetzung nach Anspruch 1, wobei das Verhältnis (Masse: N/O) zwischen Stickstoffgehalt (N) des Amin-Antioxidationsmittels und Sauerstoffgehalt (O) des phenolischen Antioxidationsmittels 0,20 bis 0,35 beträgt.
3. Zusammensetzung nach Anspruch 1, wobei der Gesamtgehalt des Amin-Antioxidationsmittels und des phenolischen Antioxidationsmittels 1,5 Masse-% oder mehr beträgt, das Verhältnis (Masse: N/O) zwischen Stickstoffgehalt (N) des Amin-Antioxidationsmittels und Sauerstoffgehalt (O) des phenolischen Antioxidationsmittels 0,20 bis 0,35 beträgt und der Gehalt an Molybdändithiocarbamat (MoDTC) als Molybdänelement (Mo) 0,055 Masse-% oder mehr beträgt.

Revendications

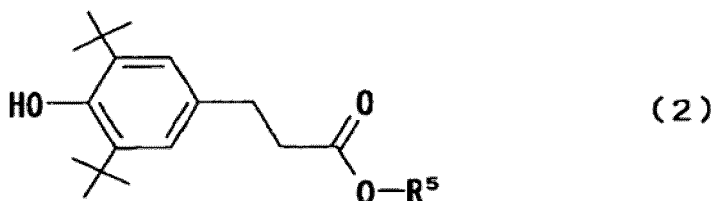
1. Composition d'huile pour moteur de longue durée économisant le carburant, comprenant :

une huile minérale et/ou une huile à base synthétique;

un antioxydant aminé consistant en diphenylamine et/ou en phénylnaphtylamine, comme il est illustré par la formule générale (4) ou (5) suivante, où chacun d'entre R⁶, R⁷, R⁸ et R⁹ peut être un groupe hydrocarbure ayant 3 à 20 atomes de carbone :



et un antioxydant phénolique illustré par la formule générale (2) suivante :



où R⁵ est un groupe hydrocarbure ayant 3-20 atomes de carbone, en une quantité de 1,2% en masse ou plus au total et selon le rapport (masse: N/O) de la teneur en azote (N) de l'antioxydant aminé à la teneur en oxygène (O) de l'antioxydant phénolique étant de 0,20 à 0,50; et du dithiocarbamate de molybdène (MoDTC) en une quantité de 0,055% en masse ou plus en tant qu'élément molybdène (Mo).

2. Composition selon la revendication 1, dans laquelle le rapport (masse: N/O) de la teneur en azote (N) de l'antioxydant aminé à la teneur en oxygène (O) de l'antioxydant phénolique est de 0,20 à 0,35.
3. Composition selon la revendication 1, dans laquelle la teneur totale en antioxydant aminé et en antioxydant phénolique est de 1,5% en masse ou plus, le rapport (masse: N/O) de la teneur en azote (N) de l'antioxydant aminé à la teneur en oxygène (O) de l'antioxydant phénolique est de 0,20 à 0,35 et la teneur en dithiocarbamate de molybdène (MoDTC) est de 0,055% en masse ou plus en tant qu'élément molybdène (Mo).

REFERENCES CITED IN THE DESCRIPTION

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