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(54) **ADDITIVE FOR LUBRICATING OIL AND LUBRICATING OIL COMPOSITION**

(57) The present invention is intended to provide a lubricating oil additive having high viscosity index improvability and shear stability and a lubricating oil composition containing the additive and having excellent viscosity index and excellent shear stability. The lubricating oil additive comprises an ethylene/ α -olefin random copolymer having the following properties:

(i) said copolymer is a copolymer of ethylene and at least one α -olefin selected from α -olefins of 3 to 20 carbon atoms and contains at least constituent units derived from ethylene in amounts of 10 to 75% by mol and constituent units derived from at least one α -olefin selected from α -olefins of 8 to 20 carbon atoms in amounts of 20 to 80% by mol,

(ii) the kinematic viscosity at 100°C is in the range of 500 to 1,000,000 mm²/s,

(iii) the intrinsic-viscosity [η] is in the range of 0.15 to 1.0 dl/g,

(iv) the molecular weight distribution (Mw/Mn), as measured by GPC, is not more than 4, and

(v) the number-average molecular weight is in the range of 5,000 to 30,000.

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DescriptionTECHNICAL FIELD

5 **[0001]** The present invention relates to an ethylene/ α -olefin random copolymer useful as an additive having high viscosity index and hardly suffering viscosity decrease attributable to permanent or temporary shear, and to a lubricating oil composition containing the copolymer.

BACKGROUND ART

10 **[0002]** An ethylene/propylene copolymer is well known as a lubricating oil additive comprising an ethylene random copolymer. Since this ethylene/propylene copolymer has no unsaturated double bond and few tertiary carbon atoms, it exhibits excellent shear stability and oxidation stability. Therefore, when this copolymer is added to a lubricating oil, such as gear oil, engine oil or grease, the life of the oil is prolonged, and hence the copolymer is widely employed.

15 **[0003]** Further, it is known that when the copolymer is added as a thickening agent to a lubricating oil containing a synthetic hydrocarbon or an ester as a base oil, the low-temperature viscosity of the oil is decreased (Japanese Patent Laid-Open Publication No. 104695/1989).

[0004] However, the lubricating oil containing a mineral oil or a hydrocarbon synthetic oil as a base oil and an ethylene/propylene copolymer as a thickening agent has a viscosity index lower than that of a lubricating oil containing PMA (polymethyl methacrylate). On this account, the temperature dependence of the viscosity of the lubricating oil is great, and if the high-temperature viscosity of the lubricating oil is designed so as to be kept constant at a certain value, the low-temperature viscosity is increased, and therefore the use of the lubricating oil in winter or in the cold district is sometimes restricted. Accordingly, a thickening agent having high viscosity index improvability is desired.

25 **[0005]** The viscosity index improvability of an ethylene random copolymer generally depends upon the molecular weight, and if the molecular weight is increased, the viscosity index improvability is also increased but the shear stability is decreased. If the ethylene content is increased, the viscosity index improvability and the shear stability are both enhanced, but the high-ethylene content portion is crystallized to make the compounded oil turbid, and hence the compounded oil cannot be used as a lubricating oil.

[0006] On the other hand, it is generally known that PMA has high viscosity index but has low shear stability.

30 **[0007]** Under such circumstances as mentioned above, the present inventors have made various studies of the types and the amounts of comonomers in ethylene random copolymers. As a result, they have found that an ethylene/ α -olefin random copolymer, which has specific ranges of an α -olefin content, a kinematic viscosity at 100°C, an intrinsic viscosity $[\eta]$, and a molecular weight distribution and a number-average molecular weight as measured by gel permeation chromatography, has both of high viscosity index improvability and excellent shear stability and is favorable as an additive to a lubricating oil. That is to say, the present inventors have found that an ethylene/ α -olefin copolymer having many branched chains of 6 or more carbon atoms has both of high viscosity index improvability and excellent shear stability.

35 **[0008]** In WO 01/85880A1, there is disclosed a viscosity modifier for lubricating oil, which is a copolymer of ethylene, an α -olefin of 3 or more carbon atoms and a higher α -olefin of 4 to 20 carbon atoms whose number of carbon atoms is larger by 1 or more than that of the α -olefin of 3 or more carbon atoms, contains 40 to 80% by weight of ethylene, 15 to 59% by weight of the α -olefin of 3 or more carbon atoms and 0.1 to 25% by weight of the higher α -olefin of 4 to 20 carbon atoms (total: 100% by weight), and has a weight-average molecular weight of 80,000 to 400,000. This copolymer, however, has an α -olefin content lower than that of the ethylene/ α -olefin copolymer of the present invention.

40 **[0009]** It is an object of the present invention to provide a lubricating oil additive having high viscosity index improvability and shear stability and a lubricating oil composition excellent in viscosity index and shear stability.

DISCLOSURE OF THE INVENTION

50 **[0010]** According to the present invention, the following lubricating oil thickening agent and lubricating oil composition capable of attaining the above object can be provided.

(1) A lubricating oil additive comprising an ethylene/ α -olefin random copolymer having the following properties:

55 (i) said copolymer is a copolymer of ethylene and at least one α -olefin selected from α -olefins of 3 to 20 carbon atoms and contains at least constituent units derived from ethylene in amounts of 10 to 75% by mol and constituent units derived from at least one α -olefin selected from α -olefins of 8 to 20 carbon atoms in amounts of 20 to 80% by mol,

(ii) the kinematic viscosity at 100°C is in the range of 500 to 1,000,000 mm²/s,

- (iii) the intrinsic viscosity $[\eta]$, as measured in decalin at 135°C, is in the range of 0.15 to 1.0 dl/g,
- (iv) the molecular weight distribution (M_w/M_n , M_w : weight-average molecular weight, M_n : number-average molecular weight), as measured by gel permeation chromatography, is not more than 4, and
- (v) the number-average molecular weight is in the range of 5,000 to 30,000.

(2) The lubricating oil additive as stated in the above (1), wherein the ethylene/ α -olefin random copolymer contains constituent units derived from ethylene in amounts of 30 to 75% by mol and constituent units derived from at least one α -olefin selected from α -olefins of 8 to 20 carbon atoms in amounts of 25 to 70% by mol.

(3) The lubricating oil additive as stated in the above (1), wherein the ethylene/ α -olefin random copolymer contains constituent units derived from ethylene in amounts of 30 to 75% by mol and constituent units derived from at least one α -olefin selected from α -olefins of 10 to 16 carbon atoms in amounts of 25 to 70% by mol.

(4) The lubricating oil additive as stated in the above (1), wherein the ethylene/ α -olefin random copolymer contains constituent units derived from ethylene in amounts of 35 to 70% by mol and constituent units derived from 1-decene in amounts of 30 to 65% by mol.

(5) The lubricating oil additive as stated in the above (1), wherein the ethylene/ α -olefin random copolymer contains constituent units derived from ethylene in amounts of 10 to 75% by mol, constituent units derived from at least one lower α -olefin selected from α -olefins of 3 to 6 carbon atoms in amounts of 5 to 50% by mol, and constituent units derived from at least one higher α -olefin selected from α -olefins of 8 to 20 carbon atoms in amounts of 20 to 85% by mol.

(6) The lubricating oil additive as stated in the above (1), wherein the ethylene/ α -olefin random copolymer contains constituent units derived from ethylene in amounts of 10 to 70% by mol, constituent units derived from at least one lower α -olefin selected from α -olefins of 3 to 6 carbon atoms in amounts of 10 to 40% by mol, and constituent units derived from at least one higher α -olefin selected from α -olefins of 8 to 20 carbon atoms in amounts of 20 to 80% by mol.

(7) The lubricating oil additive as stated in the above (1), wherein the ethylene/ α -olefin random copolymer contains constituent units derived from ethylene in amounts of 10 to 70% by mol, constituent units derived from at least one lower α -olefin selected from α -olefins of 3 to 4 carbon atoms in amounts of 10 to 40% by mol, and constituent units derived from at least one higher α -olefin selected from α -olefins of 10 to 14 carbon atoms in amounts of 20 to 80% by mol.

(8) The lubricating oil additive as stated in the above (1), wherein the ethylene/ α -olefin random copolymer contains constituent units derived from ethylene in amounts of 10 to 70% by mol, constituent units derived from propylene in amounts of 10 to 40% by mol, and constituent units derived from 1-decene in amounts of 20 to 80% by mol.

(9) A lubricating oil additive containing constituent units derived from ethylene in amounts of 30 to 75% by mol and constituent units derived from at least one α -olefin selected from α -olefins of 8 to 20 carbon atoms in amounts of 25 to 70% by mol, and having the following properties:

the shear stability (A (%)) and the viscosity index (B) satisfy the following formula:

$$B \geq 0.4 \times A + 155$$

and

A is a number satisfying the condition of $A \leq 30$.

(10) The lubricating oil additive as stated in the above (9), wherein the shear stability (A (%)) and the low-temperature viscosity (C (mPa·s)) as measured at -26°C satisfy the following formula:

$$C \leq -50 \times A + 15,000.$$

(11) A lubricating oil composition comprising:

(A) at least one base oil selected from a synthetic hydrocarbon, a mineral oil and an ester, which has a kinematic viscosity at 100°C of 1 to 20 mm²/s, in an amount of 50 to 99.8 parts by weight,

(B) the lubricating oil additive as stated in any one of the above (1) to (10), in an amount of 0.2 to 50 parts by weight,

with the proviso that the total of the component (A) and the component (B) is 100 parts by weight, and optionally,

(C) at least one additive selected from the group consisting of a dispersant, a viscosity index improver, an antioxidant, a corrosion inhibitor, an anti-wear agent, a pour point depressant, a rust preventive, an antifoaming agent and an extreme pressure agent.

BEST MODE FOR CARRYING OUT THE INVENTION

[0011] The lubricating oil additive and the lubricating oil composition according to the invention are described in detail hereinafter.

[0012] The lubricating oil additive according to the invention comprises a liquid ethylene/ α -olefin random copolymer.

[0013] The ethylene/ α -olefin random copolymer is a copolymer of ethylene and at least one α -olefin selected from α -olefins of 3 to 20 carbon atoms and contains at least constituent units derived from ethylene and constituent units derived from at least one α -olefin selected from α -olefins of 8 to 20 carbon atoms.

[0014] The ethylene/ α -olefin random copolymer that is a lubricating oil thickening agent of the invention satisfies the following requirements (i) to (v).

[0015] (i) The ethylene/ α -olefin random copolymer contains constituent units derived from ethylene in amounts of 10 to 75% by mol and constituent units derived from at least one α -olefin selected from α -olefins of 8 to 20 carbon atoms in amounts of 20 to 80% by mol.

[0016] In a preferred embodiment of the invention, the ethylene/ α -olefin random copolymer contains constituent units derived from ethylene in amounts of 30 to 75% by mol, preferably 35 to 70% by mol, more preferably 50 to 70% by mol, and constituent units derived from an α -olefin of 8 to 20 carbon atoms in amounts of 25 to 70% by mol, preferably 30 to 65% by mol, more preferably 30 to 50% by mol (copolymer (i-a)).

[0017] In another preferred embodiment of the invention, the ethylene/ α -olefin random copolymer contains constituent units derived from ethylene in amounts of 10 to 75% by mol, preferably 10 to 70% by mol, constituent units derived from at least one lower α -olefin selected from α -olefins of 3 to 6 carbon atoms in amounts of 10 to 50% by mol, preferably 10 to 40% by mol, and constituent units derived from at least one higher α -olefin selected from α -olefins of 8 to 20 carbon atoms in amounts of 20 to 85% by mol, preferably 20 to 80% by mol (copolymer (i-b)).

[0018] Examples of the α -olefins of 3 to 6 carbon atoms (lower α -olefins) include straight-chain α -olefins, such as propylene, 1-butene, 1-pentene and 1-hexene, and branched α -olefins, such as isobutylene, 3-methyl-1-butene and 4-methyl-1-pentene.

[0019] Examples of the α -olefins of 8 to 20 carbon atoms (higher α -olefins) include straight-chain α -olefins, such as 1-octene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene and 1-eicosene, and branched α -olefins, such as 8-methyl-1-nonene, 7-methyl-1-decene, 6-methyl-1-undecene and 6,8-dimethyl-1-decene.

[0020] In the copolymer (i-a), the α -olefin of 8 to 20 carbon atoms is preferably an α -olefin of 8 to 16 carbon atoms, more preferably an α -olefin of 10 to 16 carbon atoms, still more preferably an α -olefin of 10 to 12 carbon atoms, particularly preferably 1-decene.

[0021] In the copolymer (i-a), two or more kinds of α -olefins of 8 to 20 carbon atoms are employable, and for example, a combination of 1-decene and 1-dodecene and a combination of 1-decene and 1-tetradecene are preferable.

[0022] In the copolymer (i-a), an α -olefin of 3 to 7 carbon atoms may be copolymerized in a small amount (e.g., not more than 3% by mol).

[0023] In the copolymer (i-b), the lower α -olefin is preferably an α -olefin of 3 or 4 carbon atoms, particularly preferably propylene. In the copolymer (i-b), the higher α -olefin is preferably an α -olefin of 8 to 16 carbon atoms, more preferably an α -olefin of 10 to 14 carbon atoms, still more preferably an α -olefin of 10 to 12 carbon atoms, particularly preferably 1-decene.

[0024] In the copolymer (i-b), two or more kinds of lower α -olefins are employable, and two or more kinds of higher α -olefins are employable.

[0025] When the ethylene content in the ethylene/ α -olefin random copolymer is in the above range, the copolymer has excellent shear stability and high viscosity index improvability. Moreover, the copolymer does not become turbid, and the pour point thereof can be maintained low.

[0026] (ii) The kinematic viscosity at 100°C (JIS K 2283) is in the range of 500 to 1,000,000 mm²/s, preferably 500 to 500,000 mm²/s, more preferably 1,000 to 100,000 mm²/s.

[0027] When the kinematic viscosity of the ethylene/ α -olefin random copolymer at 100°C is in the above range, the copolymer exhibits an excellent balance between the shear stability and the viscosity index, so that it is practically desirable.

[0028] (iii) The intrinsic viscosity $[\eta]$, as measured in decalin at 135°C, is in the range of 0.15 to 1.0 dl/g, preferably 0.15 to 0.8 dl/g.

[0029] When the intrinsic viscosity $[\eta]$ of the ethylene/ α -olefin random copolymer is in the above range, the copolymer exhibits an excellent balance between the shear stability and the viscosity index, so that it is practically desirable.

[0030] (iv) The number-average molecular weight (M_n), as measured by GPC (molecular weight standard substance: polystyrene), is in the range of 5,000 to 30,000, preferably 5,000 to 27,000, more preferably 8,000 to 27,000, still more preferably 10,000 to 25,000.

[0031] When the number-average molecular weight of the ethylene/ α -olefin random copolymer is in the above range, the copolymer exhibits an excellent balance between the shear stability and the viscosity index, so that it is practically desirable.

[0032] (v) The molecular weight distribution (M_w/M_n , M_w : weight-average molecular weight, M_n : number-average molecular weight), as measured by GPC, is not more than 4, preferably not more than 3.5

[0033] When M_w/M_n of the ethylene/ α -olefin random copolymer is in the above range, the copolymer has excellent shear stability.

[0034] When the ethylene/ α -olefin random copolymer is the copolymer (i-a), this copolymer can become a thickening agent having high viscosity index improvability and shear stability. By blending this thickening agent, a lubricating oil composition excellent in viscosity index and shear stability and particularly free from turbidity can be obtained.

[0035] When the ethylene/ α -olefin random copolymer is the copolymer (i-b), this copolymer can become a thickening agent having high viscosity index improvability and shear stability. By blending this thickening agent, a lubricating oil composition excellent in viscosity index and shear stability and particularly having a low pour point can be obtained.

[0036] The ethylene/ α -olefin random copolymer of the invention that is a lubricating oil thickening agent of the invention preferably satisfies the above requirement (i) and the following requirement (vi), or preferably satisfies the above requirement (i) and the following requirements (vi) and (vii), or preferably satisfies the above requirements (i) to (v) and the following requirements (vi) and (vii). Such an ethylene/ α -olefin random copolymer is preferably the copolymer (i-a).

[0037] (vi) The shear stability (A (%)) and the viscosity index (B) satisfy the following formula:

$$B \geq 0.4 \times A + 155,$$

and

A is a number satisfying the condition of $A \leq 30$; preferably, they satisfy the following formula:

$$B \geq 0.4 \times A + 158,$$

and

A is a number satisfying the condition of $A \leq 25$; more preferably, they satisfy the following formula:

$$0.4 \times A + 180 \geq B \geq 0.4 \times A + 158,$$

and

A is a number satisfying the condition of $A \leq 22$.

[0038] (vii) The shear stability (A (%)) and the low-temperature viscosity (C (mPa·s)) as measured at -26°C satisfy the following formula:

$$C \leq -50 \times A + 15,000,$$

and

A is a number satisfying the condition of $A \leq 30$; preferably, they satisfy the following formula:

$$C \leq -50 \times A + 14,000,$$

and

A is a number satisfying the condition of $A \leq 25$; more preferably, they satisfy the following formula:

$$-50 \times A + 8,000 \leq C \leq -50 \times A + 14,000,$$

and

A is a number satisfying the condition of $A \leq 20$.

[0039] The ethylene/ α -olefin random copolymer satisfying the requirement (vi) and the ethylene/ α -olefin random copolymer satisfying the requirements (vi) and (vii) can each become a thickening agent excellent in shear stability and low-temperature viscosity properties.

[0040] Methods to measure the shear stability, the viscosity index and the low-temperature viscosity are described later.

Process for preparing ethylene/ α -olefin random copolymer

[0041] The ethylene/ α -olefin random copolymer that is a lubricating oil additive of the invention is desired to have a structure wherein the α -olefin units are incorporated into the polymer chain as uniformly as possible. Therefore, it is preferable to prepare the copolymer by the use of a single site catalyst system, and for example, it is preferable to prepare the copolymer by the use of a metallocene catalyst consisting of a metallocene compound and an organoaluminum oxy-compound and/or an ionizing ionic compound. Examples of the metallocene catalysts employable for the preparation of the ethylene/ α -olefin random copolymer are given below. As a matter of course, catalysts other than the following ones are employable without any problem as long as they can copolymerize α -olefins of 10 to 20 carbon atoms with high randomness.

Metallocene compound

[0042] The metallocene compound for constituting the metallocene catalyst is a metallocene compound of a transition metal selected from Group 4 of the periodic table and is, for example, a compound represented by the following formula (1):



wherein M is a transition metal selected from the Group 4 of the periodic table, x is a valence of the transition metal M, and L is a ligand.

[0043] Examples of the transition metals indicated by M include zirconium, titanium and hafnium. L is a ligand coordinated to the transition metal. At least one ligand L is a ligand having cyclopentadienyl skeleton, and the ligand having cyclopentadienyl skeleton may have a substituent.

[0044] Examples of the ligands L having cyclopentadienyl skeleton include cyclopentadienyl group; alkyl- or cycloalkyl-substituted cyclopentadienyl groups, such as methylcyclopentadienyl, ethylcyclopentadienyl, n- or i-propylcyclopentadienyl, n-, i-, sec- or t-butylcyclopentadienyl, dimethylcyclopentadienyl, methylpropylcyclopentadienyl, methylbutylcyclopentadienyl and methylbenzylcyclopentadienyl; indenyl group; 4,5,6,7-tetrahydroindenyl group; and fluorenyl group. The hydrogen in the group having cyclopentadienyl skeleton may be replaced with a halogen atom or a trialkylsilyl group.

[0045] When the metallocene compound has two or more groups having cyclopentadienyl skeleton as ligands L, two of the groups having cyclopentadienyl skeleton may be bonded to each other through, for example, an alkylene group, such as ethylene or propylene, a substituted alkylene group, such as isopropylidene or diphenylmethylenes, a silylene group, or a substituted silylene group, such as methylsilylene, diphenylsilylene or methylphenylsilylene.

[0046] Examples of the ligands L (ligands L having no cyclopentadienyl skeleton) other than the ligands having cyclopentadienyl skeleton include a hydrocarbon group of 1 to 12 carbon atoms, an alkoxy group, an aryloxy group, a sulfonic acid-containing group ($-\text{SO}_3\text{R}^1$) (R^1 is an alkyl group, an alkyl group substituted with a halogen atom, an aryl group, or an aryl group substituted with a halogen atom or an alkyl group), a halogen atom and a hydrogen atom.

Example 1 of the metallocene compound

[0047] The metallocene compound represented by the formula (1) wherein the valence of the transition metal is 4 is more specifically represented by the following formula (2):



wherein M is a transition metal selected from Group 4 of the periodic table, R^2 is a group (ligand) having cyclopentadienyl

skeleton, R^3 , R^4 and R^5 are each independently a group (ligand) having or not having cyclopentadienyl skeleton, k is an integer of 1 or more, and $k+l+m+n=4$.

[0048] Examples of the metallocene compounds having zirconium as M and containing at least two ligands having cyclopentadienyl skeleton include bis(cyclopentadienyl)zirconium monochloride monohydride, bis(cyclopentadienyl)zirconium dichloride, bis(1-methyl-3-butylcyclopentadienyl)zirconium-bis(trifluoromethanesulfonato), bis(1,3-dimethylcyclopentadienyl)zirconium dichloride and bis(*n*-butylcyclopentadienyl)zirconium dichloride.

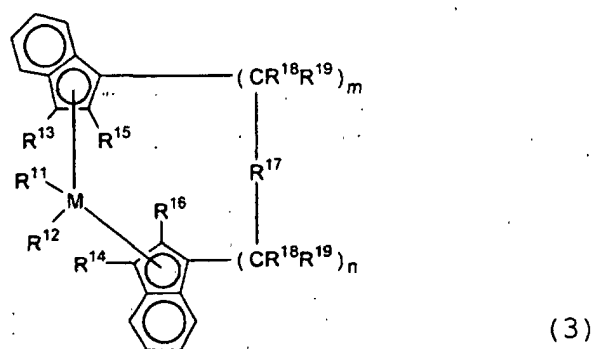
[0049] Compounds wherein the 1,3-position substituted cyclopentadienyl group in the above compounds is replaced with a 1,2-position substituted cyclopentadienyl group are also employable.

[0050] As another example of the metallocene compound, a bridge type metallocene compound of the formula (2) wherein at least two of R^2 , R^3 , R^4 and R^5 , for example, R^2 and R^3 , are each a group (ligand) having cyclopentadienyl skeleton, and these at least two groups are bonded to each other through an alkylene group, a substituted alkylene group, a silylene group, a substituted silylene group or the like is also employable. In this case, R^4 and R^5 are each independently identical with the aforesaid ligand L other than the ligand having cyclopentadienyl skeleton.

[0051] Examples of the bridge type metallocene compounds include ethylenebis(indenyl)dimethylzirconium, ethylenebis(indenyl)zirconium dichloride, isopropylidene(cyclopentadienyl-fluoroenyl)zirconium dichloride, diphenylsilylenebis(indenyl)zirconium dichloride and methylphenylsilylenebis(indenyl)zirconium dichloride.

Example 2 of the metallocene compound

[0052] Another example of the metallocene compound is a metallocene compound represented by the following formula (3), which is described in Japanese Patent Laid-Open Publication No. 268307/1992.



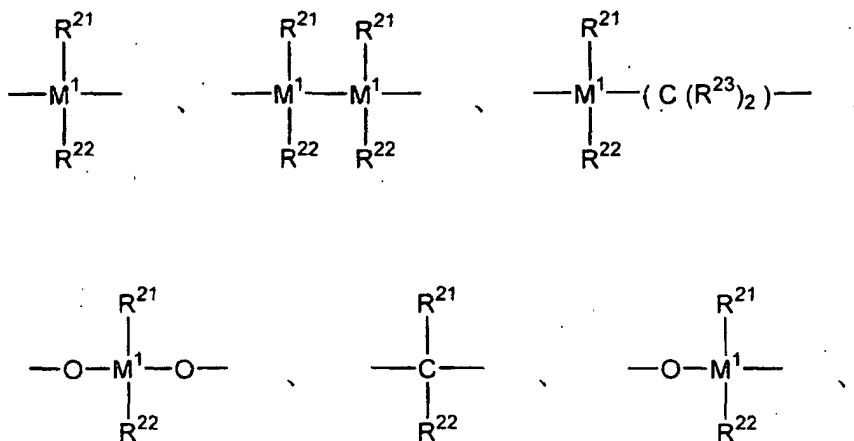
[0053] In the above formula, M is a transition metal of Group 4 of the periodic table, such as titanium, zirconium or hafnium.

[0054] R^{11} and R^{12} may be the same or different and are each a hydrogen atom, an alkyl group of 1 to 10 carbon atoms, an alkoxy group of 1 to 10 carbon atoms, an aryl group of 6 to 10 carbon atoms, an aryloxy group of 6 to 10 carbon atoms, an alkenyl group of 2 to 10 carbon atoms, an arylalkyl group of 7 to 40 carbon atoms, an alkylaryl group of 7 to 40 carbon atoms, an arylalkenyl group of 8 to 40 carbon atoms, or a halogen atom, preferably a chlorine atom.

[0055] R^{13} and R^{14} may be the same or different and are each a hydrogen atom, a halogen atom, an alkyl group of 1 to 10 carbon atoms which may be halogenated, an aryl group of 6 to 10 carbon atoms, $-N(R^{20})_2$ group, $-SR^{20}$ group, $-OSi(R^{20})_3$ group, $-Si(R^{20})_3$ group or $-P(R^{20})_2$ group. R^{20} is a halogen atom, preferably a chlorine atom, an alkyl group of 1 to 10 carbon atoms, preferably 1 to 3 carbon atoms, or an aryl group of 6 to 10 carbon atoms, preferably 6 to 8 carbon atoms. R^{13} and R^{14} are each particularly preferably a hydrogen atom.

[0056] R^{15} and R^{16} are identical with R^{13} and R^{14} except that a hydrogen atom is not included, and they may be the same as or different from each other, preferably the same as each other. R^{15} and R^{16} are each preferably an alkyl group of 1 to 4 carbon atoms which may be halogenated, specifically methyl, ethyl, propyl, isopropyl, butyl, isobutyl, trifluoromethyl or the like, particularly preferably methyl.

[0057] In the formula (3), R^{17} is selected from the group consisting of:



$=\text{BR}^{21}$, $=\text{AlR}^{21}$, $-\text{Ge}-$, $-\text{Sn}-$, $-\text{O}-$, $-\text{S}-$, $=\text{SO}$, $=\text{SO}_2$, $=\text{NR}^{21}$, $=\text{CO}$, $=\text{PR}^{21}$ and $=\text{P}(\text{O})\text{R}^{21}$. M^1 is silicon, germanium or tin, preferably silicon or germanium.

[0058] In the above formulas, R^{21} , R^{22} and R^{23} may be the same or different and are each a hydrogen atom, a halogen atom, an alkyl group of 1 to 10 carbon atoms, a fluoroalkyl group of 1 to 10 carbon atoms, an aryl group of 6 to 10 carbon atoms, a fluoroaryl group of 6 to 10 carbon atoms, an alkoxy group of 1 to 10 carbon atoms, an alkenyl group of 2 to 10 carbon atoms, an arylalkyl group of 7 to 40 carbon atoms, an arylalkenyl group of 8 to 40 carbon atoms, or an alkylaryl group of 7 to 40 carbon atoms. " R^{21} and R^{22} " or " R^{21} and R^{23} " may form a ring together with atoms to which they are bonded.

[0059] R^{17} is preferably $=\text{CR}^{21}\text{R}^{22}$, $=\text{SiR}^{21}\text{R}^{22}$, $=\text{GeR}^{21}\text{R}^{22}$, $-\text{O}-$, $-\text{S}-$, $=\text{SO}$, $=\text{PR}^{21}$ or $=\text{P}(\text{O})\text{R}^{21}$.

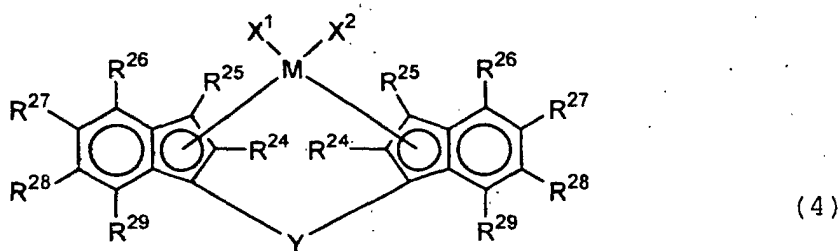
[0060] R^{18} and R^{19} may be the same or different and are each the same group as indicated by R^{21} .

[0061] m and n may be the same or different and are each 0, 1 or 2, preferably 0 or 1. $m+n$ is 0, 1 or 2, preferably 0 or 1.

[0062] Examples of the metallocene compounds represented by the formula (3) include *rac*-ethylene(2-methyl-1-indenyl)²-zirconium-dichloride, *rac*-dimethylsilylene(2-methyl-1-indenyl)²-zirconium-dichloride. These metallocene compounds can be prepared by, for example, the process described in Japanese Patent Laid-Open Publication No. 268307/1992.

Example 3 of the metallocene compound

[0063] As the metallocene compound, further, a metallocene compound represented by the following formula (4) is also employable.



[0064] In the above formula, M is a transition metal atom of Group 4 of the periodic table, specifically titanium, zirconium or hafnium.

[0065] R^{24} and R^{25} may be the same or different and are each a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, a silicon-containing group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group or a phosphorus-containing group.

[0066] R^{24} is preferably a hydrocarbon group, particularly preferably an alkyl group of 1 to 3 carbon atoms, such as methyl, ethyl or propyl.

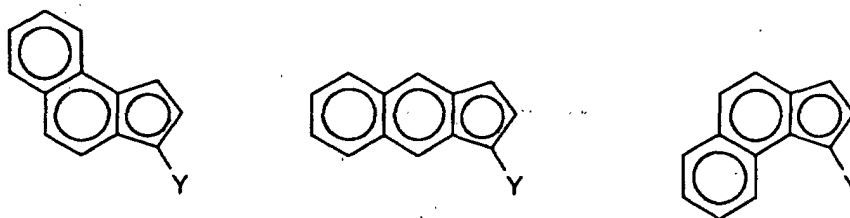
[0067] R²⁵ is preferably a hydrogen atom or a hydrocarbon group, particularly preferably a hydrogen atom or an alkyl group of 1 to 3 carbon atoms, such as methyl, ethyl or propyl.

[0068] R²⁶, R²⁷, R²⁸ and R²⁹ may be the same or different and are each a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms or a halogenated hydrocarbon group of 1 to 20 carbon atoms. Of these, hydrogen, a hydrocarbon group or a halogenated hydrocarbon group is preferable. At least one combination of "R²⁶ and R²⁷", "R²⁷ and R²⁸" and "R²⁸ and R²⁹" may form a monocyclic aromatic ring together with carbon atoms to which they are bonded. When two or more kinds of hydrocarbon groups or halogenated hydrocarbon groups are present in the groups other than the groups for forming the aromatic ring, they may be bonded to each other to form a ring. When R²⁹ is a substituent other than the aromatic group, it is preferably a hydrogen atom.

[0069] X¹ and X² may be the same or different and are each a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group or a sulfur-containing group.

[0070] Y is a divalent hydrocarbon group of 1 to 20 carbon atoms, a divalent halogenated hydrocarbon group of 1 to 20 carbon atoms, a divalent silicon-containing group, a divalent germanium-containing group, a divalent tin-containing group, -O-, -CO-, -S-, -SO-, -SO₂-, -NR³⁰-, -P(R³⁰)-, -P(O)(R³⁰)-, -BR³⁰- or -AlR³⁰- (R³⁰ is a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms or a halogenated hydrocarbon group of 1 to 20 carbon atoms).

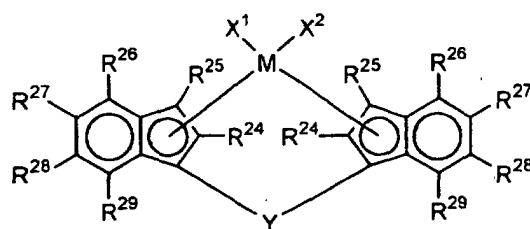
[0071] Examples of the ligands, which contain a monocyclic aromatic ring formed by bonding of at least one combination of "R²⁶ and R²⁷", "R²⁷ and R²⁸" and "R²⁸ and R²⁹" and are coordinated to M in the above formula, include ligands represented by the following formulas:



wherein Y is the same as that in the above formula.

Example 4 of the metallocene compound

[0072] As the metallocene compound, further, a metallocene compound represented by the following formula (5) is also employable.



(5)

[0073] In the above formula, M, R²⁴, R²⁵, R²⁶, R²⁷, R²⁸ and R²⁹ are the same as those in the formula (4).

[0074] Of R²⁶, R²⁷, R²⁸ and R²⁹, two groups including R²⁶ are preferably alkyl groups, and R²⁶ and R²⁸, or R²⁸ and R²⁹ are preferably alkyl groups. These alkyl groups are each preferably a secondary or tertiary alkyl group. These alkyl groups may be substituted with a halogen atom or a silicon-containing group, and examples of the halogen atoms and the silicon-containing groups include substituents exemplified for R²⁴ and R²⁵.

[0075] Of R²⁶, R²⁷, R²⁸ and R²⁹, groups other than the alkyl group are each preferably a hydrogen atom.

[0076] Two groups selected from R²⁶, R²⁷, R²⁸ and R²⁹ may be bonded to each other to form a monocyclic or

polycyclic ring other than an aromatic ring. Examples of the halogen atoms include the same atoms as described with respect to R^{24} and R^{25} .

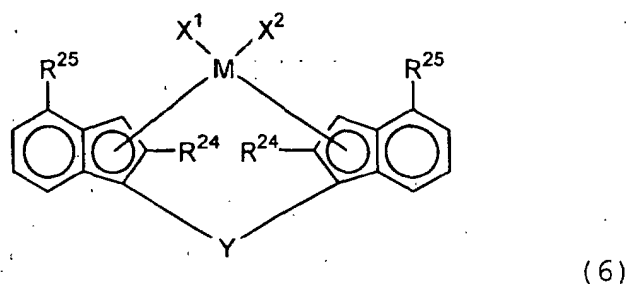
[0077] X^1 , X^2 and Y are the same as those previously described.

[0078] Examples of the metallocene compounds represented by the formula (5) include rac-dimethylsilylene-bis(4,7-dimethyl-1-indenyl)zirconium dichloride, rac-dimethylsilylene-bis(2,4,7-trimethyl-1-indenyl)zirconium dichloride and rac-dimethylsilylene-bis(2,4,6-trimethyl-1-indenyl)zirconium dichloride.

[0079] Transition metal compounds wherein the zirconium metal in the above compounds is replaced with a titanium metal or a hafnium metal are also employable. Although the transition metal compound is usually used as racemic modification, it may be used as R form or S form.

Example 5 of the metallocene compound

[0080] As the metallocene compound, a metallocene compound represented by the following formula (6) is also employable.



[0081] In the above formula, M , R^{24} , X^1 , X^2 and Y are each the same atom or group as described in the formula (4).

[0082] R^{24} is preferably a hydrocarbon group, particularly preferably an alkyl group of 1 to 4 carbon atoms, such as methyl, ethyl, propyl or butyl.

[0083] R^{25} is an aryl group of 6 to 16 carbon atoms. R^{25} is preferably phenyl or naphthyl. The aryl group may be substituted with a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms or a halogenated hydrocarbon group of 1 to 20 carbon atoms.

[0084] X^1 and X^2 are each preferably a halogen atom or a hydrocarbon group of 1 to 20 carbon atoms.

[0085] Examples of the metallocene compounds represented by the formula (6) include rac-dimethylsilylene-bis(4-phenyl-1-indenyl)zirconium dichloride, rac-dimethylsilylene-bis(2-methyl-4-phenyl-1-indenyl)zirconium dichloride, rac-dimethylsilylene-bis(2-methyl-4-(α -naphthyl)-1-indenyl)zirconium dichloride, rac-dimethylsilylene-bis(2-methyl-4-(β -naphthyl)-1-indenyl)zirconium dichloride and rac-dimethylsilylene-bis(2-methyl-4-(1-anthryl)-1-indenyl)zirconium dichloride. Transition metal compounds wherein the zirconium metal in these compounds is replaced with a titanium metal or a hafnium metal are also employable.

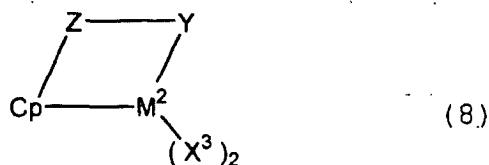
Example 6 of the metallocene compound

[0086] As the metallocene compound, further, a metallocene compound represented by the following formula (7) is also employable.



[0087] In the above formula, M^2 is a metal of Group 4 or lanthanide series of the periodic table. La is a derivative of a delocalized π bond group and is a group imparting a constrained geometric shape to the metal M^2 active site. Each X^3 may be the same or different and is a hydrogen atom, a halogen atom, a hydrocarbon group containing 20 or less carbon atoms, a silyl group containing 20 or less silicon atoms, or a germyl group containing 20 or less germanium atoms.

[0088] Of such compounds, a compound represented by the following formula is preferable.



[0089] In the above formula, M^2 is titanium, zirconium or hafnium.

[0090] X^3 is the same as that described in the formula (7).

[0091] Cp is π bonded to M^2 and is a substituted cyclopentadienyl group having a substituent Z.

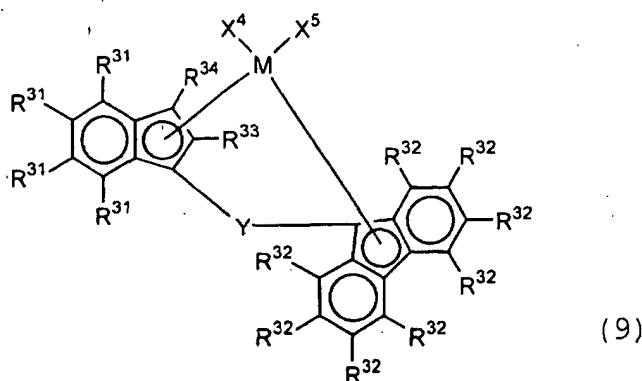
[0092] Z is oxygen, sulfur, boron or an element of Group 4 of the periodic table, such as silicon, germanium or tin.

[0093] Y is a ligand containing phosphorus, oxygen or sulfur, and Z and Y may together form a condensed ring.

[0094] Examples of the metallocene compounds represented by the above formula include (dimethyl(t-butylamido)(tetramethyl- η^5 -cyclopentadienyl)silane)titanium dichloride and ((t-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyl)titanium dichloride. Compounds wherein titanium is replaced with zirconium or hafnium in these metallocene compounds are also employable.

Example 7 of the metallocene compound

[0095] As the metallocene compound, further, a metallocene compound represented by the following formula (9) is also employable.



[0096] In the above formula, M is a transition metal atom of Group 4 of the periodic table, specifically titanium, zirconium or hafnium, preferably zirconium.

[0097] Each R^{31} may be the same or different. At least one of R^{31} is an aryl group of 11 to 20 carbon atoms, an arylalkyl group of 12 to 40 carbon atoms, an arylalkenyl group of 13 to 40 carbon atoms, an alkylaryl group of 12 to 40 carbon atoms or a silicon-containing group, or at least two neighboring groups of the groups indicated by R^{31} form one or plural aromatic rings or aliphatic rings together with carbon atoms to which they are bonded. In this case, the ring formed by R^{31} has, in total, 4 to 20 carbon atoms including carbon atoms to which R^{31} is bonded.

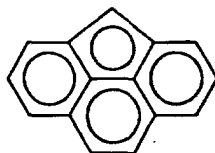
[0098] R^{31} other than R^{31} that forms an aryl group, an arylalkyl group, an arylalkenyl group, an alkylaryl group and an aromatic ring (or aliphatic ring) is a hydrogen atom, a halogen atom, an alkyl group of 1 to 10 carbon atoms or a silicon-containing group.

[0099] Each R^{32} may be the same or different and is a hydrogen atom, a halogen atom, an alkyl group of 1 to 10 carbon atoms, an aryl group of 6 to 20 carbon atoms, an alkenyl group of 2 to 10 carbon atoms, an arylalkyl group of 7 to 40 carbon atoms, an arylalkenyl group of 8 to 40 carbon atoms, an alkylaryl group of 7 to 40 carbon atoms, a silicon-containing group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group or a phosphorus-containing group.

[0100] Of the groups indicated by R^{32} , at least two neighboring groups may form one or plural aromatic rings or aliphatic rings together with carbon atoms to which they are bonded. In this case, the ring formed by R^{32} has, in total,

4 to 20 carbon atoms including carbon atoms to which R^{32} is bonded. R^{32} other than R^{32} that forms an aromatic ring or an aliphatic ring is a hydrogen atom, a halogen atom, an alkyl group of 1 to 10 carbon atoms or a silicon-containing group.

[0101] The group, which is constituted by formation of one or plural aromatic rings or aliphatic rings from two groups indicated by R^{32} , includes an embodiment wherein the fluorenyl group has the following structure.



[0102] R^{32} is preferably a hydrogen atom or an alkyl group, particularly preferably a hydrogen atom or a hydrocarbon group of 1 to 3 carbon atoms, such as methyl, ethyl or propyl. A preferred example of the fluorenyl group having such a substituent R^{32} is a 2,7-dialkyl-fluorenyl group. In this case, the alkyl group of the 2,7-dialkyl is, for example, an alkyl group of 1 to 5 carbon atoms. R^{31} and R^{32} may be the same or different.

[0103] R^{33} and R^{34} may be the same or different and are each the same hydrogen atom, halogen atom, alkyl group of 1 to 10 carbon atoms, aryl group of 6 to 20 carbon atoms, alkenyl group of 2 to 10 carbon atoms, arylalkyl group of 7 to 40 carbon atoms, arylalkenyl group of 8 to 40 carbon atoms, alkylaryl group of 7 to 40 carbon atoms, silicon-containing group, oxygen-containing group, sulfur-containing group, nitrogen-containing group or phosphorus-containing group as previously described. At least one of R^{33} and R^{34} is preferably an alkyl group of 1 to 3 carbon atoms.

[0104] X^4 and X^5 are the same or different and are each a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, or a conjugated diene residue formed from X^4 and X^5 .

[0105] Preferred examples of the conjugated diene residues formed from X^4 and X^5 include residues of 1,3-butadiene, 2,4-hexadiene, 1-phenyl-1,3-pentadiene and 1,4-diphenylbutadiene. These residues may be substituted with a hydrocarbon group of 1 to 10 carbon atoms.

[0106] X^4 and X^5 are each preferably a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms or a sulfur-containing group.

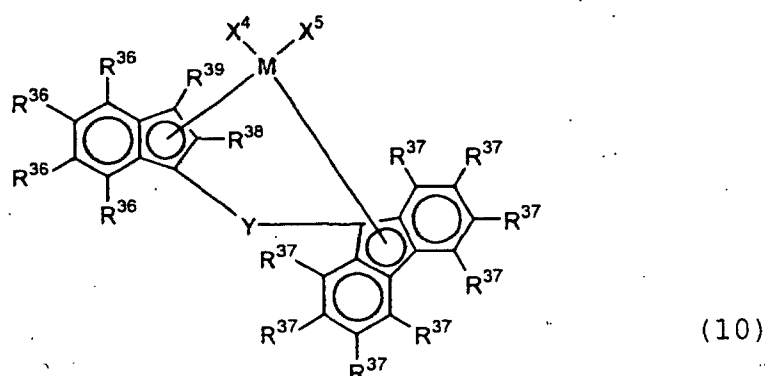
[0107] Y is a divalent hydrocarbon group of 1 to 20 carbon atoms, a divalent halogenated hydrocarbon group of 1 to 20 carbon atoms, a divalent silicon-containing group, a divalent germanium-containing group, a divalent tin-containing group, -O-, -CO-, -S-, -SO-, SO_2 -, $-NR^{35}$ -, $-P(R^{35})$ -, $-P(O)(R^{35})$ -, $-BR^{35}$ - or $-AlR^{35}$ - (R^{35} is a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms or a halogenated hydrocarbon group of 1 to 20 carbon atoms).

[0108] Of the above divalent groups, preferable is a group wherein the shortest connecting portion of -Y- consists of one or two atoms. R^{35} is a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms or a halogenated hydrocarbon group of 1 to 20 carbon atoms.

[0109] Y is preferably a divalent hydrocarbon group of 1 to 5 carbon atoms, a divalent silicon-containing group or a divalent germanium-containing group, more preferably a divalent silicon-containing group, particularly preferably alkylsilylene, alkylarylsilylene or arylsilylene.

Example 8 of the metallocene compound

[0110] As the metallocene compound, further, a metallocene compound represented by the following formula (10) is also employable.



[0111] In the above formula, M is a transition metal atom of Group 4 of the periodic table, specifically titanium, zirconium or hafnium, preferably zirconium.

[0112] Each R^{36} may be the same or different and is a hydrogen atom, a halogen atom, an alkyl group of 1 to 10 carbon atoms, an aryl group of 6 to 10 carbon atoms, an alkenyl group of 2 to 10 carbon atoms, a silicon-containing group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group or a phosphorus-containing group. The alkyl group and the alkenyl group may be substituted with a halogen atom.

[0113] R^{36} is preferably an alkyl group, an aryl group or a hydrogen atom, particularly preferably a hydrocarbon group of 1 to 3 carbon atoms, such as methyl, ethyl, n-propyl or i-propyl, an aryl group, such as phenyl, α -naphthyl or β -naphthyl, or a hydrogen atom.

[0114] Each R^{37} may be the same or different and is a hydrogen atom, a halogen atom, an alkyl group of 1 to 10 carbon atoms, an aryl group of 6 to 20 carbon atoms, an alkenyl group of 2 to 10 carbon atoms, an arylalkyl group of 7 to 40 carbon atoms, an arylalkenyl group of 8 to 40 carbon atoms, an alkylaryl group of 7 to 40 carbon atoms, a silicon-containing group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group or a phosphorus-containing group.

[0115] The alkyl group, the aryl group, the alkenyl group, the arylalkyl group, the arylalkenyl group and the alkylaryl group may be substituted with halogen.

[0116] R^{37} is preferably a hydrogen atom or an alkyl group, particularly preferably a hydrogen atom or a hydrocarbon group of 1 to 4 carbon atoms, such as methyl, ethyl, n-propyl, i-propyl, n-butyl or tert-butyl. R^{36} and R^{37} may be the same or different.

[0117] At least one of R^{38} and R^{39} is an alkyl group of 1 to 5 carbon atoms, and the other is a hydrogen atom, a halogen atom, an alkyl group of 1 to 10 carbon atoms, an alkenyl group or 2 to 10 carbon atoms, a silicon-containing group, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group or a phosphorus-containing group.

[0118] It is preferable that at least one of R^{38} and R^{39} is an alkyl group of 1 to 3 carbon atoms, such as methyl, ethyl or propyl and the other is a hydrogen atom.

[0119] X^4 and X^5 may be the same or different and are each a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms, a halogenated hydrocarbon group of 1 to 20 carbon atoms, an oxygen-containing group, a sulfur-containing group, a nitrogen-containing group, or a conjugated diene residue formed from X^4 and X^5 . Of these, preferable is a halogen atom or a hydrocarbon group of 1 to 20 carbon atoms.

[0120] Y is a divalent hydrocarbon group of 1 to 20 carbon atoms, a divalent halogenated hydrocarbon group of 1 to 20 carbon atoms, a divalent silicon-containing group, a divalent germanium-containing group, a divalent tin-containing group, -O-, -CO-, -S-, -SO-, SO_2 -, $-NR^{40}$ -, $-P(R^{40})$ -, $-P(O)(R^{40})$ -, $-BR^{40}$ - or $-AlR^{40}$ - (R^{40} is a hydrogen atom, a halogen atom, a hydrocarbon group of 1 to 20 carbon atoms or a halogenated hydrocarbon group of 1 to 20 carbon atoms).

[0121] Y is preferably a divalent hydrocarbon group of 1 to 5 carbon atoms, a divalent silicon-containing group or a divalent germanium-containing group, more preferably a divalent silicon-containing group, particularly preferably alkylsilylene, alkylarylsilylene or arylsilylene.

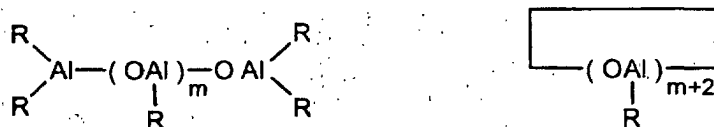
[0122] The metallocene compounds mentioned above are used singly or in combination of two or more kinds. The

metallocene compounds may be diluted with hydrocarbon, halogenated hydrocarbon or the like, prior to use.

Organoaluminum oxy-compound

[0123] The organoaluminum oxy-compound may be aluminoxane publicly known or may be a benzene-insoluble organoaluminum oxy-compound.

[0124] Such publicly known aluminoxane is represented by any one of the following formulas.



[0125] In the above formulas, R is a hydrocarbon group, such as methyl, ethyl, propyl or butyl, preferably methyl or ethyl, particularly preferably methyl, and m is an integer of 2 or more, preferably an integer of 5 to 40.

[0126] The aluminoxane may be formed from mixed alkyloxyaluminum units consisting of alkyloxyaluminum units represented by the formula (OAl(R')) and alkyloxyaluminum units represented by the formula (OAl(R'')) (R' and R'' are each the same hydrocarbon group as exemplified for R, and R' and R'' are groups different from each other). The organoaluminum oxy-compound may contain a small amount of an organic compound of a metal other than aluminum.

Ionizing ionic compound

[0127] The ionizing ionic compound (sometimes referred to as "ionic ionizing compound" or "ionic compound") is, for example, Lewis acid, an ionic compound, a borane compound or a carborane compound.

[0128] The Lewis acid is, for example, a compound represented by the formula BR_3 (R is a phenyl group, which may have a substituent such as fluorine, methyl or trifluoromethyl, or fluorine). Examples of the Lewis acids include trifluoroboron, triphenylboron, tris(4-fluorophenyl)boron, tris(3,5-difluorophenyl)boron, tris(4-fluoromethylphenyl)boron, tris(pentafluorophenyl)boron, tris(p-tolyl)boron, tris(o-tolyl)boron and tris(3,5-dimethylphenyl)boron.

[0129] The ionic compound is, for example, a trialkyl-substituted ammonium salt, a N,N-dialkylanilinium salt, a dialkylammonium salt or a triarylphosphonium salt. Examples of the trialkyl-substituted ammonium salts as the ionic compounds include triethylammoniumtetra(phenyl)boron, tripropylammoniumtetra(phenyl)boron, tri(n-butyl)ammoniumtetra(phenyl)boron. Examples of the dialkylammonium salts as the ionic compounds include di(1-propyl)ammoniumtetra(pentafluorophenyl)boron and dicyclohexylammoniumtetra(phenyl)boron.

[0130] Also available as the ionic compounds are triphenylcarbeniumtetrakis(pentafluorophenyl)borate, N,N-dimethylaniliniumtetrakis(pentafluorophenyl)borate and ferroceniumtetra(pentafluorophenyl)borate.

[0131] Examples of the borane compounds include decaborane (9), and salts of metallic borane anions, such as bis[tri(n-butyl)ammonium]nonaborate, bis[tri(n-butyl)ammonium]decaborate and bis[tri(n-butyl)ammonium]bis(dodecahydridododecaborate)niccolate(II).

[0132] Examples of the carborane compounds include 4-carbanonaborane(9), 1,3-dicarbanonaborane(8), and salts of metallic carborane anions, such as bis[tri(n-butyl)ammonium]bis(undecahydrido-7-carbaundecaborate)niccolate(IV).

[0133] The ionizing ionic compounds mentioned above are used singly or in combination of two or more kinds. The organoaluminum oxy-compound and the ionizing ionic compound may be used in the supported form on the aforesaid carrier compounds.

[0134] In the preparation of the metallocene catalyst, the following organoaluminum compound may be used together with the organoaluminum oxy-compound and/or the ionizing ionic compound.

Organoaluminum compound

[0135] As the organoaluminum compound that is used when needed, a compound having at least one Al-carbon bond in the molecule is employable. Examples of such compounds include:

an organoaluminum compound represented by the following formula (11):



wherein R^{41} and R^{42} may be the same or different and are each a hydrocarbon group of usually 1 to 15 carbon atoms, preferably 1 to 4 carbon atoms, X^6 is a halogen atom, and m , n , p and q are numbers satisfying the conditions of $0 < m \leq 3$, $0 \leq n < 3$, $0 \leq p < 3$, $0 \leq q < 3$ and $m+n+p+q=3$; and

an alkyl complex compound of a Group 1 metal and aluminum, which is represented by the following formula (12):



wherein M^3 is Li, Na or K, and R^{41} is the same as R^{41} in the formula (11).

Polymerization

[0136] The ethylene/ α -olefin random copolymer for use in the invention can be prepared by, for example, copolymerizing ethylene and an α -olefin of 3 to 20 carbon atoms in the presence of the above-mentioned metallocene catalyst usually in a liquid phase. Although a hydrocarbon solvent is generally used as a polymerization solvent, an α -olefin may be used as the solvent. The monomers used herein are those previously described.

[0137] The copolymerization reaction may be carried out batchwise or continuously. When the copolymerization is carried out batchwise, the aforesaid catalyst components are used in the following concentrations.

[0138] The concentration of the metallocene compound in the polymerization system is in the range of usually 0.00005 to 0.1 mmol/l (polymerization volume), preferably 0.0001 to 0.05 mmol/l. The organoaluminum oxy-compound is fed in such an amount that the molar ratio (Al/transition metal) of the aluminum atom to the transition metal in the metallocene compound in the polymerization system becomes 1 to 10000, preferably 10 to 5000.

[0139] The ionizing ionic compound is fed in such an amount that the molar ratio (ionizing ionic compound/metallocene compound) of the ionizing ionic compound to the metallocene compound in the polymerization system becomes 0.5 to 20, preferably 1 to 10.

[0140] The organoaluminum compound is used in an amount of usually about 0 to 5 mmol/l (polymerization volume), preferably about 0 to 2 mmol/l.

[0141] The copolymerization reaction is carried out under the conditions of a temperature of usually -20 to $+150^\circ\text{C}$, preferably 0 to 120°C , more preferably 0 to 100°C , and a pressure of more than 0 MPa and not more than 7.8 MPa (80 kgf/cm², gauge pressure), preferably more than 0 MPa and not more than 4.9 MPa (50 kgf/cm², gauge pressure).

[0142] In the copolymerization, ethylene and the α -olefin of 10 to 20 carbon atoms are fed in such amounts that an ethylene/ α -olefin random copolymer of the aforesaid specific composition is obtained. In the copolymerization, further, a molecular weight modifier such as hydrogen may be added.

Lubricating oil composition

[0143] The lubricating oil composition of the invention comprises:

(A) at least one base oil selected from a synthetic hydrocarbon, a mineral oil and an ester, which has a kinematic viscosity at 100°C of 1 to 20 mm²/s,

(B) the aforesaid ethylene/ α -olefin random copolymer, and optionally,

(C) at least one additive selected from the group consisting of a dispersant, a viscosity index improver, an antioxidant, a corrosion inhibitor, an anti-wear agent, a pour point depressant, a rust preventive, an antifoaming agent and an extreme pressure agent.

Base oil

[0144] The base oil used in the lubricating oil composition of the invention has a kinematic viscosity at 100°C of 1 to 20 mm²/s and is selected from a synthetic hydrocarbon, a mineral oil and an ester. As the synthetic hydrocarbon, the mineral oil and the ester, those conventionally known are employed.

[0145] Examples of the synthetic hydrocarbons having a kinematic viscosity at 100°C of 1 to 20 mm²/s include α -olefin oligomers, alkylbenzenes and alkylnaphthalenes. These can be used singly or in combination of two or more kinds. As the α -olefin oligomer, a low-molecular weight oligomer of at least one olefin selected from olefins of 8 to 12 carbon atoms is employable. The α -olefin oligomer can be prepared by polymerization using a Ziegler catalyst, thermal

polymerization, polymerization using free radical as a catalyst, or polymerization using BF_3 as a catalyst. Such polymerization processes are described in, for example, U.S. Patent No. 4,045,508.

[0146] Most of the alkylbenzenes or the alkylnaphthalenes employable as the base oil are usually dialkylbenzenes or dialkylnaphthalenes wherein the alkyl chains have 6 to 14 carbon atoms, and such dialkylbenzenes or alkylnaphthalenes are prepared by Friedel-Crafts alkylation of benzene or naphthalene and olefin. The alkylation olefin used in the preparation of the alkylbenzenes or the alkylnaphthalenes may be a linear olefin, a branched olefin or a combination thereof. The process for preparing them is described in, for example, U.S. Patent No. 3,909,432.

[0147] Examples of the esters having a kinematic viscosity at 100°C of 1 to 20 mm^2/s include monoesters prepared from monobasic acids such as pelargonic acid and alcohols; diesters prepared from dibasic acids and alcohols or prepared from diols and monobasic acids or acid mixtures; and polyol esters prepared by the reaction of diols, triols (e.g., trimethylolpropane), tetraols (e.g., pentaerythritol) or hexaols (e.g., dipentaerythritol) with monobasic acids or acid mixtures. Particular examples of such esters include tridecyl pelargonate, di-2-ethylhexyl adipate, di-2-ethylhexyl azelate, trimethylolpropane triheptanoate and pentaerythritol tetraheptanoate.

Other additives

[0148] Examples of other additives, which can be added to the lubricating oil composition of the invention when needed, include:

detergents, such as neutral or basic sulfonates and phenates (metal salt type);
dispersants, such as succinimide, esters, benzylamine and copolymerization type polymers (ashless type);
pour point depressants, such as condensates of chlorinated paraffin and naphthalene or phenol, polyalkyl acrylates, polyalkyl methacrylates, polybutene, polyalkylstyrene and polyvinyl acetate;
antioxidants, such as zinc thiophosphate and trialkylphenol;
viscosity index improvers, such as high-molecular weight ethylene/propylene copolymer and PMA;
emulsifying agents, such as sulfuric ester, sulfonic ester, phosphoric ester, fatty acid derivatives, amine derivatives, quaternary ammonium salt and polyoxyethylene type activators;
demulsifying agents, such as quaternary ammonium salt, sulfonated oil and phosphoric ester;
antifungal substances, such as phenolic compounds, formaldehyde donative compounds and salicylanilide type compounds;
anti-stain agents;
untoucher agents;
anti-scorching agents; and
extreme pressure agents.

Composition

[0149] In the lubricating oil composition of the invention, the content of the component (A) is in the range of 50 to 99.8 parts by weight, preferably 60 to 95 parts by weight, and the content of the component (B) is in the range of 0.2 to 50 parts by weight, preferably 5 to 40 parts by weight, with the proviso that the total of the component (A) and the component (B) is 100 parts by weight. The compounding ratio between the component (A) and the component (B) is so determined that the resulting composition has a kinematic viscosity of a prescribed value.

[0150] When the contents of the component (A) and the component (B) are in the above ranges, an economical lubricating oil composition having excellent shear stability, high viscosity index and low low-temperature viscosity can be obtained.

[0151] The lubricating oil composition of the invention has high viscosity index and shear stability and also has good appearance without turbidity.

EFFECT OF THE INVENTION

[0152] The lubricating oil thickening agent according to the invention has high viscosity index improvability and shear stability.

[0153] The lubricating oil composition according to the invention exhibits high viscosity index and shear stability and has good appearance without turbidity.

EXAMPLE

[0154] The present invention is further described with reference to the following examples, but it should be construed

that the invention is in no way limited to those examples.

[0155] The methods for evaluating the examples are as follows.

Kinematic viscosity (mm²/s)

[0156] The kinematic viscosity was measured in accordance with JIS K 2283.

Viscosity index

[0157] The viscosity index was measured in accordance with JIS K 2283.

Intrinsic viscosity [η] (dl/g)

[0158] The intrinsic viscosity was measured in decalin at 135°C.

Number-average molecular weight, Mw/Mn

[0159] The number-average molecular weight and Mw/Mn were measured by GPC using polystyrene as a molecular weight standard substance.

KRL shear stability (%)

[0160] A decrease (%) of the kinematic viscosity at 100°C was measured in accordance with the CEC test method under the conditions of 20 hours.

Pour point (°C)

[0161] The pour point was measured in accordance with JIS K 2269.

Low-temperature viscosity (mPa·s)

[0162] The viscosity at -26°C was measured in accordance with ASTM D 2983.

Appearance

[0163] The appearance was visually observed, and a lubricating oil composition free from turbidity was evaluated as good.

[0164] In the examples and the comparative examples, the following copolymers were used.

Ethylene/1-decene copolymer (1)

[0165] ethylene content: 57% by mol, kinematic viscosity (100°C): 361 mm²/s, [η]: 0.120 dl/g, Mn: 8,600, Mw/Mn: 1.7

Ethylene/1-decene copolymer (2)

[0166] ethylene content: 60% by mol, kinematic viscosity (100°C): 730 mm²/s, [η]: 0.165 dl/g, Mn: 10,700, Mw/Mn: 1.6

Ethylene/1-decene copolymer (3)

[0167] ethylene content: 60% by mol, kinematic viscosity (100°C): 1,440 mm²/s, [η]: 0.190 dl/g, Mn: 13,400, Mw/Mn: 1.8

Ethylene/1-decene copolymer (4)

[0168] ethylene content: 66% by mol, kinematic viscosity (100°C): 15,600 mm²/s, [η]: 0.375 dl/g, Mn: 26,400, Mw/Mn: 1.8

Ethylene/1-octene copolymer (5)

[0169] ethylene content: 60% by mol, kinematic viscosity (100°C): 1,460 mm²/s, [η]: 0.180 dl/g, Mn: 10,600, Mw/Mn: 1.6

Ethylene/propylene/1-decene copolymer (6)

[0170] ethylene content: 65% by mol, propylene content: 5% by mol, 1-decene content: 30% by mol, kinematic viscosity (100°C): 3,030 mm²/s, [η]: 0.240 dl/g, Mn: 16,100, Mw/Mn: 1.7

Ethylene/1-dodecene/1-tetradecene copolymer (7)

[0171] ethylene content: 65% by mol, 1-dodecene content: 20% by mol, 1-tetradecene content: 15% by mol, kinematic viscosity (100°C): 1,400 mm²/s, [η]: 0.235 dl/g, Mn: 24,700, Mw/Mn: 1.6

Ethylene/propylene copolymer (8)

[0172] ethylene content: 50% by mol, kinematic viscosity (100°C): 600 mm²/s, [η]: 0.140 dl/g, Mn: 5,220, Mw/Mn: 1.8

Ethylene/propylene copolymer (9)

[0173] ethylene content: 50% by mol, kinematic viscosity (100°C): 2,000 mm²/s, [η]: 0.190 dl/g, Mn: 7,730, Mw/Mn: 1.8

Ethylene/propylene copolymer (10)

[0174] ethylene content: 50% by mol, kinematic viscosity (100°C): 15,600 mm²/s, [η]: 0.353 dl/g, Mn: 15,000, Mw/Mn: 1.9

Ethylene/1-decene copolymer (11)

[0175] ethylene content: 65% by mol, [η]: 0.50 dl/g, Mn: 52,000, Mw/Mn: 1.6

Ethylene/propylene/1-decene copolymer (12)

[0176] ethylene content: 65% by mol, propylene content: 15% by mol, 1-decene content: 20% by mol, [η]: 0.170 dl/g, Mn: 11,500, kinematic viscosity (100°C): 933 mm²/s, Mw/Mn: 1.6

Ethylene/propylene/1-decene copolymer (13)

[0177] ethylene content: 65% by mol, propylene content: 15% by mol, 1-decene content: 20% by mol, [η]: 0.240 dl/g, Mn: 16,100, kinematic viscosity (100°C): 3,030 mm²/s, Mw/Mn: 1.7

Ethylene/1-butene/1-decene copolymer (14)

[0178] ethylene content: 50% by mol, 1-butene content: 15% by mol, 1-decene content: 35% by mol, [η]: 0.202 dl/g, Mn: 14,400, kinematic viscosity (100°C): 2,000 mm²/s, Mw/Mn: 1.7

Ethylene/propylene/1-dodecene copolymer (15)

[0179] ethylene content: 65% by mol, propylene content: 15% by mol, 1-dodecene content: 20% by mol, [η]: 0.220 dl/g, Mn: 16,000, kinematic viscosity (100°C): 2,000 mm²/s, Mw/Mn: 1.7

Ethylene/propylene/1-decene copolymer (16)

[0180] ethylene content: 15% by mol, propylene content: 15% by mol, 1-decene content: 70% by mol, [η]: 0.240 dl/g, Mn: 17,500, kinematic viscosity (100°C): 4,000 mm²/s, Mw/Mn: 1.8

Ethylene/propylene copolymer (17)

[0181] ethylene content: 50% by mol, propylene content: 50% by mol, $[\eta]$: 0.190 dl/g, Mn: 7,700, kinematic viscosity (100°C): 2,000 mm²/s, Mw/Mn: 1.9

Ethylene/1-decene copolymer (18)

[0182] ethylene content: 10% by mol, 1-decene content: 90% by mol, $[\eta]$: 0.200 dl/g, Mn: 16,500, kinematic viscosity (100°C): 2,300 mm²/s, Mw/Mn: 2.0

Ethylene/propylene/1-decene copolymer (19)

[0183] ethylene content: 80% by mol, propylene content: 5% by mol, 1-decene content: 10% by mol, $[\eta]$: 0.205 dl/g, Mn: 35,000, kinematic viscosity (100°C): 2,100 mm²/s, Mw/Mn: 1.8

[0184] In the evaluations of the examples and the comparative examples, the following base oil and additives were used.

Mineral oil (100N)

[0185] available from Fuji Kosan K.K., F-NT100 (100°C kinematic viscosity: 4.29 mm²/s, viscosity index: 100)

Pour point depressant

[0186] available from Sanyo Kasei Kogyo K.K., ACLUBE 136, amount added: 0.5%

Extreme pressure agent

[0187] available from Lubrizol, ANGRAMOL 98A, amount added: 6.5%

Examples 1 to 12, Comparative Examples 1 to 7

[0188] The components shown in Tables 1 to 4 were mixed in the formulations (unit: g) shown in Tables 1 to 4 at 100°C for 1 hour, to obtain lubricating oil compositions. Evaluation results of properties of the compositions are set forth in Tables 1 to 4.

Table 1

Formulation	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
Ethylene/1-decene copolymer (1)	18.6						
Ethylene/1-decene copolymer (2)		14.5					
Ethylene/1-decene copolymer (3)			12.4				
Ethylene/1-decene copolymer (4)				6.7			
Ethylene/1-octene copolymer (5)					12.5		
Ethylene/propylene/1-decene copolymer (6)						10.0	
Ethylene/1-dodecene/1-tetradecene copolymer (7)							10.5
Pour point depressant	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Extreme pressure agent	6.5	6.5	6.5	6.5	6.5	6.5	6.5
Mineral oil (100N)	74.4	78.5	80.6	86.3	80.5	83.0	82.5
Compounded oil properties							
Kinematic viscosity (mm ² /s, at 40°C)	85.4	85.9	85.6	83.4	88.1	84.9	79.5
Kinematic viscosity (mm ² /s, at 100°C)	14.0	14.0	14.1	14.2	14.1	13.99	13.85
Viscosity index	168	168	171	177	165	170	180
Low-temperature viscosity (mPa·s, at -26°C)	9,950	11,000	13,200	10,600	12,300	12,000	7,980
Shear stability (viscosity decrease, %)	7.1	14.1	20.9	29.1	13.6	23.6	27.8
Appearance	good	good	good	good	good	good	good

Table 2

Formulation	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Ethylene/propylene copolymer (8)	16.0			
Ethylene/propylene copolymer (9)		11.8		
Ethylene/propylene copolymer (10)			6.6	
Ethylene/1-decene copolymer (11)				5.0
Pour point depressant	0.5	0.5	0.5	0.5
Extreme pressure agent	6.5	6.5	6.5	6.5
Mineral oil (100N)	77.0	81.2	86.4	88.0
Compounded oil properties				
Kinematic viscosity (mm ² /s, at 40°C)	93.7	94.3	91.9	78.0
Kinematic viscosity (mm ² /s, at 100°C)	14.0	14.3	14.2	13.8
Viscosity index	152	157	159	183
Low-temperature viscosity (mPa·s, at -26°C)	13,200	15,600	14,700	7,980
Shear stability (viscosity decrease, %)	3.8	9.2	26.3	49.0
Appearance	good	good	good	good

Table 3

Formulation	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12
Ethylene/propylene/1-decene copolymer (12)	13.8				
Ethylene/propylene/1-decene copolymer (13)		11.5			
Ethylene/1-butene/1-decene copolymer (14)			11.2		
Ethylene/propylene/1-dodecene copolymer (15)				11.0	
Ethylene/propylene/1-decene copolymer (16)					10.1
PMA	0.5	0.5	0.5	0.5	0.5
Extreme pressure agent	6.5	6.5	6.5	6.5	6.5
Mineral oil (100N)	79.2	83.0	81.8	82.0	82.9
Compounded oil properties					
Kinematic viscosity (mm ² /s, at 40°C)	86.93	84.87	83.36	82.90	82.92
Kinematic viscosity (mm ² /s, at 100°C)	14.01	13.99	13.90	13.84	13.96
Viscosity index	166	170	172	172	174
Shear stability (viscosity decrease, %)	9.1	10.6	12.8	10.1	20.5
Pour point (°C)	-42.5	-42.5	-42.5	-40	-42.5

Table 4

Formulation	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7
Ethylene/propylene copolymer (17)	11.8		
Ethylene/1-decene copolymer (18)		12.0	
Ethylene/propylene/1-decene copolymer (19)			11.4
PMA (pour point depressant)	0.5	0.5	0.5
Extreme pressure agent	6.5	6.5	6.5
Mineral oil (100N)	81.2	81.0	81.6
Compounded oil properties			
Kinematic viscosity (mm ² /s, at 40°C)	91.02		84.90
Kinematic viscosity (mm ² /s, at 100°C)	14.01		13.83
Viscosity index	158	165	167
Shear stability (viscosity decrease, %)	9.2	32.1	9.0
Pour point (°C)	-37.5	-35	-5

Claims

1. A lubricating oil additive comprising an ethylene/ α -olefin random copolymer having the following properties:

(i) said copolymer is a copolymer of ethylene and at least one α -olefin selected from α -olefins of 3 to 20 carbon atoms and contains at least constituent units derived from ethylene in amounts of 10 to 75% by mol and constituent units derived from at least one α -olefin selected from α -olefins of 8 to 20 carbon atoms in amounts of 20 to 80% by mol,

(ii) the kinematic viscosity at 100°C is in the range of 500 to 1,000,000 mm²/s,

(iii) the intrinsic viscosity $[\eta]$, as measured in decalin at 135°C, is in the range of 0.15 to 1.0 dl/g,

(iv) the molecular weight distribution (Mw/Mn, Mw: weight-average molecular weight, Mn: number-average molecular weight), as measured by gel permeation chromatography, is not more than 4, and

(v) the number-average molecular weight is in the range of 5,000 to 30,000.

2. The lubricating oil additive as claimed in claim 1, wherein the ethylene/ α -olefin random copolymer contains con-

stituent units derived from ethylene in amounts of 30 to 75% by mol and constituent units derived from at least one α -olefin selected from α -olefins of 8 to 20 carbon atoms in amounts of 25 to 70% by mol.

3. The lubricating oil additive as claimed in claim 1, wherein the ethylene/ α -olefin random copolymer contains constituent units derived from ethylene in amounts of 30 to 75% by mol and constituent units derived from at least one α -olefin selected from α -olefins of 10 to 16 carbon atoms in amounts of 25 to 70% by mol.
4. The lubricating oil additive as claimed in claim 1, wherein the ethylene/ α -olefin random copolymer contains constituent units derived from ethylene in amounts of 35 to 70% by mol and constituent units derived from 1-decene in amounts of 30 to 65% by mol.
5. The lubricating oil additive as claimed in claim 1, wherein the ethylene/ α -olefin random copolymer contains constituent units derived from ethylene in amounts of 10 to 75% by mol, constituent units derived from at least one lower α -olefin selected from α -olefins of 3 to 6 carbon atoms in amounts of 5 to 50% by mol, and constituent units derived from at least one higher α -olefin selected from α -olefins of 8 to 20 carbon atoms in amounts of 20 to 85% by mol.
6. The lubricating oil additive as claimed in claim 1, wherein the ethylene/ α -olefin random copolymer contains constituent units derived from ethylene in amounts of 10 to 70% by mol, constituent units derived from at least one lower α -olefin selected from α -olefins of 3 to 6 carbon atoms in amounts of 10 to 40% by mol, and constituent units derived from at least one higher α -olefin selected from α -olefins of 8 to 20 carbon atoms in amounts of 20 to 80% by mol.
7. The lubricating oil additive as claimed in claim 1, wherein the ethylene/ α -olefin random copolymer contains constituent units derived from ethylene in amounts of 10 to 70% by mol, constituent units derived from at least one lower α -olefin selected from α -olefins of 3 to 4 carbon atoms in amounts of 10 to 40% by mol, and constituent units derived from at least one higher α -olefin selected from α -olefins of 10 to 14 carbon atoms in amounts of 20 to 80% by mol.
8. The lubricating oil additive as claimed in claim 1, wherein the ethylene/ α -olefin random copolymer contains constituent units derived from ethylene in amounts of 10 to 70% by mol, constituent units derived from propylene in amounts of 10 to 40% by mol, and constituent units derived from 1-decene in amounts of 20 to 80% by mol.
9. A lubricating oil additive containing constituent units derived from ethylene in amounts of 30 to 75% by mol and constituent units derived from at least one α -olefin selected from α -olefins of 8 to 20 carbon atoms in amounts of 25 to 70% by mol, and having the following properties:

the shear stability (A (%)) and the viscosity index (B) satisfy the following formula:

$$B \geq 0.4 \times A + 155,$$

and

A is a number satisfying the condition of $A \leq 30$.

10. The lubricating oil additive as claimed in claim 9, wherein the shear stability (A (%)) and the low-temperature viscosity (C (mPa·s)) as measured at -26°C satisfy the following formula:

$$C \leq -50 \times A + 15,000.$$

11. A lubricating oil composition comprising:

(A) at least one base oil selected from a synthetic hydrocarbon, a mineral oil and an ester, which has a kinematic viscosity at 100°C of 1 to 20 mm²/s, in an amount of 50 to 99.8 parts by weight,

(B) the lubricating oil additive of any one of claims 1 to 10, in an amount of 0.2 to 50 parts by weight, with the proviso that the total of the component (A) and the component (B) is 100 parts by weight, and optionally,

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(C) at least one additive selected from the group consisting of a dispersant, a viscosity index improver, an antioxidant, a corrosion inhibitor, an anti-wear agent, a pour point depressant, a rust preventive, an antifoaming agent and an extreme pressure agent.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/11366

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ C10M143/08, 169/04/(C10M169/04, 101:02, 105:02, 105:32) C10N20:02, 20:04, 30:02 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁷ C10M143/08, 101/02, 105/02-105/06, 105/32-105/48, 169/04, C10N20:02-20:04, 30:02 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2003 Kokai Jitsuyo Shinan Koho 1971-2003 Jitsuyo Shinan Toroku Koho 1996-2002 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01/58968 A1 (Idemitsu Petrochemical Co., Ltd.), 16 August, 2001 (16.08.01), Claims; examples (Family: none)	1-11
X	EP 1043341 A2 (MITSUI CHEMICALS, INC.), 11 October, 2000 (11.10.00), Claims; examples & CN 1270180 A & JP 2000-351813 A & KR 2000071607 A & US 6459005 B1	1-11
X	WO 01/85880 A1 (MITSUI CHEMICALS, INC. et al.), 15 November, 2001 (15.11.01), Claims; examples & AU 200156686 A & BR 200106323 A	1-11
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 28 January, 2003 (28.01.03)		Date of mailing of the international search report 12 February, 2003 (12.02.03)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/11366

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1205243 A (E.I. DU PONT DE NEMOURS AND CO.), 16 September, 1970 (16.09.70), Claims; examples & CA 889834 A & DE 1644941 C1 & FR 1537571 A5 & JP 47-40530 B1 & NL 6712998 A	1-11
X	GB 1337475 A (ESSO RESEARCH AND ENGINEERING CO.), 14 November, 1973 (14.11.73), Claims; examples & CA 969529 A & DE 2126952 A1 & FR 2093989 A1 & JP 47-177 A & NL 7107500 A & US 3697429 A	1-11
X	GB 1246585 A (E.I. DU PONT DE NEMOURS AND CO.), 15 September, 1971 (15.09.71), Claims; examples & CA 902594 A & DE 1963039 A1 & FR 2026594 A1 & JP 50-10322 B1 & NL 6919111 A & US 3691078 A	1-11
X	EP 21634 A1 (MOBIL OIL CORP.), 07 January, 1981 (07.01.81), Claims; examples & JP 56-2398 A	1-11
X	EP 1103568 A1 (PENNZOIL QUAKER STATE CO.), 30 May, 2001 (30.05.01), Claims; examples & AU 200012508 A & CA 2292360 A1 & CN 1297949 A & JP 2001-151820 A & KR 2001049193 A & NO 200000194 A	1-11
X	JP 57-49697 A (Nippon Oil Co., Ltd.), 23 March, 1982 (23.03.82), Claims; examples (Family: none)	1-11
X	JP 2000-72825 A (Idemitsu Petrochemical Co., Ltd.), 07 March, 2000 (07.03.00), Claims; examples (Family: none)	1-11

Form PCT/ISA/210 (continuation of second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/11366

Box I Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 3 of first sheet)This International Searching Authority found multiple inventions in this international application, as follows:
(See extra sheet)

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest.
☒ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (1)) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/11366

Continuation of Box No.II of continuation of first sheet(1)

An additive for lubricating oils which comprises an ethylene/ α -olefin random copolymer comprising, in a specific proportion, structural units derived from ethylene and structural units derived from an α -olefin having a specific number of carbon atoms, which is a matter common to the subject matter of claims 1 to 8 and the subject matter of claims 9 and 10, is known because it is disclosed in the following document A. Since it is within the scope of the prior art, it does not fall under the category of special technical features in the meaning of Rule 13.2 of the Regulations under the PCT. Consequently, between the two groups of inventions, there is no technical relationship involving any identical or corresponding special technical feature.

Additionally, the subject matter of claim 11 involves the two groups of inventions.

Therefore, this international application involves two groups of inventions not so linked as to form a single general inventive concept.

Document A: JP 1-104695 A (Mitsui Petrochemical Industries, Ltd.),
1989.04.21