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(54) Lubricating oil composition

(57) The present invention provides a lubricating oil composition comprising a base oil made of synthetic oil and/or mineral oil, admixed with an antioxidant and a polymethacrylate having a phosphate ester added to a terminal position.

In a further aspect the present invention provides the use of the lubricating oil composition as a transmission oil, in particular as an automatic transmission oil.

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Description

[0001] The present invention relates to a lubricating oil composition, and in particular to a lubricating oil composition having excellent frictional properties and abrasion resistance, and also in which oxidative stability and heat stability are required.

[0002] A lubricating oil composition, in particular an automatic transmission oil, is a lubricating oil composition used for automatic transmission devices including torque converters, wet type clutches, gear bearing mechanisms and oil pressure mechanisms, wherein in order for the smooth operation of such automatic transmission devices, various well balanced functions are required as regards for example power conduction media, gear and other lubrication, heat transfer medium, maintenance of constant frictional properties and the like.

[0003] In such automatic transmission devices, it is necessary to regulate the lubricating oil viscosity and to regulate the friction in order to achieve reduced shock during gear change, and also to display a good torque transmission function and to reduce energy losses.

[0004] In order to carry out such regulation in lubricating oil, polymethacrylate system viscosity regulator (Kokai 2001-181664) and phosphate ester compounds (Kokai 3-39399, Kokai 7-268375 and Kokai 2000-63869) have been used.

[0005] Furthermore, recently, an additive has been proposed which rather than regulation by individual friction regulators and viscosity index improvers as in the prior art, achieves both a viscosity index improvement and friction regulation at the same time, however the oxidation stability is not satisfactory, and problems of thermostability at high temperature remain to be overcome.

[0006] The present inventors reached the conclusion that the problem of oxidation at high temperature was caused as a result of poor combination compatibility present with friction regulator and oxidation inhibitor combinations, and therefore tried to prepare lubricating oil compositions demonstrating small fluctuation change bands in kinetic viscosity and viscosity index even at high temperature oxidation, and which can be used at all times under similar conditions.

[0007] The present invention provides a lubricating oil composition comprising a base oil made of synthetic oil and/or mineral oil, admixed with an antioxidant and a polymethacrylate having a phosphate ester added to a terminal position

[0008] According to a further aspect, the present invention provides the use of the lubricating oil composition as a transmission oil, in particular as an automatic transmission oil.

[0009] The lubricating oil composition of the present invention is a lubricating oil composition with dramatically improved oxidation stability but with which the frictional properties are still maintained, and wherein the fluctuation ranges for the changes in kinetic viscosity and viscosity index are small even at high temperature oxidation. Moreover, various well balanced functions are demonstrated as regards for example power conduction media, gear and other lubrication, heat transfer media, the maintenance of constant frictional properties and the like. Therefore the present lubricant oil composition can be used at any time under similar conditions over long periods of time.

[0010] Moreover, the present lubricant oil composition can be used widely and effectively as a transmission device oil such as a gear oil for automobiles, AT (automatic transmission) oil, MT oil, CVT (constant velocity joint) oil and the like, a lubricating oil for internal combustion engines such as diesel engines, gasoline engines, gas engines and the like, and a lubricating oil in industry such as an industrial gear oil, oil pressure hydraulic oil, compressor oil and the like.

[0011] Mineral oils and synthetic oils which are usually used in lubricating oils can be used as the base oil of this lubricating oil composition, and in particular, oils belonging to Group 1, Group 2, Group 3, Group 4 and the like in the API (American Petroleum Institute) base oil categories can be used, alone or as mixtures thereof. A suitable content of elemental sulphur in the base oil used here is less than 700 ppm, and preferably less than 500 ppm. Moreover, a favourable density is 0.8-0.9. A favourable aromatic content is 5 % or less, and preferably 3 % or less.

[0012] Group 1 base oils, for example, include paraffinic mineral oil obtained by applying an appropriate combination of purification means, such as solvent refining, hydrofining, wax removal and the like, to the lubricating oil fraction obtained by distilling crude oil at atmospheric pressure. A good viscosity index is 80-120, preferably 95-120. The kinematic viscosity at 40°C is preferably 2-680 mm^2/s, more preferably 8-220 mm^2/s. Moreover, a preferred total sulfur content is less than 700 ppm, preferably less than 500 ppm. Also, a preferred total nitrogen content is less than 300 ppm, preferably less than 100 ppm. Furthermore, good such oils to use have an aniline point of 80-150°C, preferably 90-120°C.

[0013] Group 2 base oils, for example, include paraffinic mineral oil obtained by applying an appropriate combination of purification means, such as hydrogenolysis, wax removal and the like, to the lubricating oil fraction obtained by distilling crude oil at atmospheric pressure. A Group 2 oil purified by the hydrofining process of the Gulf Co. process and the like, whose total sulphur content is less than 10 ppm, and aromatic content is 5 % or less, is ideal for this invention. The viscosity of these base oils is not limited in particular, but a good viscosity index is 80-120, preferably 100-120. The kinematic viscosity at 40°C is preferably 2-680 mm^2/s and more preferably 8-220 mm^2/s. Moreover, a good total sulfur content is less than 300 ppm, preferably less than 200 ppm, more preferably less than 10 ppm. A good total nitrogen content is less than 10 ppm, preferably less than 1 ppm. Furthermore, good such oils to use have an aniline point of 80-150°C, preferably 100-135°C.

[0014] As far as Group 3 and Group 2+ base oils are concerned, for example paraffinic mineral oil obtained by high degree hydrogenolysis of the lubricating oil fraction obtained by distilling crude oil at atmospheric pressure, base oil refined by the ISODEWAX process wherein the wax produced in the dewaxing process is isomerised to isoparaffin and dewaxed, the base oil refined by the Mobil wax isomerization process are ideal. Oils which can be represented as 'synthetic oils' as decided by NAD (National Advertising Division) in charge of reviewing American advertising are included. The viscosity of these base oils is not limited in particular, but a good viscosity index is 95-160, preferably 100-160. The kinematic viscosity at 40°C is preferably 2-680 mm^2/s and more preferably 8-220 mm^2/s. Moreover, a good total sulphur content is 0-100 ppm, preferably less than 10 ppm. A good total nitrogen content is less than 10 ppm, preferably less than 1 ppm. Furthermore, good oils to use have an aniline point of 80-150°C, and preferably 100-135°C.

[0015] A GTL (Gas to Liquid) derived base oil which has been synthesised by the Fischer-Tropsch Method liquid fuel technique for (amongst others) natural gas, is ideal as the base oil of this invention, because compared with mineral oil base oil purified from crude oil, GTL has excellent oxidation stability because its sulphur content and aromatic content are extremely low and the proportion of paraffin structure is extremely high, and also GTL has an unusually low vaporization loss. The viscosity properties of a GTL base oil are not limited in particular, but usually, the viscosity index is 130-180, more preferably 135-180. Moreover, the kinematic viscosity at 40°C is preferably 2-680 mm^2/s, more preferably 5-120 mm^2/s. Moreover, usually, the total sulphur content is less than 10 ppm and the total nitrogen content is less than 1 ppm. As an example of such a GTL base oil commercial product, SHELL XHVI (Registered Trade Name) may be proposed.

[0016] As synthetic oil, for example, polyolefin, alkylbenzene, alkyl naphthalene, ester, polyoxyalkylene glycol, polyoxyalkylene glycol ester, polyoxyalkylene glycol ether, polyphenyl ether, dialkyl diphenyl ether, fluorine-containing compounds (perfluoropolyether, fluorinated polyolefin and the like), silicone oil and the like may be proposed.

[0017] Polymers of various olefins or their hydrogenated materials are included in the aforesaid polyolefins. Any olefin may be used as the olefin, for example, ethylene, propylene, butene, α-olefin of carbon number 5 or more and the like may be proposed. In the polyolefin production, a single species of the aforesaid olefins may be used, or a combination of two or more of the olefins may be used. In particular, the polyolefins known as poly α-olefins (PAO) are ideal, and these comprise Group 4 oils.

[0018] The viscosity of these synthetic base oils is not limited in particular, but the kinematic viscosity at 40°C is preferably 2-680 mm^2/s, more preferably 8-220 mm^2/s.

[0019] The content of the aforesaid base oil in the lubricating oil composition of this invention is not limited in particular, but is 60 wt % or more, preferably 80 wt % or more, more preferably 90 wt % or more, even more preferably 95 wt % or more, based on the total amount of the lubricating oil composition.

[0020] The aforesaid polymethacrylate having phosphate ester added to a terminal position preferably comprises an oil-soluble copolymer having a weight average molecular weight of 3,000-500,000 obtainable by copolymerising at least one species of a monomer represented by following general formula (1) and at least one species of a monomer represented by general formula (2) :

$$CH_2 =C(R^1)\text{-}Q\text{-}(Z\text{-}A^1)\ m\text{-}X \qquad (1)$$

$$CH_2 =C(R^3)\text{-}CO\text{-}(O\text{-}A^2)\ n\text{-}OR^4 \qquad (2)$$

wherein X is a polar group represented by formula -(O) a-P (=O)b $(OR^2)_2$, wherein either one of a and b is 1 and the other is 0 or 1, and the two R^2s are the same or different and denote H, a C1-24 alkyl group, a group represented by formula $-(A^1\text{-}Z)m\text{-}Q\text{-}C(R^1)=CH_2$ or a cation of formula M_1/f, wherein M is a cation with a valency of f (monovalent or divalent);

wherein R^1 is H or a methyl group, Z is -O- or -NH-, A^1 is a C2-18 alkylene group, m is 0 or 1 or an integer of 2-50, and Q is -CO- or a divalent hydrocarbon group of carbon number 1-22, and when m is 0, then Q is a divalent hydrocarbon group of carbon number 1-22; and

wherein R^3 is H or a methyl group, n is 0 or an integer of 1-30, A^2 is a C2-18 alkylene group and R^4 is an aliphatic hydrocarbon group of carbon number 1-32, an alicyclic hydrocarbon group of carbon number 5-7 or a C7-32 aralkyl group, and when present in plurality, A^1, Z, Q, R^1, m and A^2 each independently may be the same or different.

[0021] According to a preferred embodiment of the present invention, in the aforesaid formula (1), R^2 in X of formula -(O)a-P(=O)b $(OR^2)_2$, is a C1-24 alkyl group, preferably C1-4 alkyl group, and in particular a methyl or ethyl group.

[0022] When R^2 is $-(A^1\text{-}Z)m\text{-}Q\text{-}C(R^1)=CH_2$, the following may be proposed as Q, Z and A^1.

[0023] The divalent hydrocarbon group of carbon number 1-22 of Q may be a straight chain or branched aliphatic hydrocarbon group (for example, a methylene, ethylene, 1,2-propylene, 1,3-propylene, 1,2-butylene, 1,3-butylene, 1,4-butylene, 1,2-hexylene, 1,6-hexylene and 1,2-dodecylene group), an alicyclic hydrocarbon group (for example, a cyclohexylene, cyclohexyl methylene, cyclohexyl ethylene and cyclooctyl hexylene group) and an aromatic hydrocarbon group (for example, a phenylene, phenylmethylene, phenylethylene, phenyl hexylene, phenylbis methylene and phenylbis ethylene group). Among these hydrocarbon groups, preferred species are of C1-10 and in particular C1-2.

[0024] Preferred species for Q comprise aliphatic hydrocarbon groups (and in particular, a methylene group) and in particular -CO-. Z is preferably -O-.

[0025] Among the divalent aliphatic hydrocarbon groups of the aforesaid Q, examples of A^1 include 2-18C alkylene groups. A preferred species is 2-4C alkylene group.

- $(Z\text{-}A^1)m$- denotes m entities of amino alkylene group or oxyalkylene group. When Q is -CO-, m is preferably 1 or 2-20, more preferably 1 or 2-6 and in particular preferably 1. When Q is a hydrocarbon group of carbon number 1-22, m may be 0 and is preferably 0 or 1.

  In the aforesaid formula (1), the same aforesaid examples are proposed for Q, Z and A^1 in $CH_2{=}C(R^1)\text{-}Q\text{-}(Z\text{-}A^1)m$-, and the same preferred examples are also proposed.

  The polar group represented by formula $\text{-}(O)a\text{-}P({=}O)b(OR^2)_2$ of X includes phosphoric acid groups, phosphonic acid groups, phosphorous acid groups, esters thereof and salts thereof. Preferred species comprise groups wherein b is 1, and groups wherein both a and b are 1 are particularly preferred.

  As examples of the monomer wherein X is $\text{-}(O)a\text{-}P({=}O)b(OR^2)_2$, in the aforesaid formula (1), the following species may be proposed.

  Monomers wherein a = 1, b = 1 and all R^2 are H: Mono alkenyl (C3-12) phosphate [for example, mono (meth)allyl, mono (iso) propenyl, mono butenyl, mono pentenyl, mono octenyl, mono decenyl and mono dodecenyl phosphate], mono (meth)acryloyloxy alkyl (C2-12) phosphate [for example, mono methacryloyloxy ethyl phosphate (hereinafter abbreviated to EPMA), mono acryloyloxy ethyl phosphate and mono (meth)acryloyloxy isopropyl phosphate], and mono methacryloyl poly (degree of polymerisation 2-20) oxyethylene phosphate (hereinafter abbreviated to PEPMA). Commercial products include "Light-Ester P-1M" made by Kyoeisha Chemical Co. Ltd. (an EPMA composition), "Phosmer PE" made by Uni Chemical Co. (composition of PEPMA with a degree of polymerisation of 4-5) and the like.

[0026] Monomers wherein a = 1, b= 1 and at least one of R^2 is an alkyl group:

Mono alkenyl (C3-12) mono alkyl (C1-24) phosphate [for example, allyl monomethyl and allyl mono ethyl phosphate], mono alkenyl (C3-12) dialkyl (C1-24) phosphate [for example, allyl dimethyl and allyl diethyl phosphate], and mono (meth)acryloyloxy alkyl (C2-12) mono alkyl (C1-24) phosphate [for example, mono (meth)acryloyloxy ethyl monomethyl phosphate].

Monomers wherein a = 1, b = 1 and at least one of R^2 is $\text{-}(A^1\text{-}Z)m\text{-}Q\text{-}C(R^1){=}CH_2$:

Di(meth)acryloyloxy alkyl (C2-12) phosphate [for example, dimethacryloyloxy ethyl phosphate (hereinafter abbreviated to DEPMA), diacryloyloxy ethyl and di(meth)acryloyloxy isopropyl phosphate]. Commercial products include "Light-Ester P-2M" made by Kyoeisha Chemical Co. (a DEPMA composition) and the like.

[0027] Monomers wherein a = 0, b = 1 and all R^2 are H:

Alkene (C3-12) phosphonic acid [for example, 2-propene-1-, 1-propene, decene, dodecene phosphonic acid], mono (meth)acryloyloxy alkane (C2-12) phosphonic acid [for example, mono (meth)acryloyloxy ethane and mono (meth) acryloyloxy isopropane phosphonic acid], and mono (meth)acryloyl poly (degree of polymerisation 2-20) oxyethylene phosphonic acid.

[0028] Monomers wherein a = 0, b = 1 and at least one of R^2 is alkyl group:

Mono alkyl (C1-24) mono alkene (C3-12) phosphonate [for example, mono methyl and mono ethyl 2-propene-1-phosphonate], dialkyl (C1-24) alkene (C3-12) phosphonate [for example, dimethyl and diethyl 2-propene-1-phosphonate], and mono alkyl (C1-24) mono (meth)acryloyloxy alkane (C2-12) phosphonate [for example, monomethyl mono (meth)acryloyloxy ethane phosphonate].

[0029] Monomers wherein a = 0, b = 1 and at least one of R^2 is $\text{-}\ (A^1\text{-}Z)\ m\text{-}Q\text{-}C\ (R^1) = CH_2$:

(meth)acryloyloxy alkyl (C2-12) (meth)acryloyloxy alkane (C2-12) phosphonate [for example, (meth)acryloyloxy ethyl (meth)acryloyloxy ethane and (meth)acryloyloxy propyl (meth)acryloyloxy propane phosphonate].

[0030] Monomer wherein a = 1, b = 0 and all R^2 are H:

Mono alkenyl (C3-12) phosphite [for example, mono allyl, mono propenyl, mono decenyl and mono dodecenyl phosphate], mono (meth)acryloyloxy alkyl (C2-12) phosphite [for example, mono (meth)acryloyloxy ethyl and mono (meth)acryloyloxy isopropyl phosphite], and mono (meth)acryloyl poly (degree of polymerisation 2-20) oxyethylene phosphite and the like.

[0031] Monomers wherein a = 1, b = 0 and at least one of R^2 is alkyl group:

Mono alkenyl (C3-12) mono alkyl (C1-24) phosphite [for example, allyl monomethyl and allyl mono ethyl phosphite], mono alkenyl (C3-12) dialkyl (C1-24) phosphite [for example, allyl dimethyl and allyl diethyl phosphite], and mono (meth)acryloyloxy alkyl (C2-12) mono alkyl (C1-24) phosphite [for example, mono (meth)acryloyloxy alkyl ethyl monomethyl phosphite].

[0032] Monomers wherein a = 1, b = 0 and at least one of R^2 is $-(A^1\text{-}Z)m\text{-}Q\text{-}C(R^1){=}CH_2$:

Di (meth)acryloyloxy alkyl (C2-12) phosphite [for example, di (meth)acryloyloxy ethyl and di (meth)acryloyloxy isopropyl phosphite].

[0033] From the viewpoint of the friction regulation effect, preferred species among the aforesaid monomers of formula (1) comprise those of the aforesaid (a=1, b=1) and (a=0, b=1) and particularly (a=1, b=1). Preferred species among (a=1, b=1) comprise monomers wherein a=1, b=1 and all R^2 are H, and monomers wherein a=1, b=1 and at least one of R^2 is $-(A^1\text{-}Z)m\text{-}Q\text{-}C(R^1){=}CH_2$ and the co-use of both, and in particular, EPMA, DEPMA, PEPMA and co-use of these. In the case of co-use, a combination of both in at least 50% (wt.%, the same hereinafter) and in particular 60-95% is preferred.

[0034] In the aforesaid general formula (2), R^3 is a hydrogen atom or methyl group, and preferably a methyl group. A^2 is an alkylene group of C2-18, and for example, the same groups as proposed for aforesaid A^1 may be proposed. Preferred examples are the same as well. n is preferably 0 or 1-10 and more preferably 0 or 1.

[0035] As the aliphatic hydrocarbon group of carbon number 1-32 for R^4, straight or branched chain C1-32 alkyl groups, or straight or branched chain C2-32 alkenyl groups may be proposed.

[0036] As far as alkyl groups are concerned, in addition to the aforesaid alkyl groups, hexacosyl, octacosyl (2-dodecyl hexadecyl and the like), triacosyl group and dotriacosyl group (2-tetradecyl octadecyl group and the like) may be proposed. As alkenyl groups, vinyl, (meth)allyl, isopropenyl, butenyl, octenyl, decenyl, dodecenyl, pentadecenyl, octadecenyl, dococenyl, tetracocenyl, octacocenyl and triacocenyl group may be proposed.

[0037] As alicyclic hydrocarbon groups of carbon number 5-7 of R^4, cyclopentyl, cyclohexyl and cycloheptyl group and the like may be proposed, and as aralkyl groups of carbon number 7-32 (the alkyl group is straight or branched chain), benzyl, phenylethyl, phenylbutyl, phenyl nonyl and phenyl dodecyl group and the like may be proposed.

[0038] When A^2 is C2-3, from the viewpoint of oil solubility, n is preferably 0 or an integer of 1-10, and more preferably 0 or 1 and particularly preferably 0.

[0039] Monomers represented by aforesaid general formula (2) include the following.

(2-1):

[0040] (Meth)acrylic ester containing C1-7 (preferably C1-6, more preferably C1-4 and particularly C1) alkyl group, C2-7 (preferably C2-3) alkenyl group, C5-7 (preferably C6) cycloalkyl group or C7-8 aralkyl group: for example, methylacrylate, methyl methacrylate, ethyl, butyl and hexyl (meth)acrylate; allyl and isopropenyl (meth)acrylate; cyclopentyl (meth)acrylate, cyclohexyl acrylate and cyclohexyl methacrylate; benzyl and phenylethyl (meth)acrylate.

(2-2):

[0041] (Meth)acrylic ester containing C8-32 (preferably C8-24, more preferably C12-24) alkyl group or alkenyl group, or C9-32 (preferably C9-18) aralkyl group: for example, dodecyl methacrylate (hereinafter abbreviated to MA-12), tetradecyl methacrylate, hexadecyl methacrylate, octadecyl methacrylate, 2-decyl tetradecyl methacrylate, dodecyl, tetradecyl, hexadecyl, octadecyl and 2-decyl tetradecyl acrylate, 2-ethylhexyl, n-octyl, decyl, isodecyl, tri decyl, eicosyl and tetracosyl (meth)acrylate, octenyl, decenyl, dodecenyl and octadecenyl (meth)acrylate and the like.

(2-3):

[0042] Mono (meth)acrylic ester of (poly) alkylene (C2-18) glycol mono alkyl (C1-32, preferably C1-8), alkenyl (C2-32, preferably C2-3) or aralkyl (C7-32, preferably C7-8) ether: wherein as alkylene groups, alkyl groups, alkenyl groups and aralkyl groups, the same aforesaid groups may be proposed, and the degree of polymerisation of alkylene glycol is preferably 1-20, more preferably 1-10.

[0043] Examples include (poly)ethylene glycol (degree of polymerization 1-9) monomethyl ether, (poly)propylene glycol (degree of polymerization 1-5) mono ethyl ether, ethylene glycol mono-2-ethylhexyl ether and polypropylene glycol (degree of polymerization 2-4) monobutyl ether mono (meth)acrylate and the like.

[0044] Preferred species among monomers of the aforesaid formula (2) comprise combinations of two or more species of the aforesaid (2-1), (2-2) and (2-3), and more preferably a combination of 1-2 species of (2-1) and 2 or more species, in particular, 2-4 species of (2-2).

[0045] The weight ratio of combinations of (2-1)/(2-2) is preferably 50/50-2/98, and in particular 35/65-3/97. The copolymer is readily made oil soluble if (2-2) is 50 or more, and a friction regulation effect can be displayed particularly well if 98 or less. Moreover, the amount of [(2-1) + (2-2)] in the monomer of the aforesaid formula (2) is preferably 80-100% and more preferably 100% based on the weight of monomers of the said formula (2).

[0046] Moreover, a preferred combination is one of 2-50% of monomer (2-1) wherein in the formula of monomer of aforesaid formula (2), n is 0 or 1, and R^4 is a C1-7 alkyl group, C2-7 alkenyl group, C5-7 cycloalkyl group or C7-8 aralkyl group, and, 50-98% of monomer (2-2) wherein, in general formula (2), n is 0 or 1, and R^4 is a C8-32 alkyl group or alkenyl group or C9-32 aralkyl group.

[0047] The content of monomer of the aforesaid formula (1) based on the weight of copolymer is preferably 0.01-50%, more preferably 0.05-40%, in particular 0.1-15% and most preferably 0.2-5%. When the monomer of aforesaid formula (1) is 0.01% or more, this is preferred from the point of view of the excellent friction regulation effect, and when 50% or less, this is preferred from the point of view of being readily made oil soluble.

[0048] The content of monomer of the aforesaid formula (2) based on the weight of copolymer is preferably 50-99.99%, more preferably 60-99.95%, in particular 85-99.9% and most preferably 95-99.8%.

[0049] This polymethacrylate having phosphate ester added to the terminals can be produced using well-known prior art radical polymerisation processes, for example, a solution polymerisation method, emulsion polymerisation method, suspension polymerisation method, reverse phase suspension polymerisation method, thin film polymerisation method or spray polymerisation method, but preferably by a solution polymerisation method. Usually, production is possible by radically-polymerising the monomers of said formula (1) and monomers of said formula (2) in a solvent in the presence of initiator and in accordance with requirements, a chain transfer agent.

[0050] Examples of solvent include high flash point solvents (a flash point of at least 130°C) such as, a mineral oil [solvent refined oil, hydrogenation reformate (for example, high viscosity index oil of viscosity index 100-160) or naphthenic oil] and synthetic oil [hydrocarbon synthetic lubricating oil (poly α-olefinic synthetic lubricating oil or the like) and ester synthetic lubricating oil] and the like; other solvent [aliphatic hydrocarbon (pentane, hexane and the like), aromatic hydrocarbon (toluene, xylene and the like), alcohol solvent (isopropyl alcohol, octanol, butanol and the like), ketone solvent (methyl isobutyl ketone, methyl ethyl ketone and the like), amide solvent (N,N-dimethylformamide, N-methylpyrrolidone and the like), sulfoxide solvent (dimethylsulfoxide and the like)] and combinations of 2 or more thereof. Preferred solvents are high flash point solvents, aromatic hydrocarbon and alcohol solvents and in particular isopropyl alcohol.

[0051] As initiator, azo initiators, peroxide initiators and redox type initiators may be proposed.

[0052] As azo initiator, 2,2'-azobis (2,4-dimethyl valeronitrile) (hereinafter abbreviated to AVN) 2,2'-azobisisobutyronitrile, 2,2'-azobis (2-methyl butyronitrile), azobis cyano valeric acid and salts thereof (for example, hydrochloride and the like), 2,2'-azobis (2-amidino propane) hydrochloride, 2,2'-azobis (2-methyl-N-(2-hydroxyethyl) propionamide and the like may be proposed.

[0053] As far as peroxide initiators are concerned, inorganic peroxide (for example, hydrogen peroxide, ammonium persulphate, potassium persulphate, sodium persulphate and the like), organic peroxide (for example, benzoyl peroxide, di-t-butyl peroxide, cumene hydroperoxide, succinic acid peroxide, di (2-ethoxyethyl) peroxydicarbonate, t-butyl peroxy pivalate, t-hexyl peroxy pivalate, t-butyl peroxy neoheptanoate, t-butyl peroxy neodecanoate, t-butyl peroxy 2-ethyl hexanoate, t-butyl peroxy isobutyrate, t-amyl peroxy 2-ethyl hexanoate, 1,1,3,3-tetramethylbutyl peroxy 2-ethyl hexanoate, dibutyl peroxy trimethyl adipate, lauryl peroxide and the like) may be proposed.

[0054] Examples of redox type initiators include combinations of a reducing agent such as alkali metal sulphite and bisulphite (for example, ammonium sulphite, ammonium bisulphite and the like), ferrous chloride, ferrous sulphate, ascorbic acid and the like, and, an oxidising agent such as alkali metal persulphate, ammonium persulphate, hydrogen peroxide, organic peroxide and the like. Examples of chain transfer agents include for example, mercaptan species (n-lauryl mercaptan, mercaptoethanol, mercapto propanol or the like), thiocarboxylic acid species (thioglycollic acid, thiomalic acid and the like), secondary alcohol species (isopropanol and the like), amines (dibutyl amine and the like), hypophosphite species (sodium hypophosphite and the like) and the like.

[0055] The polymerisation temperature is preferably 30-140°C, more preferably 50-130°C and particularly 70-120°C. The polymerisation temperature may be controlled using an adiabatic polymerisation method or temperature controlled polymerisation method.

[0056] Moreover, processes wherein the polymerisation is started by irradiation of radiation, electron beam, ultraviolet ray and the like can be adopted as well as polymerization initiation using heat. A temperature-controlled solution polymerisation method is preferred.

[0057] Moreover, the copolymerisation may be either one of random addition polymerisation or alternating copolymerisation, and moreover either graft copolymerisation or block copolymerisation.

[0058] The polymethacrylate as used in the present invention and having phosphate ester added to a terminal position is readily soluble in base oil by dissolution / dilution with diluent.

[0059] As diluent, the solvents proposed in the process for the production of the said copolymer are usable, and the solvent used in the polymerisation step may be allowed to remain without being eliminated. Among these diluents, mineral oils and synthetic oils are preferred.

[0060] Dissolution into the diluent may be carried out under heating in accordance with requirements (preferably 40-150°C).

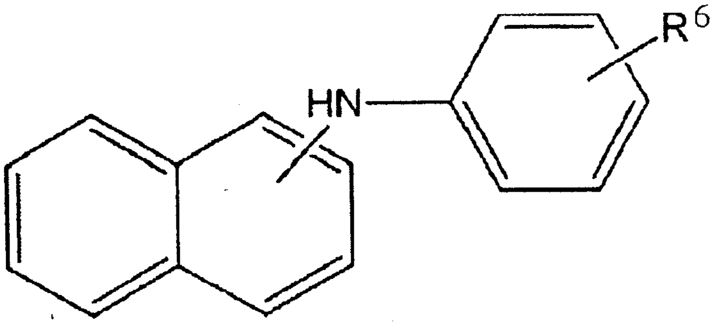
[0061] The amount of this additive with terminally added phosphate ester is preferably 0.0001%-15% and more preferably 0.001%-10%.

[0062] Preferable examples of the aforesaid phenolic antioxidant to be formulated into the lubricating oil composition include, 4,4'-methylene bis (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'-butylidene bis (3-methyl-6-tert-butylphenol), 4,4'-isopropylidene bis (2,6-di-tert-butylphenol), 2,2'-methylenebis (4-methyl-6-nonylphenol), 2,2'-iso butylidene bis (4,6-dimethylphenol), 2,2'-methylenebis (4-methyl-6-cyclohexyl phenol), 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butylphenol, 2,6-di-tert-alfa-dimethylamino-p-cresol, 2,6-di-tert-butyl-4 (N,N'-dimethylaminomethyl phenol), 4,4'-thio bis (2-methyl-6-tert-butylphenol), 4,4'-thio bis (3-methyl-6-tert-butylphenol), 2,2'-thio bis (4-methyl-6-tert-butylphenol), bis (3-methyl-4-hydroxy-5-tert-butyl benzyl) sulphide, bis (3,5-di-tert-butyl-4-hydroxybenzyl) sulphide, 2,2'-thio-diethylenebis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], tri decyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, pentaerythrityltetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate], octyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, octyl-3-(3-methyl-5-tert-butyl-4-hydroxyphenyl) propionate and the like. These can be used by admixing two or more species thereof.

[0063] The content of these phenolic antioxidants is preferably 0.01%-5% and more preferably 0.05%-2%. If less than 0.01%, there is no effect, and no additional effect thereby results if contained in a greater amount than 5%.

[0064] Examples of the aforesaid amine antioxidant, include as aromatic amine, phenyl-α-naphthylamine compounds and dialkyl diphenylamine compounds.

[0065] As such phenyl-α-naphthylamine compounds, the phenyl-α-naphthylamines represented by following general formula (3) are preferably used.



(3)

in formula (3), R^6 denotes a hydrogen atom or a straight chain or branched alkyl group of carbon number 1-16).

[0066] When R^6 in general formula (3) is an alkyl group, the said alkyl group is C1-16 of straight chain or branched form as described above. Examples of such alkyl groups include a methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, octyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group, tetradecyl group, pentadecyl group and hexadecyl group (these alkyl groups may be straight chain or branched form). Moreover, if the carbon number of R6 exceeds 16, the proportion of functional group present within the molecule becomes low, and there is the danger that an unfavourable influence may be exerted on the antioxidant properties.

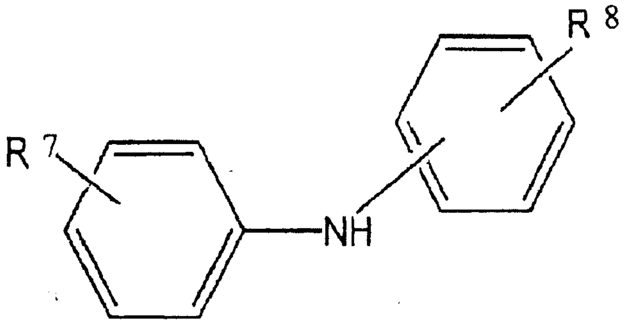
[0067] When R6 in general formula (3) is an alkyl group, from the viewpoint of excellent solubility, R6 is preferably a branched alkyl group of carbon number 8-16, and moreover, more preferably, a branched alkyl group of carbon number 8-16 derived from an oligomer of an olefin of carbon number 3 or 4. Examples of olefins of carbon number 3 or 4 include propylene, 1-butene, 2-butene and isobutylene, and from the viewpoint of solubility, preferred examples comprise propylene or isobutylene.

[0068] In order to obtain even more excellent solubility, R^6 is more preferably a branched octyl group derived from a dimer of isobutylene, a branched nonyl group derived from a trimer of propylene, a branched dodecyl group derived from a trimer of isobutylene, a branched dodecyl group derived from a tetramer of propylene or a branched pentadecyl group derived from a pentamer of propylene, and particularly preferably a branched octyl group derived from a dimer of isobutylene, a branched dodecyl group derived from a trimer of isobutylene or a branched dodecyl group derived from a tetramer of propylene.

[0069] Moreover, when R^6 is an alkyl group, the said group can be bonded at an arbitrary position on the phenyl group, but preferably is at the p-position with respect to the amino group. Furthermore, although the amino group can be bonded at an arbitrary position on the naphthyl group, it is preferably bonded at the α-position.

[0070] As phenyl-α-naphthylamine represented by general formula (3), either commercial products or synthesised products may be used. Synthesised products can be readily synthesised by carrying out the reaction of phenyl-α-naphthylamine with an alkyl halide compound of carbon number 1-16, or the reaction of phenyl-α-naphthylamine with an olefin of carbon number 2-16 or an olefin oligomer of carbon number 2-16 using a Friedel-Krafts catalyst. Examples of Friedel-Krafts catalyst which can be used include metal halides such as aluminium chloride, zinc chloride, ferric chloride and the like, and acidic catalysts such as sulphuric acid, phosphoric acid, phosphorus pentoxide, boron fluoride, acid clay, activated clay and the like.

[0071] As dialkyl diphenylamine compound, a dialkyl diphenylamine represented by following general formula (4) is preferably used.



(4)

(in formula (4), R^7 and R^8 may be the same or different and respectively denote 1-16C alkyl groups).

[0072] As the alkyl groups represented by R^7 and R^8, for example, a methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, octyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group, tetradecyl group, pentadecyl group, hexadecyl group (these alkyl groups may be straight chain or branched form) may be proposed.

[0073] Among these, from the viewpoint of excellent solubility, R^7 and R^8 are preferably a C3-16 branched alkyl group, more preferably a C3-16 branched alkyl group derived from C3 or 4 olefin or oligomer thereof. As examples of olefin of carbon number 3 or 4, propylene, 1-butene, 2-butene and isobutylene and the like may be proposed, wherein propylene or isobutylene is preferred from the viewpoint of affording excellent solubility.

[0074] Moreover, because a more excellent solubility is afforded, R^7 or R^8 is preferably respectively an isopropyl group derived from propylene, a tert-butyl group derived from isobutylene, a branched hexyl group derived from a dimer of propylene, a branched octyl group derived from a dimer of isobutylene, a branched nonyl group derived from a trimer of propylene, a branched dodecyl group derived from a trimer of isobutylene, a branched dodecyl group derived from a tetramer of propylene or a branched pentadecyl group derived from a pentamer of propylene, and most preferably a tert-butyl group derived from isobutylene, a branched hexyl group derived from a dimer of propylene, a branched octyl group derived from a dimer of isobutylene, a branched nonyl group derived from a trimer of propylene, a branched dodecyl group derived from a trimer of isobutylene or a branched dodecyl group derived from a tetramer of propylene.

[0075] Moreover, if the compound wherein one or both of R^7 and R^8 are hydrogen atoms is used, there is danger of sludge being generated due to oxidation of the said compound itself. Moreover, if the carbon number of the alkyl group exceeds 16, the proportion of functional group present within the molecule becomes low, and there is the danger that the antioxidation properties will be depressed at high temperatures.

[0076] The alkyl groups represented by R^7 or R^8 can be respectively bonded at arbitrary positions on the phenyl groups, but preferably are bonded at the p-position with respect to the amino group, in other words, a dialkyl diphenylamine represented by general formula (4) is preferably a p,p'-dialkyl diphenylamine.

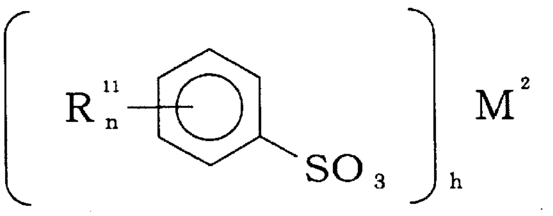
[0077] Commercial or synthesised products may be used as the dialkyl diphenylamine represented by general formula (4). Synthesised products can be readily synthesised by reacting diphenylamine and an alkyl halide compound of carbon number 1-16 and diphenylamine (sic) or the reaction of diphenylamine and olefin of carbon number 2-16 or olefin of carbon number 2-16 (sic) or an oligomer thereof using a Friedel-Krafts catalyst. As Friedel-Krafts catalyst, metal halide and acid catalyst and the like as exemplified in the description of the aforesaid phenyl-alfa-naphthylamine system compound may be used.

[0078] Aromatic amine represented by the aforesaid general formulae (3) and (4) may be used singly or mixtures of two or more species thereof with differing structures may be used. However, a phenyl-alfa-naphthylamine represented by general formula (3) and a dialkyl diphenylamine represented by general formula (4) are preferably co-used because antioxidant properties can be maintained at high temperatures over even a more longer period of time. Wherein, the mixed proportions are arbitrary, but a range of 1/10-10 /1 by weight ratio is preferred.

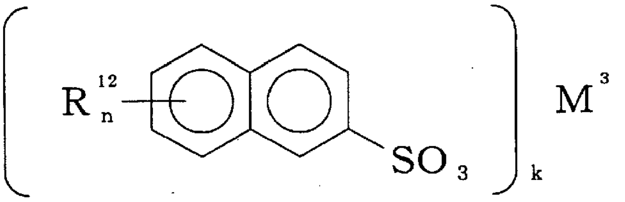
[0079] The content of these amine antioxidants is preferably 0.01% to 5% and more preferably 0.05% to 2%. If less than 0.01%, there is no effect, and no additional effect thereby results if contained in a greater amount than 5%.

[0080] Alkaline earth metal salts such as sulphonate, phenate, salicylate, naphthenate and the like, known as metal detergents, comprise species formulated into this lubricating oil composition. These may be used alone or in combinations of two or more species. As alkaline earth metal, calcium, magnesium may be proposed. Usually sulphonates, phenates and salicylates of calcium or magnesium are preferably used.

[0081] As sulphonate, compounds represented by general formula (5) or general formula (6) may be proposed for alkaline earth metal salts of the aforesaid alkylbenzene sulphonic acid or alkyl naphthalene sulphonic acid.



(5)



(6)

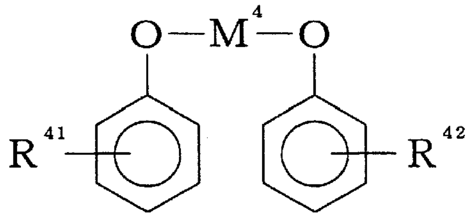
[0082] In the aforesaid general formula (5) and general formula (6), M^2 and M^3 are alkaline earth metals, and Rn^{11} and Rn^{12} denote hydrogen atoms or C1-30 alkyl groups and are preferably C6-18 alkyl groups. When present as a plurality thereof, these may be the same or different. Moreover, h and k are 1-2.

[0083] A basic sulphonate which has been obtained by the reaction of an excess of alkaline earth metal salt and the borate or carbonate of alkaline earth metal salt with respect to the normal salt, in the presence of carbon dioxide, can also be used as an overbased alkaline earth metal sulphonate.

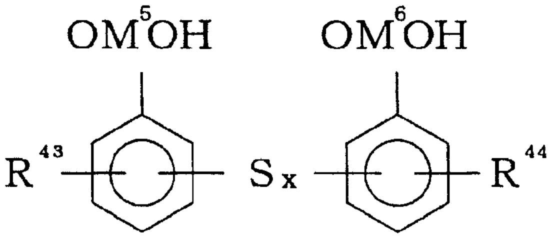
[0084] These alkaline earth metal sulphonates are sulphonates whose base number (BN) is 50-500 mgKOH/g and which contain an alkaline earth metal salt. The said base number can be measured by the hydrochloric acid method of JIS K2501.

[0085] As alkaline earth metal phenate, for example, an alkaline earth metal salt of an alkylphenol, alkylphenol sulphide or an alkylphenol Mannich reactant, and in particular a magnesium salt or calcium salt and the like may be proposed. Examples include the compounds represented by following general formulae (7) and (8).

[0086] The phenate of the overbased alkaline earth metal is an alkaline earth metal salt of alkylphenol or sulphurised alkylphenol, and is usually obtained by a process of carbonating the alkaline earth metal salt of the alkylphenol or sulphurised alkylphenol.



(7)



(8)

[0087] In the aforesaid general formulae (7) and (8), R^{41}, R^{42}, R^{43} and R^{44}, which may each be the same or different, denote C4-30, preferably C6-18, straight chain or branched alkyl groups. M^4, M^5 and M^6, which may each be the same or different, denote alkaline earth metals, preferably calcium or magnesium, and x denotes 1 or 2.

[0088] Examples of the alkyl group represented by the aforesaid R^{41}, R^{42}, R^{43} and R^{44} include a butyl group, pentyl group, hexyl group, heptyl group, octyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group, tetradecyl group, pentadecyl group, hexadecyl group, heptadecyl group, octadecyl group, nonadecyl group, eicosyl group, heneicosyl group, docosyl group, tricosyl group, tetracosyl group, pentacosyl group, hexacosyl group, heptacosyl, octacosyl group, nonacosyl group and triacontyl group and the like. These may be straight chain or branched. Moreover these may be primary alkyl groups, secondary alkyl groups or tertiary alkyl groups.

[0089] Base number (BN) of alkaline earth metal phenate is 40-400 mgKOH/g, preferably 60-300 mgKOH/g.

[0090] When this base number is less than 40 mgKOH/g, the admixture of a large amount becomes necessary in order to increase the total base number for the lubricating oil, and this is not preferred from the point of view of economy, and on the other hand, when this base number exceeds 400mgKOH/g, the phenate component which is present in the lubricating oil is decreased and a satisfactory detergent effect may not be demonstrated.

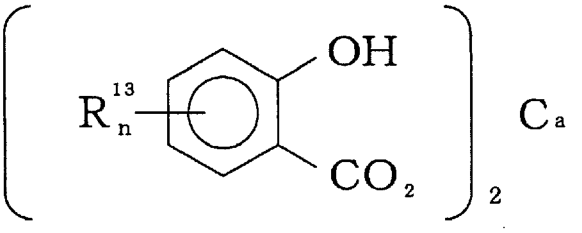
[0091] In the aforesaid metal detergent which has been added to the aforesaid base oil, there may also be metal salicylate, and this is an alkaline earth metal salicylate salt. The base number of the alkaline earth metal salicylate is 40-400 mgKOH/g and is preferably 100-300 mgKOH/g.

[0092] When this base number is less than 40 mgKOH/g, the admixture of a large amount becomes necessary in order to increase the total base number for the insulating oil, and this is not preferred from the point of view of economy, and on the other hand, when this base number exceeds 400mgKOH/g, the salicylate component which is present in the lubricating oil decreases and there may not be sufficient detergent effect.

[0093] Calcium and magnesium are preferred as the alkali metal (sic) of the alkaline earth metal salt of the aforesaid salicylate. Calcium (Ca) is more preferred.

[0094] If the base number of this Ca type salicylate is in the aforesaid range, the normal salt can be used as it is, but basic Ca salicylate which has been obtained by reacting the normal salt of Ca type salicylate with excess calcium salt and calcium base in the presence of water under heating; and overbased calcium salicylate obtained by reacting the normal salt of Ca type salicylate with calcium type carbonate and borate salt in the presence of carbon dioxide gas may also be used.

[0095] As an example of this component, a Ca salicylate of general formula (9) and the like may be proposed.



(9)

[0096] In formula (9), R^{13} denotes a hydrogen atom or C1-30 alkyl group, and a C6-18 alkyl group is preferred, and when a plurality of these are present, they each may be the same or different. n is an integer of 1-4.

[0097] This Ca salicylate may be used alone, or in accordance with requirements a plurality thereof may be mixed and used. Moreover, metal type detergents other than Ca salicylate may be co-used, depending on the circumstances.

[0098] The content of each of the aforesaid metal system detergents can be freely selected to conform with the kind lubricating oil in accordance with the object thereof, but the content is preferably 0.1-10.0 %, and more preferably 0.5-3 %.

[0099] When the aforesaid amine antioxidant is formulated into the lubricating oil composition, an alkaline earth metal salt of a salicylate, namely, the alkaline earth metal salt of an alkyl salicylic acid is preferably used.

Examples

[0100] The following materials were located in order to produce the Examples and Comparative Examples shown in Table 1 and Table 2.

1. Polymethacrylate (PMA) having phosphate ester added to the terminals: (weight average molecular weight; about 30000, content of monomer of formula (1) 0.5% - content of monomer of formula (2) 99.5%), "PAS-447" (made by Sanyo Chemical Industries Ltd.).
   The content of additive phosphorus (P) used herein was 0.03% (0.05% as polymer, because the additive is diluted into mineral oil).
2. Prior art polymethacrylate (PMA): non-dispersing polymethyl methacrylate (polymer of weight average molecular weight, about 33000 and 100% formula (2))
3. Calcium (Ca) sulphonate: base number, about 400 mgKOH/g
4. Calcium (Ca) salicylate: base number, about 160 mgKOH/g
5. Calcium (Ca) phenate: base number, about 250 mgKOH/g
6. Phenolic antioxidant: octyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate.
7. Amine antioxidant A: dialkyl diphenylamine wherein the alkyl group is octyl group and butyl group.
8. Amine antioxidant B: phenyl-α-naphthylamine.
9. Base oil A: paraffinic hydrogenated refined mineral oil with 100°C kinematic viscosity of 4.2 mm^2/s and viscosity index of 120 (ring analysis result by ASTM-D3238, % C_P=78, % C_N=22, % C_A=0).
10. Base oil B: GTL base oil synthesised by Fischer-Tropsch method, classified as Group 3 by API (American Petroleum Institute) base oil classification. (Properties: kinematic viscosity at 100°C degrees of 5.10 mm^2/s; kinematic viscosity at 40°C of 23.5 mm^2/s; viscosity index of 153; density at 15°C of 0.821; sulphur content of less than 10 ppm (calculated as elemental sulphur); nitrogen content less than 1 ppm (calculated as elemental nitrogen); aromatic content of ring analysis by ASTM D3238 method of less than 1%).

Example 1

[0101] In accordance with the formulation shown in Table 1, 22.5 pts. (parts by weight, same hereinafter) polymethacrylate having phosphate ester added to the terminals, 0.5 pts. calcium sulphonate and 1.25 pts. phenolic antioxidant were added to 225.75 pts. base oil A, and a lubricating oil composition was obtained by mixing with stirring.

Examples 2, 3 and 4

[0102] Lubricating oil compositions were prepared in accordance with Example 1 except that the 0.5 pts. calcium sulphonate of Example 1 was replaced by 1.25 pts. calcium salicylate in Example 2 and by 0.8 (sic) calcium phenate in Example 3, while nothing was used instead of this in Example 4. Moreover, the calcium salts used were ones which were formulated so that their calcium quantity was the same as in Example 1, and were adjusted so that the total amount in the base oil comprised 250 pts.

Example 5

[0103] To 225 pts. base oil A were added 22.5 pts. polymethacrylate having phosphate ester added to the terminals, 1.25 pts. calcium salicylate and 1.25 pts. amine antioxidant A, and a lubricating oil composition was prepared by mixing with stirring.

Examples 6 and 7

[0104] Example 6 was an Example in which base oil B was used instead of base oil A in Example 4, and Example 7 was an Example in which amine antioxidant B was used instead of amine antioxidant A of Example 5, and lubricating oil compositions were obtained using otherwise the same procedures as in aforesaid Examples 1 ~ 5 by stirring and mixing well.

Comparative Examples 1, 2, 3 and 4

[0105] Comparative Example 1 was an example in which Example 1 was repeated but amine antioxidant A was used instead of the phenolic antioxidant of Example 1. Comparative Example 2 was an example in which Example 3 was repeated but amine antioxidant A was used instead of the phenolic antioxidant of Example 3. Comparative Example 3 was an example in which Example 1 was repeated but without the use of the phenolic system antioxidant. Comparative Example 4 was an example in which prior art type PMA and calcium sulphonate were used.

Oxidation Performance Test

[0106] An oxidation performance test was carried out on the lubricating oil compositions produced in the Examples and Comparative Examples.

[0107] In the oxidation performance test, a heat test at 165.5°C was carried out for 60 hours using a test method in accordance with the oxidation stability test for lubricating oils for internal combustion engine (ISOT), as stipulated in JIS K2514, and the following items before and after the test were measured.

1. Kinematic viscosity at 100 °C.
2. Kinematic viscosity at 40 °C
3. Viscosity index (VI).
4. Acid number (AN).
5. Base number (BN); Hydrochloric acid method specified in JIS K2501.
6. Hue (in accordance with ASTM)

Moreover, a numerical value was determined for the following items.

7. Kinematic viscosity increase ratio at 100 °C.
8. Acid value (AN) increase or decrease.

Results

[0108] The results of the aforesaid test are shown in Table 1 and Table 2.

Discussion

[0109] As shown in Table 1, each Example showed good results with little change in any of kinematic viscosity at 100°C, kinematic viscosity at 40°C, viscosity index (VI), acid number (AN), base number (BN) and the hue before and after the test.

[0110] On the other hand, as shown in Table 2, large increases in the kinematic viscosity at 100°C and kinematic viscosity at 40°C and a large fall in the viscosity index was seen in the Comparative Examples. Moreover, in Comparative Example 2, a large increase in acid number (AN) and a fall in base number (BN) were seen. In this way, in each of the Comparative Examples it is assessed that the thermal oxidation stability is inferior, and a reduction in performance is produced.

[0111] From these results, it may be assessed that, for formulations into base oil, a combination of terminal phosphate ester bonded PMA and phenolic antioxidant as shown in Examples 4 and 6 is a good combination, and moreover, additional admixture thereto of calcium sulphonate, calcium salicylate and calcium phenate and the like as shown in Examples 1, 2 and 3, is also beneficial. And moreover a combination of terminal phosphate ester bonded PMA, amine antioxidant and calcium salicylate as shown in Examples 5 and 7 is also a good combination.

[0112] On the other hand, it may be assessed in each case, that a combination of terminal phosphate ester bonded PMA, amine antioxidant and calcium sulphonate such as in Comparative Example 1, a combination of terminal phosphate ester bonded PMA, amine antioxidant and calcium phenate such as in Comparative Example 2, a combination of terminal phosphate ester bonded PMA and calcium sulphonate such as in Comparative Example 3 and a combination of prior art type PMA and calcium sulphonate such as in Comparative Example 4, are not preferred.

Table 1

	Ex.1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
Terminal phosphate ester bond PMA	22.50	22.50	22.50	22.50	22.50	22.50	22.50
Prior art PMA							
Ca sulphonate	0.50						
Ca salicylate		1.25			1.25		1.25
Ca phenate			0.80				
Phenolic antioxidant	1.25	1.25	1.25	1.25		1.25	
Amine antioxidant A					1.25		
Amine antioxidant B							1.25
Base oil A	225.75	225.00	225.45	226.25	225.00		225.00
Base oil B						226.25	
Novel oil sample							
100°C kinematic viscosity	7.08	7.9	8.024	6.797	7.86	7.674	7.522
40°C kinematic viscosity	32.85	36.79	35.85	31.71	36.57	36.41	36.47
Viscosity index: VI	186	194	207	181	194	187	180
Acid number: AN	0.22	0.38	0.16	0.25	0.37	0.42	0.43
Base number: BN	0.17	0.55	0.33	0.03	0.55	0.03	0.60
Hue (ASTM)	L0.5	L0.5	L0.5	L0.5	L0.5	L0.5	L0.5
Sample after the test							
(ISOT 165.5°C, after 60 hrs)							
100°C kinematic viscosity	7.073	7.535	7.38	6.747	7.51	7.92	7.705
100°C kinematic viscosity increase (%)	-0.1	-4.6	-8.0	-0.7	-4.5	3.2	2.4
40°C kinematic viscosity	33.05	35.02	34.46	31.53	35.08	37.39	36.1
Viscosity index: VI	184	191	188	180	190	191	193
Acid number: AN	0.20	0.21	0.22	0.27	0.18	0.35	0.25
Acid number: AN fluctuation (mg KOH/g)	-0.02	-0.17	0.06	0.02	-0.19	-0.07	-0.18
Base number: BN	0.01	0.29	0.05	0.03	0.24	0.00	0.34
Hue (ASTM)	1.0	L2.5	1.5	3.0	3.5	1.5	3.5
Note : Ex = Example							

Table 2.

	Comp. Ex.1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Terminal phosphate ester bond PMA	22.50	22.50	22.50	
Prior art PMA				22.50
Ca sulphonate	0.50		0.50	0.50
Ca salicylate				
Ca phenate		0.80		
Phenolic antioxidant				
Amine antioxidant A	1.25	1.25		
Base oil A	225.75	225.45	227.00	227.00
Novel oil sample				
100°C kinematic viscosity	7.056	8.232	7.052	6.666
40°C kinematic viscosity	32.93	36.94	32.67	30.97
Viscosity index: VI	184	207	186	180
Acid number: AN	0.23	0.16	0.22	0.11
Base number: BN	0.19	0.46	0.22	0.78
Hue (ASTM)	L0.5	L0.5	L0.5	L0.5
Sample after test				
(ISOT 165.5°C, after 60 hrs)				
100°C kinematic viscosity	16.92	11.7	28.07	12.82
100°C kinematic viscosity increase (%)	139.8	42.1	298.0	92.3
40°C kinematic viscosity	178.6	94.5	394.5	112.2
Viscosity index: VI	100	113	98	108
Acid number: AN	0.02	20.21	0.04	22.49
Acid number: AN fluctuation (mg KOH/g)	-0.21	20.05	-0.18	22.38
Base number: BN	0	0	0	0
Hue (ASTM)	L6.5	5.5	D8.0	8.0
Note: Comp. Ex. = Comparative Example				

Claims

1. A lubricating oil composition comprising a base oil made of synthetic oil and/or mineral oil, admixed with an antioxidant and a polymethacrylate having a phosphate ester added to a terminal position.

2. A lubricating oil composition according to claim 1, wherein the antioxidant is selected from the group comprising a phenolic antioxidant and an amine antioxidant, or a combination thereof.

3. A lubricating oil composition according to claim 1 or 2, further comprising a compound selected from the group comprising an alkaline earth metal salt of a sulphonate, phenate or a salicylate; preferably an alkyl salicylic acid alkaline earth metal salt.

4. A lubricating oil composition according to any one of the preceding claims, wherein said polymethacrylate comprises an oil-soluble copolymer having a weight average molecular weight of 3,000-500,000 obtainable by copolymerising at least one species of a monomer represented by following general formula (1) and at least one species of a monomer represented by general formula (2) :

$$CH^2 = C(R^1)\text{-}Q\text{-}(Z\text{-}A^1)\ m\text{-}X \qquad (1)$$

$$CH^2 = C(R^3)\text{-}CO\text{-}(O\text{-}A^2)\ n\text{-}OR^4 \qquad (2)$$

wherein X is a polar group represented by formula - (O)a-P(=O)b(OR^2)$_2$, wherein either one of a and b is 1 and the other is 0 or 1, and the two R^{2}s are the same or different and denote H, a C1-24 alkyl group, a group represented by formula -(A^1-Z)m-Q-C(R^1)=CH$_2$ or a cation of formula M$_1$/f, wherein M is a cation with a valency of f (monovalent or divalent);
wherein R^1 is H or a methyl group, Z is -O- or -NH-, A^1 is a C2-18 alkylene group, m is 0 or 1 or an integer of 2-50, and Q is -CO- or a divalent hydrocarbon group of carbon number 1-22, and when m is 0, then Q is a divalent hydrocarbon group of carbon number 1-22; and
wherein R^3 is H or a methyl group, n is 0 or an integer of 1-30, A^2 is a C2-18 alkylene group and R^4 is an aliphatic hydrocarbon group of carbon number 1-32, an alicyclic hydrocarbon group of carbon number 5-7 or a C7-32 aralkyl group, and when present in plurality, A^1, Z, Q, R^1, m and A^2 each independently may be the same or different.

5. A lubricating oil composition according to claim 4, wherein, in formula (1), R^2 in X of formula -(O)a-P (=O) b (OR^2) 2, is a C1-24 alkyl group, preferably C1-4 alkyl group, and in particular a methyl or ethyl group.

6. A lubricating oil composition according to any one of the preceding claims, comprising a base oil made of synthetic oil and/or mineral oil, admixed with a phenolic antioxidant and a polymethacrylate having a phosphate ester added to a terminal position.

7. A lubricating oil composition according to any one of the preceding claims, comprising a base oil made of synthetic oil and/or mineral oil, admixed with an amine antioxidant, an alkyl salicylic acid alkaline earth metal salt and a polymethacrylate having a phosphate ester added to a terminal position.

8. A lubricating oil composition according to any one of the preceding claims, wherein the base oil is a Fischer-Tropsch derived base oil.

9. Use of the lubricating oil composition according to any one of the preceding claims 1 to 8 as a transmission oil, in particular as an automatic transmission oil.

10. Method of improving the lubrication in a transmission device, in particular an automatic transmission device, by lubricating said transmission device with a lubricating oil composition according to any one of the preceding claims 1 to 8.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2001181664 A **[0004]**
- JP 3039399 A **[0004]**
- JP 7268375 A **[0004]**
- JP 2000063869 A **[0004]**