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(54) **GREASE COMPOSITION**

(57) Provided are a grease composition which inhibits simultaneously a bearing wear and a fretting wear under a high load to make it possible to elongate a life of the bearing; a grease composition which can inhibit a fretting wear caused by a change in a load in a thrust direction in addition to an usual fretting wear caused by small vibration in an oscillating direction; and a grease composition which is excellent in low-temperature char-

acteristics.

The grease compositions contain a base oil and a thickener, wherein the base oil contains a poly- α -olefin (component A) which has a kinetic viscosity of 300 mm²/s or more at 40°C and which is produced by using a metallocene catalyst.

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Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a grease composition. It relates specifically to a grease composition used for a main bearing which receives a main shaft mounted in a wind power generation apparatus and a pitch bearing which receives a blade shaft.

RELATED ART

[0002] A grease composition is used for lubrication in a bearing to which a large load is applied, such as a main bearing which receives a main shaft mounted in a wind power generation apparatus and a pitch bearing which receives a blade shaft. In these main bearing and pitch bearing, a fluctuation and a small oscillation are always brought about due to a change in a wind speed and refined controlling of blades, and therefore they stay in an environment in which a fretting wear is liable to be caused. Large times and costs are required for exchanging a bearing when it is in trouble, and therefore a lubricant which are excellent in a fretting resistance and which are less liable to cause damage of bearings over a long period of time is demanded.

Accordingly, a grease composition in which a base oil comprises an ester base synthetic oil having the kinetic viscosity of 200 to 2500 mm²/s at 100°C is proposed for the purpose of enhancing a fretting resistance (refer to a patent document 1).

Further, a grease composition in which a high-viscosity base oil is used for the grease composition in order to improve a durability against a large load and into which an extreme pressure agent are blended if necessary, is also disclosed (refer to non-patent documents 1 and 2).

Also, a composition containing a base oil, a thickener and an oleoylsarcosine (refer to a patent document 2) and a composition containing a base oil having the kinetic viscosity of 70 to 250 mm²/s at 40°C, a thickener and a carboxylic acid based rust preventive additive are proposed as a grease composition which is used for a wind power generation apparatus (refer to a patent document 3).

PRIOR ART DOCUMENTS

Patent documents

[0003]

Patent document 1: Japanese Patent Application Laid-Open No. 2003-206939

Patent document 2: Japanese Patent Application Laid-Open No. 2008-38088

Patent document 3: Japanese Patent Application Laid-Open No. 2007-63423

Non-patent documents

[0004]

Non-patent document 1: 「Researches on Evaluation of Fretting Resistance of Lubricant Grease Used for Thrust Ball Bearing」, Tribologist Vol. 54, No. 1 (2009) 64

Non-patent document 2: 「Fretting Wear Resistant Characteristic of Lithium Soap Grease in Oscillating Thrust Ball Bearing」, Tribologist Vol. 42, No. 6 (1997) 492

[0005] A main bearing and a pitch bearing which are used for a wind power generation apparatus are not only required to be reduced in a fretting wear caused by rotation of a main shaft and a blade shaft but also required at the same time to be reduced in a bearing wear caused by receiving the main shaft and the blade shaft each having a high weight. However, it is difficult to inhibit the bearing wear and the fretting wear at the same time with the grease compositions disclosed in the patent documents 1 to 3 and the non-patent documents 1 and 2. In addition, when a high-viscosity base oil is used, there are the problems that comparing with a low-viscosity base oil, a low-temperature startability is deteriorated and the fretting wear is increased. Further, it is known that the fretting wears includes a fretting wear caused by a small vibration in an oscillating direction and a wear caused by a change in a load in a thrust direction (see in non-patent document 1), but it has been difficult to reduce two kinds of fretting wears described above at the same time with the technology disclosed in the patent document 1, although the fretting wear caused by a small vibration in an oscillating direction can be improved.

[0006] An object of the present invention is to provide a grease composition which inhibits simultaneously the bearing

wear and the fretting wear brought about by applying a high load, and which can elongate a life of a bearing.

Also, an object of the present invention is to provide a grease composition which can inhibit the fretting wear caused by a change in a load in a thrust direction in addition to the fretting wear caused by a small vibration in an oscillating direction. Further, an object of the present invention is to provide a grease composition which is excellent in low-temperature characteristics.

[0007] The present invention relates to:

(1) a grease composition comprising a base oil and a thickener, the base oil containing a poly- α -olefin (component A) that has a kinetic viscosity of 300 mm²/s or more at 40°C and that is produced by a metallocene catalyst;

(2) the grease composition according to the item (1), wherein a kinetic viscosity of the component A at 40°C is 600 mm²/s or more;

(3) the grease composition according to the item (1) or (2), containing 20 % by mass or more of the component A based on a whole amount of the composition,

(4) the grease composition according to any of the items (1) to (3), wherein the base oil has a kinetic viscosity of 150 to 2000 mm²/s at 40°C and a worked penetration of 220 to 385,

(5) the grease composition according to any of the items (1) to (4), wherein the base oil contains a component B having a kinetic viscosity of 70 mm²/s or less at 40°C in a proportion of 10 to 70 % by mass based on a whole amount of the composition,

[0008]

(6) the grease composition according to any of the items (1) to (5), containing 17 % by mass or less of the thickener based on a whole amount of the composition,

(7) the grease composition according to any of the items (1) to (6), wherein the thickener is a soap base thickener,

(8) the grease composition according to any of the items (1) to (7), wherein the thickener is produced by reacting carboxylic acid with alkali in the component B,

(9) the grease composition according to any of the items (1) to (8), wherein an extreme pressure additive containing sulfur is blended therein in a proportion of 0.01 to 10 % by mass based on a whole amount of the composition and

(10) the grease composition according to any of the items (1) to (9), wherein the grease composition is used for a wind power generation apparatus, and is used in at least one of a main bearing contacted with a main shaft with which a blade of the wind power generation apparatus is connected, and a pitch bearing contacted with a blade shaft mounted in the blade.

[0009] According to the grease composition of the present invention, the bearing wear and the fretting wear under a high load can be inhibited at the same time, which can elongate a life of the bearings.

Also, according to the present invention, a grease composition which can inhibit the fretting wear caused by a change in a load in a thrust direction in addition to the fretting wear caused by a small vibration in an oscillating direction can be provided. Further, a grease composition in which a low-temperature torque is small and which is excellent in low-temperature characteristics can be provided.

BRIEF EXPLANATION of THE DRAWING

[0010] Fig. 1 is a schematic view showing a wind power generation apparatus in which the grease composition of the present invention is used.

MODE FOR CARRYING OUT THE INVENTION

[0011] The present invention shall more specifically be explained below.

[Component A]

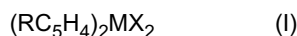
[0012] The grease composition of the present invention contains a base oil and a thickener, and the base oil contains a poly- α -olefin (component A) that has a kinetic viscosity of 300 mm²/s or more at 40°C and that is produced by using a metallocene catalyst.

[0013] In the present invention, a polymer having a kinetic viscosity of 300 mm²/s or more at 40°C is used as the poly- α -olefin produced by using the metallocene catalyst, from the viewpoints that the bearing wear and the fretting wear can be inhibited at the same time so as to elongate a life of the bearing, and that the fretting wear caused by a change in a load in the thrust direction can be inhibited as well as the fretting wear caused by a small vibration particularly in an

oscillating direction.

[0014] If the kinetic viscosity of the component A at 40°C is lower than 300 mm²/s, it is difficult to obtain an excellent wear resistance in the grease composition, and the fretting wear, in particular the fretting wear caused by a change in a load in a thrust direction is not sufficiently improved. In the present invention, a kinetic viscosity of the component A at 40°C is preferably 600 mm²/s or more, more preferably 1000 mm²/s or more from the viewpoints described above. An upper limit thereof shall not specifically be restricted, but it is approximately 200000 mm²/s from the viewpoint of suitably maintaining a viscosity of the base oil. In addition, the kinetic viscosity thereof at 100°C is preferably 32 mm²/s or more, more preferably 90 mm²/s or more from the same viewpoints as described above.

[0015] The metallocene catalyst for obtaining the component A includes a catalyst containing a combination of a metallocene compound and a promoter. The metallocene compound is preferably a metallocene compound represented by Formula (I):



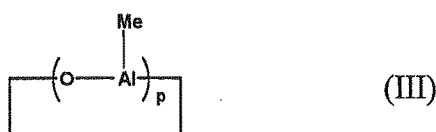
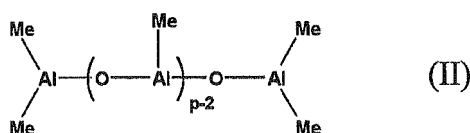
In Formula (I), R represents a hydrogen atom or a hydrocarbon group having 1 to 10 carbon atoms; M represents a transition metal element of the fourth group in the periodic table; and X represents a covalent bonding or ionic bonding ligand.

[0016] In Formula (I), R is preferably a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms. The examples of M include titanium, zirconium and hafnium. Among these, zirconium is preferred. The examples of X include a hydrogen atom; a halogen atom; a hydrocarbon group having 1 to 20 carbon atoms, preferably having 1 to 10 carbon atoms; an alkoxy group having 1 to 20 carbon atoms, preferably having 1 to 10 carbon atoms; an amino group; a phosphorus-containing hydrocarbon group having 1 to 20 carbon atoms, preferably having 1 to 12 carbon atoms (for example, a diphenylphosphine group and the like); a silicon-containing hydrocarbon group having 1 to 20 carbon atoms, preferably having 1 to 12 carbon atoms (for example, a trimethylsilyl group and the like); and a boron compound that contains a hydrocarbon group having 1 to 20 carbon atoms, preferably having 1 to 12 carbon atoms, or that contains a halogen (for example, B(C₆H₅)₄, BF₄ and the like). Among these, a group that is selected from the hydrogen atom, the halogen atom, the hydrocarbon group and the alkoxy group is preferred.

[0017] The examples of the metallocene compound represented by Formula (I) include bis(cyclopentadienyl)zirconium dichloride, bis(methylcyclopentadienyl)zirconium dichloride, bis(ethylcyclopentadienyl)zirconium dichloride, bis(iso-propylcyclopentadienyl)zirconium dichloride, bis(n-propylcyclopentadienyl)zirconium dichloride, bis(n-butylcyclopentadienyl)zirconium dichloride, bis(t-butylcyclopentadienyl)zirconium dichloride, bis(thexylcyclopentadienyl)zirconium dichloride, bis(trimethylsilylcyclopentadienyl)zirconium dichloride, bis(trimethylsilylmethylcyclopentadienyl)zirconium dichloride, bis(cyclopentadienyl)zirconium chlorohydride, bis(cyclopentadienyl)methylzirconium chloride, bis(cyclopentadienyl)ethylzirconium chloride, bis(cyclopentadienyl)methoxyzirconium chloride, bis(cyclopentadienyl)phenylzirconium chloride, bis(cyclopentadienyl)dimethylzirconium, bis(cyclopentadienyl)diphenylzirconium, bis(cyclopentadienyl)dineopentylzirconium, bis(cyclopentadienyl)dihydrozirconium, bis(cyclopentadienyl)dimethoxyzirconium, compounds obtained by replacing a chlorine atom of the above compounds with a bromine atom, an iodine atom, a hydrogen atom, a methyl group, a phenyl group or the like in the compounds described above, and compounds obtained by replacing zirconium which is central metal of the compounds described above with titanium or hafnium.

[0018] The promoter described above is preferably a methylaluminoxane. The methylaluminoxane shall not specifically be restricted, and methylaluminoxanes which have been publicly known can be used. The examples thereof include a linear or cyclic methylaluminoxane represented by Formula (II) and Formula (III):

[0019]



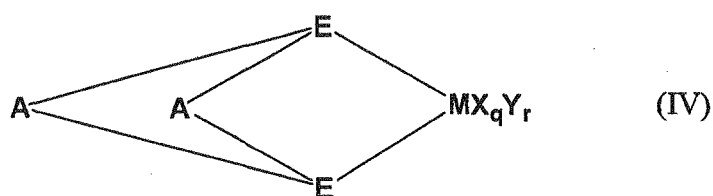
[0020] In Formula (II) and Formula (III), p represents a polymerization degree, and it is usually 3 to 50, preferably 7 to 40.

Methods for producing the methylaluminoxane include a method in which a methylaluminum is brought into contact with a condensing agent such as water and the like, and means thereof shall not specifically be restricted and can be carried out according to publicly known methods.

[0021] A blend proportion of the metallocene compound and the methylaluminoxane is usually 15 to 150, preferably 20 to 120 and more preferably 25 to 100 in terms of methylaluminoxane/metallocene compound (mole ratio). If it is 15 or more, the catalytic activity is exerted, and a yield of a trimer or higher of the α -olefin which is suited as the base oil for the lubricant is prevented from being reduced due to the production of a dimer thereof. On the other hand, if it is 150 or less, the catalyst is prevented from being incompletely removed by deashing.

[0022] The Metallocene catalyst other than the catalysts described above include metallocene catalysts in which metallocene compounds having a cross-linking group is used, for example. As these metallocene compounds, metallocene compound having two cross-linking groups is preferred, and metallocene compound having a meso symmetry is particularly preferred. The examples of the metallocene catalyst in which the metallocene compound having a meso symmetry is used include a metallocene catalyst containing (a) a metallocene compound represented by the following Formula (IV); and (b) at least one component selected from (b-1) a compound which is capable of forming an ionic complex by reacting with the metallocene compound of the above component (a) or a derivative thereof, and (b-2) an aluminoxane.

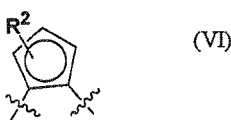
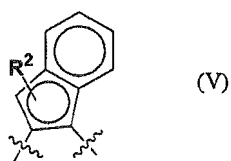
[0023]



[0024] The compound represented by Formula (IV) is a compound of a meso symmetric type, wherein in Formula (IV), M represents a metal element of the third to tenth group in the periodic table; X represents a σ -bonding ligand, and when plural X are present plural X may be the same or different; Y represents a Lewis base, and when plural Y are present plural Y may be the same or different; A represents a cross-linking group selected from a hydrocarbon group having 1 to 20 carbon atoms, a halogen-containing hydrocarbon group having 1 to 20 carbon atoms, a silicon-containing group, a germanium-containing group, a tin-containing group, -O-, -CO-, -S-, -SO₂-, -Se-, -NR¹-, -PR¹-, -P(O)R¹-, -BR¹-, and -AlR¹-, and two A in Formula (IV) may be the same or different; R¹ represents a hydrogen atom, a halogen atom, a hydrocarbon group having 1 to 20 carbon atoms or a halogen-containing hydrocarbon group having 1 to 20 carbon atoms; q is an integer of 1 to 5 and represents [(atomic valence of M) - 2]; r is an integer of 0 to 3; E represents a group represented by the following Formulas (V) and (VI), and two E in Formula (IV) are the same.

Incidentally, the compound of the meso symmetric type described above means a transition metal compound in which two cross-linking groups cross-link two E by a bonding mode of (1,1') (2,2').

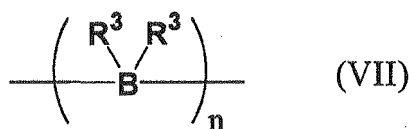
[0025]



[0026] In Formulas (V) and (VI), R² represents a group selected from a hydrogen atom, a halogen atom, a hydrocarbon group having 1 to 20 carbon atoms, a halogen-containing hydrocarbon group having 1 to 4 carbon atoms, a silicon-containing group and a hetero atom-containing group. When plural R² are present, they may be the same as or different from each other. A bond shown by a wavy line represents the bond with the cross-linking group A.

[0027] The cross-linking group A in Formula (IV) is preferably a group represented by the following Formula (VII):

[0028]

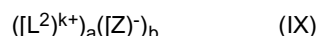
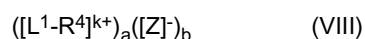


[0029] B in Formula (VII) is a skeleton of the cross-linking group and represents a carbon atom, a silicon atom, a boron atom, a nitrogen atom, a germanium atom, a phosphorus atom or an aluminum atom; R^3 represents a hydrogen atom, a carbon atom, an oxygen atom, an aliphatic hydrocarbon group, an aromatic hydrocarbon group, an amine-containing group or a halogen-containing group; and n is 1 or 2.

[0030] The examples of the metallocene compound represented by Formula (IV) include (1,1'-ethylene) (2,2'-ethylene)-bis(indenyl)zirconium dichloride, (1,1'-methylene) (2,2'-methylene)-bis(indenyl)zirconium dichloride, (1,1'-isopropylidene) (2,2'-isopropylidene)-bis(indenyl)zirconium dichloride, (1,1'-ethylene) (2,2'-ethylene)-bis(3-methylindenyl)zirconium dichloride, (1,1'-ethylene) (2,2'-ethylene)-bis(4,5-benzoidenyl)zirconium dichloride, (1,1'-ethylene) (2,2'-ethylene)-bis(4-isopropylindenyl)zirconium dichloride, (1,1'-ethylene) (2,2'-ethylene)-bis(5,6-dimethylindenyl) zirconium dichloride, (1,1'-ethylene) (2,2'-ethylene)-bis(4,7-diisopropylindenyl)zirconium dichloride, (1,1'-ethylene) (2,2'-ethylene)-bis(4-phenylindenyl)zirconium dichloride, (1,1'-ethylene) (2,2'-ethylene)-bis(3-methyl-4-isopropylindenyl)zirconium dichloride, (1,1'-ethylene) (2,2'-ethylene)-bis(5,6-benzoidenyl)zirconium dichloride,

[0031] (1,1'-dimethylsilylene) (2,2'-dimethylsilylene)bis(cyclopentadienyl) zirconium dichloride, (1,1'-dimethylsilylene) (2,2'-dimethylsilylene)bis(indenyl) zirconium dichloride, (1,1'-dimethylsilylene) (2,2'-dimethylsilylene)bis(3-methylindenyl)zirconium dichloride, (1,1'-dimethylsilylene) (2,2'-dimethylsilylene)bis(3-n-butylindenyl)zirconium dichloride, (1,1'-dimethylsilylene) (2,2'-dimethylsilylene)bis(3-i-propylindenyl) zirconium dichloride, (1,1'-dimethylsilylene) (2,2'-dimethylsilylene) bis(3-trimethylsilylmethylindenyl)zirconium dichloride, (1,1'-dimethylsilylene) (2,2'-dimethylsilylene)bis(3-phenylindenyl) zirconium dichloride, (1,1'-dimethylsilylene) (2,2'-dimethylsilylene)bis(4,5-benzoidenyl)zirconium dichloride, (1,1'-dimethylsilylene) (2,2'-dimethylsilylene)bis(4-isopropylindenyl)zirconium dichloride, (1,1'-dimethylsilylene) (2,2'-dimethylsilylene)bis(5,6-dimethylindenyl)zirconium dichloride, (1,1'-dimethylsilylene) (2,2'-dimethylsilylene) bis(4,7-di-isopropylindenyl)zirconium dichloride, (1,1'-dimethylsilylene) (2,2'-dimethylsilylene)bis(4-phenylindenyl) zirconium dichloride, (1,1'-dimethylsilylene) (2,2'-dimethylsilylene)bis(3-methyl-4-i-propylindenyl)zirconium dichloride, (1,1'-dimethylsilylene) (2,2'-dimethylsilylene) bis(5,6-benzoidenyl)zirconium dichloride and compounds obtained by replacing zirconium in the above compounds with titanium or hafnium. It is a matter of course that the examples thereof shall not be restricted to the above compounds.

[0032] Any compounds can be used for the component (b-1) in the component (b) described above as long as they are capable of forming an ionic complex by reacting with the metallocene compound of the component (a) described above. The components represented by the following Formulas (VIII) and (IX) can be suitably used:



[0033] In Formulas (VIII) and (IX), L^1 represents a Lewis base, and L^2 represents M^2 , $R^5R^6M^3$, R^7_3C or R^8M^3 . $[Z]^-$ represents a non-coordinating anion $[Z^1]^-$ or $[Z^2]^-$. Here, $[Z^1]^-$ represents an anion in which plural groups are bonded to an element, namely $[M^1G^1G^2 \cdots G^f]^-$ (wherein M^1 represents the 5th to 15th group element, preferably the 13th to 15th group element in the periodic table; each of G^1 to G^f represents a hydrogen atom, a halogen atom, an alkyl group having 1 to 20 carbon atoms, a dialkylamino group having 2 to 40 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, an aryloxy group having 6 to 20 carbon atoms, an alkylaryl group having 7 to 40 carbon atoms, an arylalkyl group having 7 to 40 carbon atoms, a halogen-substituted hydrocarbon group having 1 to 20 carbon atoms, an acyloxy group having 1 to 20 carbon atoms, an organic metalloid group or a hetero atom-containing hydrocarbon group having 2 to 20 carbon atoms. Two or more groups among G^1 to G^f may form a ring. f represents an integer of [(atomic valence of central metal M^1) + 1]; $[Z^2]^-$ represents a conjugate base of a Brønsted acid alone in which a logarithm (pKa) of an inverse number of an acid dissociation constant is -10 or less or a combination of the Brønsted acid and a Lewis acid or a conjugate salt of an acid that is usually defined as a superstrong acid; or a Lewis base may be coordinated. In addition, R^4 represents a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, an alkylaryl group or an arylalkyl group; each of R^5 and R^6 represents a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group or a fluorenyl group; R^7 represents an alkyl group having 1 to 20 carbon atoms, an aryl group, an alkylaryl group or an arylalkyl group; R^8 represents a macrocyclic ligand such as tetraphenylporphyrin, phthalocyanine and the like; k is an ionic valence of $[L^1-R^4]$ and $[L^2]$ and is an integer of 1 to 3; a is an integer of 1 or more; b = (k×a); M^2 is one that contains the 1st to 3rd, 11th to 13th and 17th group elements in the periodic table; and M^3 represents the 7th to 12th group elements in the periodic table.

[0034] Here, the examples of L^1 include ammonia; amines such as methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, N,N-dimethylaniline, trimethylamine, triethylamine, tri-n-butylamine, methyldiphenylamine, pyridine, p-bromo-N,N-dimethylaniline, p-nitro-N,N-dimethylaniline and the like; phosphines such as triethylphosphine, triphenylphosphine, diphenylphosphine and the like; thioethers such as tetrahydrothiophene and the like; esters such as ethyl benzoate and the like; and nitriles such as acetonitrile, benzonitrile and the like.

[0035] The examples of R^4 includes a hydrogen, a methyl group, an ethyl group, a benzyl group, a trityl group and the like; and the examples of R^5 and R^6 includes a cyclopentadienyl group, a methylcyclopentadienyl group, an ethylcyclopentadienyl group, a pentamethylcyclopentadienyl group and the like. The examples of R^7 include a phenyl group, a p-tolyl group, a p-methoxyphenyl group and the like; the examples of R^8 include a tetraphenylporphyrin, phthalocyanine, allyl, methallyl and the like. In addition, the examples of M^2 include Li, Na, K, Ag, Cu, Br, I, I_3 and the like; and the examples of M^3 include Mn, Fe, Co, Ni, Zn and the like. In $[Z^1]$, namely in $[M^1G^1G^2\cdots G^f]$, the examples of M^1 include B, Al, Si, P, As, Sb and the like, preferably B and Al. In addition, the examples of G^1 , $G^2\cdots G^f$ include a dimethylamino group, a diethylamino group and the like as the dialkylamino group; a methoxy group, an ethoxy group, a n-butoxy group, a phenoxy group and the like as the alkoxy group or the aryloxy group; a methyl group, an ethyl group, a n-propyl group, an isopropyl group, a n-butyl group, an isobutyl group, a n-octyl group, a n-eicosyl group, a phenyl group, a p-tolyl group, a benzyl groups, a 4-t-butylphenyl group, a 3,5-dimethylphenyl group and the like as the hydrocarbon group; fluorine, chlorine, bromine and iodine as the halogen atom; a p-fluorophenyl group, a 3,5-difluorophenyl group, a pentachlorophenyl group, a 3,4,5-trifluorophenyl group, a pentafluorophenyl group, a 3,5-bis(trifluoromethyl)phenyl group, a bis(trimethylsilyl)methyl group and the like as the hetero atom-containing hydrocarbon group; and a pentamethylantimony group, a trimethylsilyl group, a trimethylgermyl group, a diphenylarsine group, a dicyclohexylantimony group, diphenylboron and the like as the organic metalloid group.

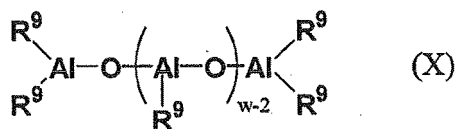
[0036] The examples of the non-coordinating anion, namely, the conjugate base of Brønsted acid alone having a pKa of -10 or less or the combination of the Brønsted acid and a Lewis acid; include a trifluoromethanesulfonic acid anion, $(CF_3SO_3)^-$; a bis(trifluoromethanesulfonyl)methyl anion; a bis(trifluoromethanesulfonyl)benzyl anion; bis(trifluoromethanesulfonyl)amide; a perchloric acid anion, $(ClO_4)^-$; a trifluoroacetic acid anion, $(CF_3CO_2)^-$; a hexafluoroantimony anion, $(SbF_6)^-$; a fluorosulfonic acid anion, $(FSO_3)^-$; a chlorosulfonic acid anion, $(ClSO_3)^-$; a fluorosulfonic acid anion/antimony pentafluoride, $(FSO_3/SbF_5)^-$; a fluorosulfonic acid anion/arsenic pentafluoride, $(FSO_3/AsF_5)^-$; a trifluoromethanesulfonic acid/antimony pentafluoride, $(CF_3SO_3/SbF_5)^-$; and the like.

[0037] The examples of the ionic compound which is reacted with the metallocene compound of the above component (a) to form an ionic complex, namely the component (b-1) compound, include N,N-dimethylanilinium tetrakis(pentafluoroborate), triethylammonium tetraphenylborate, tri-n-butylammonium tetraphenylborate, trimethylammonium tetraphenylborate, tetraethylammonium tetraphenylborate, methyl(tri-n-butyl)ammonium tetraphenylborate, benzyl(tri-n-butyl)ammonium tetraphenylborate, dimethyldiphenylammonium tetraphenylborate, triphenyl(methyl)ammonium tetraphenylborate, trimethylanilinium tetraphenylborate, methylpyridinium tetraphenylborate, benzylpyridinium tetraphenylborate, methyl(2-cyanopyridinium) tetraphenylborate, triethylammonium tetrakis(pentafluorophenyl)borate, tri-n-butylammonium tetrakis(pentafluorophenyl)borate, triphenylammonium tetrakis(pentafluorophenyl)borate, tetra-n-butylammonium tetrakis(pentafluorophenyl)borate, tetraethylammonium tetrakis(pentafluorophenyl)borate, benzyl(tri-n-butyl)ammonium tetrakis(pentafluorophenyl)borate, methyldiphenylammonium tetrakis(pentafluorophenyl)borate, triphenyl(methyl)ammonium tetrakis(pentafluorophenyl)borate, methylanilinium tetrakis(pentafluorophenyl)borate, dimethylanilinium tetrakis(pentafluorophenyl)borate, trimethylanilinium tetrakis(pentafluorophenyl)borate, methylpyridinium tetrakis(pentafluorophenyl)borate, benzylpyridinium tetrakis(pentafluorophenyl)borate, methyl(2-cyanopyridinium) tetrakis(pentafluorophenyl)borate, benzyl(2-cyanopyridinium) tetrakis(pentafluorophenyl)borate, methyl(4-cyanopyridinium) tetrakis(pentafluorophenyl)borate, triphenylphosphonium tetrakis(pentafluorophenyl)borate, dimethylanilinium tetrakis[bis(3,5-difluoromethyl)phenyl]borate, ferrocenium tetraphenylborate, silver tetraphenylborate, trityl tetraphenylborate, tetraphenylporphyrinmanganese tetraphenylborate, ferrocenium tetrakis(pentafluorophenyl)borate, (1,1'-dimethylferrocenium) tetrakis(pentafluorophenyl)borate, decamethylferrocenium tetrakis(pentafluorophenyl)borate, silver tetrakis(pentafluorophenyl)borate, trityl tetrakis(pentafluorophenyl)borate, lithium tetrakis(pentafluorophenyl)borate, sodium tetrakis(pentafluorophenyl)borate, tetraphenylporphyrinmanganese tetrakis(pentafluorophenyl)borate, silver tetrafluoroborate, silver hexafluorophosphate, silver hexafluoroarsenate, silver perchlorate, silver trifluoroacetate, silver trifluoromethanesulfonate and the like.

The component (b-1) compounds may be used alone or in combination of two or more kinds thereof.

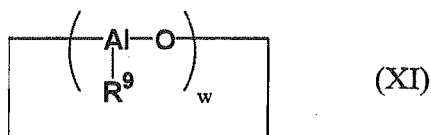
[0038] On the other hand, the examples of the aluminoxane of the component (b-2) include a linear aluminoxane represented by Formula (X):

[0039]



[0040] (wherein R^9 represents a hydrocarbon group having 1 to 20 carbon atoms, preferably having 1 to 12 carbon atoms, such as an alkyl group, an alkenyl group, an aryl group, an arylalkyl group and the like, or a halogen atom; w represents an average polymerization degree and is usually an integer of 2 to 50, preferably 2 to 40; and respective R^9 may be the same or different) and a cyclic aluminosiloxane represented by Formula (XI):

[0041]



[0042] (wherein R^9 and w are the same as those in Formula (X) described above).

[0043] A method for producing the aluminosiloxanes described above includes a method in which alkylaluminum is brought into contact with a condensing agent such as water and the like. However, the means therefor shall not specifically be restricted and can be carried out according to publicly known methods.

For example, they may include (1) a method in which an organic aluminum compound is dissolved in an organic solvent and then the solution is brought into contact with water; (2) a method in which an organic aluminum compound is added at first in polymerization and water is then added thereto; (3) a method in which crystal water contained in a metal salt or the like or water adsorbed into an inorganic substance or an organic substance is reacted with an organic aluminum compound; (4) a method in which a trialkylaluminum is reacted with a tetraalkyldialuminosiloxane and then water is further reacted therewith; and the like. Furthermore, the aluminosiloxane may be insoluble in toluene. These aluminosiloxanes may be used alone or in combination of two or more kinds thereof.

[0044] A proportion of the catalyst component (a) to the catalyst component (b) falls in a range of preferably 10 : 1 to 1 : 100, more preferably 2 : 1 to 1 : 10 in terms of a mole ratio when the compound (b-1) is used as the catalyst component. When it is outside the ranges described above, the catalyst cost per a unit mass of the polymer grows high and is not practical. Furthermore, when the compound (b-2) is used, the proportion falls in a range of preferably 1 : 1 to 1 : 1000000, more preferably 1 : 10 to 1 : 10000 in terms of a mole ratio. When it is outside these ranges, the catalyst cost per a unit mass of the polymer grows high and is not practical. Furthermore, the components (b-1) and (b-2) can be used as the catalyst component (b) solely or in combination of two or more kinds thereof.

[0045] The component (a) and the component (b) may be contained as the principal components, or the component (a), the component (b) and an organic aluminum compound (c) may be contained as the principal components as for the catalyst in the present invention. In this regard, a compound represented by Formula (XII):



(wherein R^{20} represents an alkyl group having 1 to 10 carbon atoms; Q represents a hydrogen atom, an alkoxy group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms or a halogen atom; and v is an integer of 1 to 3) is used as the organic aluminum compound of the component (c).

[0046] The examples of the compound represented by Formula (XII) include trimethylaluminum, triethylaluminum, triisopropylaluminum, triisobutylaluminum, dimethylaluminum chloride, diethylaluminum chloride, methylaluminum dichloride, ethylaluminum dichloride, dimethylaluminum fluoride, diisobutylaluminum hydride, diethylaluminum hydride, ethylaluminum sesquichloride and the like. These organic aluminum compounds may be used alone or in combination of two or more kinds thereof. A proportion of the component (a) to the component (c) is preferably 1 : 1 to 1 : 10,000, more preferably 1 : 5 to 1 : 2,000 and most preferably 1 : 10 to 1 : 1,000 in terms of a mole ratio. The use of the component (c) makes it possible to enhance the activity per the transition metal. However, if it is too much, the organic aluminum compound is used in vain and remains in the α -olefin polymer in a large amount, and therefore it is not preferred.

[0047] An α -olefin having 3 to 14 carbon atoms is usually used as a monomer for producing the component A (poly- α -olefin produced by using the metallocene catalyst) in the present invention, and the examples thereof include propylene, 1-butene, 3-methyl-1-butene, 4-methyl-1-butene, 4-phenyl-1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 3,3-dimethyl-1-pentene, 3,4-dimethyl-1-pentene, 4,4-dimethyl-1-pentene, 1-hexene, 4-methyl-1-hexene, 5-methyl-1-hexene, 6-phenyl-1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene and the like. Among them, the α -olefin

selected from 1-octene, 1-decene and 1-dodecene is preferred since a poly- α -olefin having a targeted kinetic viscosity is liable to be obtained, and 1-decene is particularly preferred. Furthermore, a copolymer obtained by using two or more kinds of the α -olefins having 3 to 14 carbon atoms may be used as the component A, and in such a case, the α -olefin selected from 1-octene, 1-decene and 1-dodecene is particularly preferred.

[0048] A blend proportion [metallocene compound (mmol)/ α -olefin (L)] of the metallocene compound represented by Formula (I) or (IV) to the α -olefin having 3 to 14 carbon atoms is usually 0.01 to 0.4, preferably 0.05 to 0.3 and more preferably 0.1 to 0.2. If it is 0.01 or more, the sufficiently high catalytic activity is obtained. On the other hand, if it is 0.4 or less, a yield of the oligomer of a trimer or higher which is suited as the base oil for the lubricant is improved, and the catalyst is prevented from being incompletely removed by deashing.

[0049] The polymerization of the α -olefin having 3 to 14 carbon atoms described above is preferably conducted in the presence of hydrogen. An addition amount of the hydrogen is usually 0.1 to 500 kPa, preferably 0.5 to 300 kPa and more preferably 1 to 200 kPa. If the addition amount of the hydrogen is 0.1 kPa or more, the sufficiently high catalytic activity is obtained. On the other hand, if it is 500 kPa or less, the generation of a saturated substance from the raw material α -olefin can be reduced, and a yield of the targeted α -olefin is improved.

[0050] A reaction method of polymerizing the α -olefin having 3 to 14 carbon atoms described above shall not be restricted, but may be carried out under the absence of a solvent or may be carried in a solvent, and any methods may be used. When a reaction solvent is used, the examples thereof include an aromatic hydrocarbon such as benzene, toluene, xylene, ethylbenzene and the like; an alicyclic hydrocarbon such as cyclopentane, cyclohexane, methylcyclohexane and the like; an aliphatic hydrocarbon such as pentane, hexane, heptane, octane and the like; and a halogenated hydrocarbon such as chloroform, dichloromethane and the like. A temperature of the polymerization reaction is usually 0 to 200°C, preferably 20 to 180°C and more preferably 30 to 150°C. If it falls in the ranges described above, the sufficiently high catalytic activity is obtained, and a yield of the oligomer of a trimer or higher which is suited as the base oil for the lubricant is improved. The component A in which a selectivity of a trimer or higher is 50 % or more can be produced by carrying out the polymerization by the method described above.

[0051] As shown above, the component A, which is different from conventional poly- α -olefins in terms of a structure of molecules and a high homogeneity thereof, exhibits a high oxidation stability and a high viscosity index, and it is excellent as a base oil for lubricants. A viscosity index of the component A is preferably 150 to 350, more preferably 165 to 300 from the viewpoint of improving the fluidity at low temperature.

Accordingly, the grease composition of the present invention is different from grease compositions prepared by using a conventional poly- α -olefin, and hence the low-temperature viscosity characteristics are improved and the dependence on a viscosity index-improving agent is reduced, by increasing the viscosity index. As the result, the grease composition of the present invention can inhibit the fretting wear caused by a change in a load in a thrust direction as well as the fretting wear caused by a small vibration in an oscillating direction.

[Component B]

[0052] It is preferable that the grease composition of the present invention contains the component B having the kinetic viscosity of 70 mm²/s or less at 40°C as well as the component A, from the viewpoint of improving the fretting wear and a pumping property. From the viewpoint described above, the kinetic viscosity of the component B at 40°C is preferably 10 to 50 mm²/s, more preferably 20 to 45 mm²/s and most preferably 20 to 40 mm²/s. The kinetic viscosity of the component B at 100°C is preferably 13 mm²/s or less, more preferably 3 to 9 mm²/s. In addition, the viscosity index of the component B is preferably 70 to 250, more preferably 120 to 200, from the viewpoint of improving the fluidity at low temperature.

[0053] The component B is an olefin oligomer, such as an oligomer of an α -olefin (which can be either a single matter or a mixture) having 4 to 18 carbon atoms, preferably having 6 to 14 carbon atoms and most preferably having 8 to 12 carbon atoms; a co-oligomer of 1-decene and ethylene; and the like. These may be used alone or in a mixture. These olefin oligomers may be one that is synthesized by known production methods, or may be one that is synthesized by production methods described in Japanese Patent Application Laid-Open No. 07-133234 and Japanese Patent Application Laid-Open No. 03-131612. Furthermore, arbitrary base oil, such as a diester, a polyol ester, an aromatic ester, an alkyl-substituted diphenyl ether, a mineral oil and the like may be used, but the synthetic oil having a fluid point of -35°C or lower are preferred from the viewpoint of a low-temperature fluidity.

[Base oil]

[0054] If necessary, the base oil may contain other synthetic oil or mineral oil as well as the component A, preferably in addition to the component B.

[0055] The examples of the other synthetic oil include alkylbenzenes such as monoalkylbenzenes, dialkylbenzenes and the like; and alkylnaphthalenes such as monoalkylnaphthalenes, dialkylnaphthalenes, polyalkylnaphthalenes and

the like. The ester base oil includes a diester oil such as dibutyl sebacate, di-2-ethylhexyl sebacate, dioctyl adipate, diisodecyl adipate, dtridecyl adipate, dtridecyl glutarate, methyl-acetyl sinolate and the like; an aromatic ester oil such as trioctyl trimellitate, tridecyl trimellitate, tetraoctyl pyromellitate and the like; a polyol ester oil such as trimethylolpropane caprylate, trimethylolpropane pelargonate, pentaerythritol-2-ethylhexanoate, pentaerythritol pelargonate and the like; and a complex ester oil which are oligoesters of polyhydric alcohols with mixed fatty acids of dibasic acids and monobasic acids; and the like. The ether base oil include a polyglycol such as polyethylene glycol, polypropylene glycol, polyethylene glycol monoethers, polypropylene glycol monoethers and the like; a phenyl ether oil such as monoalkyl triphenyl ethers, alkyl diphenyl ethers, dialkyl diphenyl ethers, pentaphenyl ether, tetraphenyl ether, monoalkyl tetraphenyl ethers, dialkyl tetraphenyl ethers and the like; and olefin base oligomers such as co-oligomers of normal paraffins, isoparaffins, polybutene, polyisobutylene, 1-decene oligomers and 1-decene with ethylene.

Each of the synthetic oils described above may be used alone or in a mixture.

[0056] As the mineral oil, compounds that are refined by suitably combining distillation under reduced pressure, oil solution deasphalting, solvent extraction, hydrocracking, solvent dewaxing, sulfuric acid washing, white clay refining, hydrogenation refining and the like can be used.

[0057] In the present invention, the kinetic viscosity of the base oil at 40°C is preferably 150 to 2000 mm²/s, more preferably 200 to 1000 mm²/s and most preferably 300 to 700 mm²/s, from the viewpoint of an excellent fretting wear and an excellent bearing wear property. Furthermore, the kinetic viscosity of the base oil at 100°C is preferably 14 to 300 mm²/s, more preferably 16 to 150 mm²/s. A viscosity index of the base oil is preferably 90 to 350, more preferably 120 to 350, from the viewpoint of enhancing the fluidity at low temperatures.

[0058] The grease composition of the present invention preferably contains the component A in a proportion of 20 % by mass or more, more preferably contains it in a proportion of 30 % by mass or more and most preferably contains it in a proportion of 50 % by mass or more, based on a whole amount of the composition, from the viewpoint of inhibiting simultaneously the bearing wear and the fretting wear to elongate a life of a bearing, and from the viewpoint of making it possible to inhibit the fretting wear caused by a change in a load in a thrust direction as well as the fretting wear brought about by a small vibration particularly in an oscillating direction. The upper limit thereof shall not specifically be restricted, but it is usually 90 % by mass, from the viewpoint of a blend ratio of the base oil. In addition, a content of the component A in the base oil is preferably 35 % by mass or more, more preferably 45 to 85 % by mass or more, from the same viewpoints as described above.

[0059] Furthermore, the base oil contains the component B preferably in a proportion of 10 to 70 % by mass, more preferably 15 to 60 % by mass, and most preferably 20 to 50 % by mass, based on a whole amount of the composition, from the viewpoints of becoming excellent in the fretting wear and the pumping property and being readily adjusted to a high viscosity. In addition, the content of the component B in the base oil is preferably 12 to 65 % by mass, more preferably 12 to 60 % by mass, and most preferably 17 to 55 % by mass, from the same viewpoints as described above.

[0060] When the component B is contained in the present invention, a proportion of the component A to the component B contained in the base oil is preferably 0.45 to 9.0, more preferably 1.0 to 5.0 in terms of a mass ratio (component A/component B) from the viewpoints of easiness in producing the grease and a pertinent viscosity of the base oil.

[Thickener]

[0061] The grease composition of the present invention contains a thickener. Any thickeners of an organic base and an inorganic base can be used as the thickener, and a soap base thickener are preferred from the viewpoint of the wear resistance. To be specific, it is preferably any of Li soap, Li complex soap, Ca soap, Ca sulfonate complex soap, and Ca complex soap, and it is more preferably soap containing 12-hydroxystearate in fatty acid constituting the soap. Above all, the soap preferably contains Li, and it is more preferably Li complex soap. The Li complex soap is excellent in a performance balance at low temperature to high temperature.

Furthermore, urea compounds, bentonite, silica, carbon black, PTFE and the like may be used as the thickener. They may be used alone or in a mixture.

[0062] The content of the thickener shall not be restricted as long as it falls in a range so that the thickener can form and maintain grease together with the base oil. However, it is preferably 17 % by mass or less based on a whole amount of the composition of the present invention, from the viewpoints of making it possible to inhibit the fretting wear caused by a change in a load in a thrust direction as well as the fretting wear caused by a small vibration in an oscillating direction and becoming excellent in a pumping property. From the viewpoints described above, the blend amount of the thickener is more preferably 14 % by mass or less, particularly preferably 12 % by mass or less, based on a whole amount of the composition.

In this connection, the content of the thickener is expressed as the amount of carboxylic acid constituting the thickener in a case of a soap base thickener. In a case of a urea base thickener, it is expressed as the amount of a reaction product of isocyanate and amine.

[0063] Furthermore, in respect to a method for producing the thickener, it is preferable to obtain the thickener by mixing

a carboxylic acid and an alkali and then conducting saponification reaction in the component B of the base oil.

The carboxylic acid includes a crude fatty acid obtained by hydrolyzing oil and fat and then removing glycerin; a mono-carboxylic acid such as stearic acid and the like; a monohydroxycarboxylic acid such as 12-hydroxystearic acid and the like; a dibasic acid such as azelaic acid and the like; and an aromatic carboxylic acid such as terephthalic acid, salicylic acid, benzoic acid and the like. Furthermore, an ester of the carboxylic acid may be used. These may be used alone or in combination of two or more kinds thereof.

The alkali described above includes a metal hydroxide of an alkali metal or an alkaline earth metal. The metal includes sodium, potassium, calcium, lithium, aluminum and the like.

[Other components]

[0064] It is preferable that an extreme pressure agent containing sulfur is blended into the grease composition of the present invention in a proportion of 0.01 to 10 % by mass, based on a whole amount of the composition from the viewpoint of obtaining a blend effect such as prevention of seizing.

The extreme pressure agent includes zinc dialkyldithiophosphate (ZnDTP), molybdenum dialkyldithiophosphate (MoDTP), zinc dithiocarbamate (ZnDTC), molybdenum dithiocarbamate (MoDTC), dithiocarbamine (DTC), thiophosphate, sulfurized oil and fat, dibenzyl disulfide, thiadiazole and the like. These compounds may be used alone or in a mixture of two or more kinds thereof.

[0065] Furthermore, resins and waxes which are soluble in the base oil, such as a petroleum resin, polyethylene and the like, may be blended into the grease composition of the present invention and the petroleum resin is preferred among these. The blend amount of the petroleum resin is preferably 0.5 to 35 % by mass based on a whole amount of the composition from the viewpoints of maintaining the suitable viscosity and obtaining a good low-temperature torque. From the viewpoints described above, the blend amount of the petroleum resin is more preferably 1 to 30 % by mass, most preferably 2 to 25 % by mass based on a whole amount of the composition.

[0066] As the petroleum resin, for example cyclopentadiene type is preferred, and materials obtained by thermally copolymerizing a cyclopentadiene compound with an α -olefin or a monovinyl aromatic hydrocarbon, materials obtained by hydrogenating these by an ordinary method if necessary, or mixtures thereof are preferred.

Cyclopentadiene, multimers thereof, their alkyl-substituted compounds, or mixtures thereof can be used as the cyclopentadiene compound described above, and it is industrially advantageous to use cyclopentadiene based fractions (CPD fraction) containing about 30 % by mass or more, preferably about 50 % by mass or more of the cyclopentadiene compound that is obtained by steam cracking of naphtha and the like. This CPD fraction may contain an olefinic monomer that is copolymerizable with these alicyclic dienes. The examples of the olefinic monomer include an aliphatic diolefin such as isoprene, piperylene, butadiene and the like; and an alicyclic olefin such as cyclopentene and the like. The concentration of the olefin is preferably lowered, and about 10 % by mass or less with respect to the cyclopentadiene compound is permissible.

[0067] An α -olefin having 4 to 18 carbon atoms, preferably having 4 to 12 carbon atoms or a mixture thereof is used as the α -olefin that is the raw materials for copolymerization with the cyclopentadiene compound. Above these, a derivative obtained from ethylene, propylene, 1-butene or the like, or a decomposition product of paraffin wax, or the like is preferably used. It is industrially preferable that the α -olefin is blended in an amount of less than about 4 mole per a mole of the cyclopentadiene compound.

[0068] Styrene, o, m, or p-vinyltoluene, α,β -methylstyrene or the like is used as the monovinyl aromatic hydrocarbon that is the other raw materials for the copolymerization. This monovinyl aromatic hydrocarbon may contain indenenes such as indene, methylindene, ethylindene and the like, and it is industrially advantageous to use a so-called C9 fraction obtained by steam cracking of naphtha and the like. It is industrially preferable that the monovinyl aromatic hydrocarbon is blended in an amount of less than about 3 moles per a mole of the cyclopentadiene compound, when it is used as the raw material for the copolymerization.

[Grease composition]

[0069] A worked penetration of the grease composition of the present invention is preferably 220 to 350 from the viewpoints of controlling a hardness of the grease, maintaining a good low temperature torque and preventing the bearing wear and the fretting wear. The worked penetration is more preferably 250 to 340, further preferably 265 to 320 from the viewpoints described above.

[0070] In the grease composition of the present invention, additives such as an antioxidant, a rust preventive, a solid lubricant, a filler, an oil agent, a metal deactivator, a water resistant agent, another extreme pressure agent, a wear resistant agent, a viscosity index-improving agent, a colorant and the like may be blended, if necessary, as long as the objects of the present invention are achieved.

The examples of the antioxidant include an amine base antioxidant such as alkylated diphenylamines, phenyl- α -naph-

thylamine, alkylated α -naphthylamines and the like; a phenol base antioxidant such as 2,6-di-*t*-butyl-4-methylphenol, 4,4'-methylenebis(2,6-di-*t*-butylphenol) and the like; and a peroxide decomposition agent such as sulfur base ZnDTP and the like. These are used usually in a proportion of 0.05 to 10 % by mass.

[0071] The rust preventive includes sodium nitrite, sulfonates, sorbitan monooleate, a fatty acid soap, an amine compound, succinic acid derivatives, thiadiazole, benzotriazole, benzotriazole derivatives and the like.

The examples of the other extreme pressure agent and wear resistant agent include a phosphorus base compound such as phosphoric esters, acid phosphates, phosphorous esters, acid phosphites, alkyl hydrogen phosphites, phosphoric ester amine salts, phosphorous ester amine salts and the like; a chlorine base compound such as chlorinated oil and fat, chlorinated paraffins, chlorinated fatty acid esters, chlorinated fatty acids and the like; an ester base compound such as alkyl- or alkenylmaleic esters, alkyl- or alkenylsuccinic esters and the like, organic an acid base compound such as alkyl- or alkenylmaleic acids, alkyl- or alkenylsuccinic acids and the like and an organic metal base compound such as naphthenic acid salts and the like.

[0072] The solid lubricant includes polyimides, PTFE, graphite, metal oxides, boron nitride, melamine cyanurate (MCA), molybdenum disulfide and the like.

Various kinds of the above additives may be blended alone or in combination of several kinds thereof, and the lubricant additives according to the present invention shall not inhibit the effect thereof.

[Grease Composition for Wind Power Generation]

[0073] The grease composition of the present invention is used suitably for a wind power generation apparatus. Fig. 1 is a schematic view showing a wind power generation apparatus for which the grease composition of the present invention is used. As shown in Fig. 1, the wind power generation apparatus 1 comprises blades 5; a main shaft 4 fixing the blades 5; an electric generator 31 driven by a rotation of the main shaft 4; a nacell 3 storing a main bearing 33 contacted with the main shaft 4 and a yaw-bearing 32; and a tower 2 supporting the nacell 3. Further, a pitch bearing 41 is contacted with a blade shaft 51. For example, the blades 5 can be controlled by rotating the blade shaft 51 so that they are liable to receive wind or hard to receive wind, and therefore the rotation of the main shaft 4 is stabilized. Due to this, a stable electric power can be obtained from the electric generator 31.

[0074] It is preferable that the grease composition of the present invention is used for the main bearing 33 and the pitch bearing 41. Although a wear is liable to be caused on a roller of the bearing, a retainer, a bearing race and the like, due to high loads applied by the blade 5 and the main shaft 4 each having a high weight, and a fretting wear of the bearing race is liable to be caused due to a fluctuation and an oscillation of the rotation in the main bearing 33 and the pitch bearing 41, the bearing wear and fretting wear can be prevented by using the grease of the present invention. Moreover, if the wind power generation apparatus 1 is a small size apparatus having an output power of less than 300 kW, the load thereon is small, and therefore the effect is reduced. It is preferable that the wind power generation apparatus 1 is a medium size apparatus or a large size apparatus, preferably having an output power of 300 kW or more, more preferably 700 kW or more.

Furthermore, the main bearing 33 and the pitch bearing 41 may be connected with a pump for supplying the grease via a pipe which is not shown in Figure. The grease can be readily supplied to the main bearing 33 and the pitch bearing 41 by operating the pump. Accordingly, a work in a high place is unnecessary, which improves the workability.

[0075] The grease composition of the present invention can be used for various gears, various bearings (a ball bearing, a roller bearing, a sliding bearing, a pin-bush and the like), a roller for a paper machine, a bearing for iron and steel facility, a swing bearing for a construction machine, a geared motor, a bearing for an automobile wheel, a bearing for an electric generator, a motor bearing, a ball screw and the like.

In particular, it may be used for an apparatus in which a rolling motion is carried out, such as a rolling bearing, a ball screw, a linear guide and the like in a high-load application. For example, it can be used for an electric cylinder, an electric linear actuator, a jack, a linear operating machine and the like.

EXAMPLES

[0076] Next, the present invention shall be specifically explained with reference to examples, but the present invention shall not be restricted by these examples. Incidentally, the respective base oils and additives used in the following examples and comparative examples are as shown in the following Table 1.

[0077]

[Table 1]

5	Component A	M-PAO-1200	Kinetic viscosity (40°C/100°C): 1221/124 mm ² /s, density (15°C): 0.850 g/cm ³ , viscosity index: 207
		M-PAO-400	Kinetic viscosity (40°C/100°C): 407/47.0 mm ² /s, density (15°C): 0.846 g/cm ³ , viscosity index: 175
10 15	Component B	M-PAO-30 (manufactured by Idemitsu Kosan Co., Ltd., LINEALENE® PAO)	Kinetic viscosity (40°C/100°C): 29.5/5.79 mm ² /s, density (15°C): 0.824 g/cm ³ , viscosity index: 142
		M-PAO-45 (manufactured by Idemitsu Kosan Co., Ltd., LINEALENE® PAO)	Kinetic viscosity (40°C/100°C): 44.6/7.79 mm ² /s, density (15°C): 0.829 g/cm ³ , viscosity index: 145
		PAO-30	Kinetic viscosity (40°C/100°C): 30.1/5.78 mm ² /s, density (15°C): 0.826 g/cm ³ , viscosity index: 137
20	Other components	PAO-400	Kinetic viscosity (40°C/100°C): 402/40.6 mm ² /s, density (15°C): 0.849 g/cm ³ , viscosity index: 152
		Olefin oligomer (manufactured by Mitsui Chemicals, Inc.)	Kinetic viscosity (40°C): 37500/2000 mm ² /s, density (15°C): 0.853 g/cm ³ , viscosity index: 299
25 30	Antioxidant		p,p'-dioctyldiphenylamine
	Rust preventive		Calcium sulfonate
	Extreme pressure agent		Zinc diamyldithiocarbamate

[0078] Incidentally, the component A in Table 1 is a poly- α -olefin produced by using the metallocene catalyst. M-PAO-400 and M-PAO-1200 used in the present examples were produced by the following methods.

M-PAO-400

[0079] After a stainless-made reactor having an internal volume of 107 liters was sufficiently dried and was replaced with nitrogen, 16.6 liters of 1-octene and 23.4 liters of 1-dodecene followed by 20 millimole of triisobutylaluminum were put therein, and then it was heated to 105°C. After putting 80 ml of a catalyst mixed solution therein that was separately prepared (700 ml of dehydrated toluene, 40 millimole of triisobutylaluminum, 0.8 millimole of (1,1'-dimethylsilylene)(2,2'-dimethylsilylene)-bis(cyclopentadienyl) zirconium dichloride, and 1.6 millimole of N,N-dimethylaniline tetrakis(pentafluorophenyl)borate in the form of powder were put in a glass-made Shlenk bottle having a volume of 2 liters under nitrogen atmosphere and stirred at room temperature for about 1 minute, and then 100 ml of 1-decene was added thereto and further stirred at room temperature for 1 hour), 0.02 MPaG of hydrogen was introduced thereto, and then the temperature was elevated to 107°C to initiate polymerization. Subsequently, while 80 ml of the catalyst mixed solution was added thereto every 60 minutes, they were reacted at 107°C for 300 minutes, and then 100 ml of methanol was added thereto to terminate the polymerization.

[0080] The content was discharged in two stainless-made vessels of 100 L by 20 liters, respectively, and 20 liters of toluene and 20 liters of a 1 mass % NaOH aqueous solution were added to each vessel and stirred for 1 hour. After the solution was left standing still for 1 hour, the aqueous phase was discharged; and 20 liters of purified water was then newly added thereto and stirred for 1 hour, and then the solution was left standing still for 1 hour, and the aqueous phase was discharged. This operation was repeated twice. The organic layer was filtrated through a filter of 2 μ m and then transferred into a stainless-made reactor having an internal volume of 107 liters. Next, light components such as toluene, the raw materials, methanol and the like were removed by distillation at 140°C under a reduced pressure of about 3.0×10^{-1} MPa to obtain 23.1 kg of a clear and colorless viscous liquid. The obtained viscous liquid 5 kg was distilled at 180°C under a reduced pressure of about 5×10^{-6} MPa by using a thin film distillation apparatus (short path distillation apparatus KDL-5, manufactured by UIC Inc.) to obtain 4.5 kg of a clear and colorless viscous liquid from which components having 20 or less carbon atoms were completely removed.

3.0 kg of the obtained viscous liquid was put in a stainless-made autoclave having an internal volume of 5 liters, and then 1 % by mass of a stabilized nickel catalyst (SN750, manufactured by Sakai Chemical Industry Co., Ltd.) in terms of a weight ratio was added thereto, followed by carrying out reaction at 130°C for 6 hours under hydrogen of 2 MPa. After finishing the reaction, the temperature was lowered to the vicinity of 80°C, and then the content was taken out. The catalyst component was separated by filtrating at 70°C through a filter of 1 μm to obtain 3.0 kg of a hydride (M-PAO-400).

M-PAO-1200

[0081] The same operation as in the production of M-PAO-400 was conducted, except that the polymerization temperature was changed to 90°C, so as to obtain 24.2 kg of a clear and colorless viscous liquid from which light components were removed. Then, 4.7 kg of a clear and colorless viscous liquid from which components having 20 or less carbon atoms were completely removed was obtained, and then 3.0 kg of a hydride (M-PAO-1200) was obtained.

Examples 1 to 5 and Comparative Example 1.

[0082]

(1) PAO-30 (or M-PAO-30, or M-PAO-45), 12-hydroxystearic acid, azelaic acid and the rust preventive in the amounts shown in Table 1 were heated at 95°C in a reaction vessel while stirring them.

(2) Lithium hydroxide (monohydrate) was dissolved in water having five times its amount (mass ratio). This aqueous solution was added to the solution of (1) and mixed while heating. After a temperature of the mixture reached 195°C, it was held for 5 minutes.

(3) Next, after the remaining base oil (M-PAO-1200, M-PAO-400 or an olefin oligomer) was added thereto, the mixture was cooled down to 80°C at 50°C/hour, and an antioxidant and an extreme pressure agent in the amounts shown in Table 2 were added and mixed.

(4) In addition, the mixture was left cooling naturally down to room temperature and then subjected to finishing treatment by using a three-roll equipment to obtain a grease composition for Examples 1 to 5 and Comparative Example 1.

Comparative Examples 2 to 4

[0083]

(1) A part (50 % by mass based on the amount of the finished grease) of the base oil shown in Table 2 and 12-hydroxystearic acid, azelaic acid and the rust preventive in the amounts as shown in Table 2 were heated at 95°C in a reaction vessel while stirring.

(2) Lithium hydroxide (monohydrate) was dissolved in water having five times its amount (mass ratio). This aqueous solution was added to the solution of (1) and mixed while heating. After a temperature of the mixture reached 195°C, it was held for 5 minutes.

(3) Next, after the remaining base oil was added thereto, the mixture was cooled down to 80°C at 50°C/hour, and the antioxidant and the extreme pressure agent in the amounts as shown in Table 1 were added and mixed.

(4) In addition, the mixture was left cooling naturally down to room temperature and then subjected to finishing treatment by using a three-roll equipment to obtain the grease composition for Comparative Examples 2 to 4.

Example 6 and Comparative Example 5

[0084]

(1) 1 mole of Diphenylmethane-4,4'-diisocyanate (MDI) was heated and dissolved in 2/3 mass of a whole amount of the base oil to prepare a raw material 1.

(2) Furthermore, 2 moles of cyclohexylamine was dissolved in the remaining base oil while stirring to prepare a raw material 2.

(3) Next, the raw material 2 was gradually added to the raw material 1 which was heavily stirring at 50 to 60°C in a grease reaction vessel. The mixture was heated while stirring, and after a temperature of the grease composition reached 165°C, it was held for 1 hour.

(4) Then, the mixture was cooled down to 80°C at 50°C/hour, and the antioxidant and the extreme pressure agent in the amounts shown in Table 1 were added thereto and mixed. The mixture was left cooling naturally down to

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room temperature and then subjected to finishing treatment by using a three-roll equipment to obtain the grease composition for Example 6 and Comparative Example 5.

The grease composition that was obtained in each of Examples 1 to 6 and Comparative Examples 1 to 5 was evaluated for the following properties. The results are shown in Table 2.

[0085]

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Table 2

			Example					
			1	2	3	4	5	6
Blend composition (% by mass)								
Thickener		12-hydroxy-stearic acid	5.00	5.50	7.50	5.00	5.00	Urea 14 %
		Azelaic acid	4.00	4.40	4.00	4.00	4.00	
		Lithium hydroxide Monohydrate	2.60	2.86	2.95	2.60	2.60	
Additive		Antioxidant	1.00	1.00	1.00	1.00	1.00	1.00
		Rust preventive	1.00	1.00	1.00	1.00	1.00	1.00
		Extreme pressure agent	3.00	3.00	3.00	3.00	3.00	3.00
Base oil	Component A	M-PAO-1200	62.55	61.68	53.70	53.40	-	60.75
		M-PAO-400	-	-	-	-	71.40	-
	Other components	PAO-400	-	-	-	-	-	-
		Olefin oligomer	-	-	-	-	-	-
	Component B	M-PAO-30	-	20.56	-	-	12.00	-
		M-PAO-45	-	-	26.85	-	-	-
		PAO-30	20.85			30.00	-	20.25
Total			100.00	100.00	100.00	100.00	100.00	100.00
Base oil kinetic viscosity (40°C) mm ² /s			400	460	400	260	260	400
Thickener amount (*)			9.0	9.9	11.5	9.0	9.0	14.0
Worked penetration 25°C, 60 times worked			304	290	276	298	284	287
Dropping point °C			290 or more	290 or more	290 or more	290 or more	290 or more	290 or more
Fretting wear test (ASTM D4170 method) mg			2.1	2.6	7.0	2.0	2.5	11.2
Fretting wear test (thrust load change method)			o	o	o	o	o	o
Low temperature torque test (-40°C) mN•m			360/85	360/88	510/90	300/82	450/136	590/120
High-load bearing wear test								
Rolling element wear amount m _{w50} mg			8	6	8	13	15	44
Bearing ring wear amount m ₅₀ mg			8	7	6	13	17	38
Retainer wear amount m _{k50} mg			29	23	27	44	84	110
Grease pumping property Pump discharge pressure, MPa			23.5	25.9	26.8	24.3	25.0	27.3
Pressure oil separation (IP121 method) 40°C, 42 hours, wt %.			0.7	0.4	0.2	1.5	1.4	0.3

Table 2 (continued)

			Comparative Example				
			1	2	3	4	5
Blend composition (% by mass)							
Thickener		12-hydroxy-stearic acid	6.00	14.00	5.00	5.00	Urea 14 %
		Azelaic acid	4.00	5.00	4.00	4.00	
		Lithium hydroxide Monohydrate	2.70	4.35	2.60	2.60	
Additive		Antioxidant	1.00	1.00	1.00	1.00	1.00
		Rust preventive	1.00	1.00	1.00	1.00	1.00
		Extreme pressure agent	3.00	3.00	3.00	3.00	3.00
Base oil	Component A	M-PAO-1200	-	-	-	-	-
		M-PAO-400	-	-	-	-	-
	Other components	PAO-400	-	69.86	-	-	-
		Olefin oligomer	24.28	1.79	-	-	23.89
	Component B	M-PAO-30	-	-	-	83.40	-
		M-PAO-45	-	-	-	-	-
		PAO-30	58.02	-	83.40	-	57.11
Total			100.00	100.00	100.00	100.00	100.00
Base oil kinetic viscosity (40°C) mm ² /s			460	460	30	30	400
Thickener amount (*)			10.0	19.0	9.0	9.0	14.0
Worked penetration 25°C, 60 times worked			305	294	290	284	2286
Dropping point °C			290 or more	265	290 or more	290 or more	290 or more
Fretting wear test (ASTM D4170 method) mg			2.6	43.6	1.9	1.0	13.4
Fretting wear test (thrust load change method)			Δ	o	x	x	Δ
Low-temperature torque test (-40°C) mN•m			370/ 90	1460/ 1200	130/ 38	120/ 35	600/ 120
High-load bearing wear test							
Rolling element wear amount m _{w50} mg			-	20	56	-	68
Bearing ring wear amount m _{w50} mg			-	27	46	-	52
Retainer wear amount m _{w50} mg			-	65	166	-	146
Grease pumping property Pump discharge pressure MPa			-	29.6	-	-	27.9
Pressure oil separation (IP121 method) 40°C, 42 hours, wt %			1.3	1.2	16.3	15.7	0.3

(*) A carboxylic acid amount (12-hydroxystearic acid + azelaic acid) was defined as the thickener amount.

In Table 2, the thickener blend amount was defined as the carboxylic acid amount (12-hydroxystearic acid + azelaic acid).

[Evaluation methods]

[0086] The specific evaluation methods shall be shown below. (

- (1) Kinetic viscosity: measured by a method prescribed in JIS K 2283.
- (2) Worked penetration: measured by a method prescribed in JIS K 2220.7 (25°C, 60 W).
- (3) Dropping point: measured by a method prescribed in JIS K 2220.8.
- (4) Fretting wear test: measured by a method prescribed in ASTM D4170. The sample was set in a test room controlled to $(22 \pm 2^\circ\text{C})$, and the temperature was not controlled after the test was started.

[0087]

- (5) Fretting wear test (thrust load changing method): a thrust load of 0.01 to 0.69 kN was applied to a thrust ball bearing of Designation 51103 (manufactured by NSK Ltd.) in which the number of balls was reduced to 3 balls at a frequency of 10 Hz.

The test was carried out for 8 hours in a room controlled to $22 \pm 2^\circ\text{C}$. A trace of wear which looked elliptical in the bearing after the test was observed and was evaluated according to the following criteria:

- ×: clear wear is observed, and the trace of wear is formed in a doughnut form over a whole periphery of the elliptical trace of wear.
- Δ: clear wear is observed
- : only dent(s) are observed or the wear is not observed

[0088]

- (6) Low-temperature torque test: measured by a method prescribed in JIS K 2220.18. The test was carried out at a temperature of -40°C .
- (7) High-load bearing wear test: measured by a method prescribed in DIN 51819-2. (test condition: DIN 51819-2-C-75/50-120, load 50 kN, temperature 120°C , revolution 75 rpm), the weights of bearing rings (inside ring + outside ring), a rolling element (total of 16 rollers), and the retainer were measured before and after the test, and a reduction in a weight per one bearing was determined as a 50 % probability of wear which is prescribed in DIN 51819-2.11.

[0089]

- (8) Pressure oil separation: measured by a method prescribed in IP121 (40°C , 42 hours).
- (9) Grease pumping property: evaluated by a discharge pressure observed when the grease was pushed out by using an automatic feeding pump for a grease. A pressure meter (for measuring a discharge pressure) and a pipe (10 m) having an inner diameter of 4 mm were connected in this order with a grease discharge port of an automatic feeding pump (Quicklub Pump model 203, manufactured by Lincoln Industrial Corp.), and was further divided into two lines by using a distribution valve. A pipe having an inner diameter of 4 mm and a length of 4 m was connected with the lines, respectively, and the grease was discharged via a relief valve (12 MPa). The grease was filled in the pump and the pipes in a room controlled to 20 to 25°C . After the discharge pressure was stabilized, the pump was operated for 2 hours and the average discharge pressure (MPa) during this period was measured. The grease having a smaller discharge pressure can be discharged with a smaller pressure and therefore is more excellent in a pumping property.

[Evaluation results]

[0090] As apparent from the results shown in Table 2, it can be found that all of the grease compositions prepared in Examples 1 to 6 were excellent in a bearing wear characteristic, a fretting wear characteristic, a low-temperature performance and a pumping property. It can be found that particularly in Examples 3 and 6, the grease compositions were excellent in a low-temperature torque property and that they can suitably be used for wind power generation apparatuses which are installed outdoors as well. On the other hand, since the high-viscosity component A was not contained in Comparative Examples 1 to 5, they cannot achieve the reduction both in the fretting wear caused by the small vibration to an oscillating direction and in the fretting wear caused by a change in a load in a thrust direction, and they are also inferior in a bearing characteristic.

INDUSTRIAL APPLICABILITY

[0091] The grease composition of the present invention can be used for various gears, various bearings (a ball bearing, a roller bearing, a sliding bearing, a pin-bush and the like), a roller for a paper machine, a bearing for iron and steel facility, a swing bearing for construction machine, a geared motor, a bearing for a automobile wheel, a bearing for an electric generator, a motor bearing, a ball screw and the like. In particular, it can suitably be used as a grease composition used for a main bearing and a pitch bearing which are mounted in a wind power generation apparatus and the like.

EXPLANATION OF REFERENCES

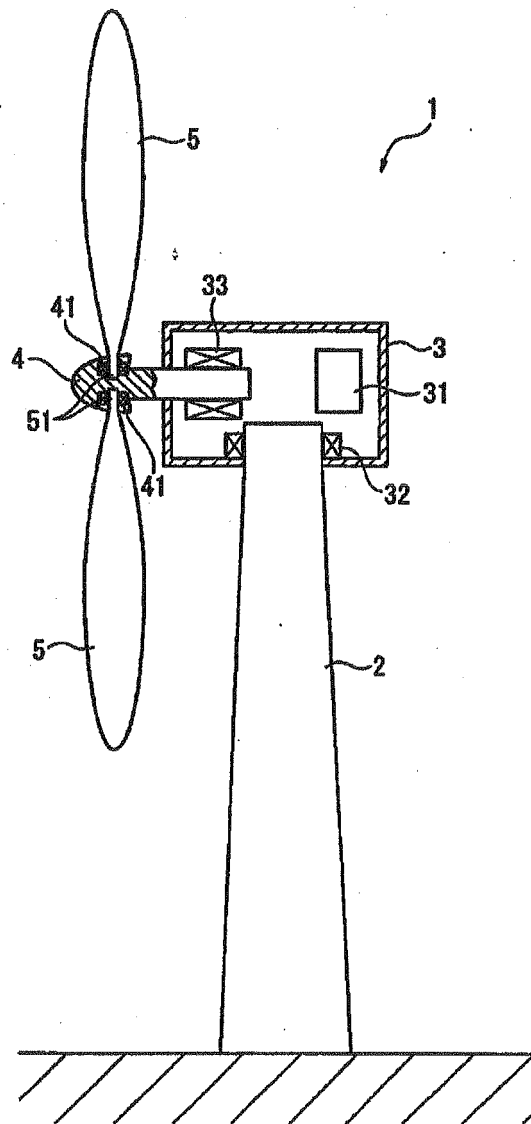
[0092]

- 1: wind power generation apparatus
- 2: tower
- 3: nacell
- 4: main shaft
- 5: blade
- 31: electric generator
- 32: yaw bearing
- 33: main bearing
- 41: pitch bearing
- 51: blade bearing

Claims

1. A grease composition comprising a base oil and a thickener, the base oil containing a poly- α -olefin (component A) that has a kinetic viscosity of 300 mm²/s or more at 40°C and that is produced by a metallocene catalyst.
2. The grease composition according to claim 1, wherein the kinetic viscosity of the component A at 40°C is 600 mm²/s or more.
3. The grease composition according to claim 1 or 2, containing 20 % by mass or more of the component A based on a whole amount of the composition.
4. The grease composition according to any of claims 1 to 3, wherein the base oil has a kinetic viscosity of 150 to 2000 mm²/s at 40°C and a worked penetration of 220 to 385.
5. The grease composition according to any of claims 1 to 4, wherein the base oil contains a component B having a kinetic viscosity of 70 mm²/s or less at 40°C in a proportion of 10 to 70 % by mass based on a whole amount of the composition.
6. The grease composition according to any of claims 1 to 5, containing 17 % by mass or less of the thickener based on a whole amount of the composition.
7. The grease composition according to any of claims 1 to 6, wherein the thickener is a soap base thickener.
8. The grease composition according to any of claims 1 to 7, wherein the thickener is produced by reacting a carboxylic acid with an alkali in the component B.
9. The grease composition according to any of claims 1 to 8, wherein an extreme pressure additive containing sulfur is blended therein in a proportion of 0.01 to 10 % by mass based on a whole amount of the composition.
10. The grease composition according to any of claims 1 to 9, wherein the grease composition is used for a wind power generation apparatus, and is used in at least one of a main bearing contacted with a main shaft with which a blade of the wind power generation apparatus is connected and a pitch bearing contacted with a blade shaft mounted in the blade.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2011/057462

A. CLASSIFICATION OF SUBJECT MATTER

C10M169/00(2006.01)i, C10M107/02(2006.01)n, C10M117/00(2006.01)n,
C10N20/00(2006.01)n, C10N20/02(2006.01)n, C10N30/00(2006.01)n, C10N30/06
(2006.01)n, C10N40/02(2006.01)n, C10N50/10(2006.01)n

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)

C10M169/00, C10M107/02, C10M117/00, C10N20/00, C10N20/02, C10N30/00,
C10N30/06, C10N40/02, C10N50/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2011
Kokai Jitsuyo Shinan Koho	1971-2011	Toroku Jitsuyo Shinan Koho	1994-2011

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 2007/069659 A1 (NSK Ltd.), 21 June 2007 (21.06.2007), claims; paragraphs [0018] to [0025]; examples & US 2010/0132499 A1 & EP 1972681 A1 & WO 2007/069304 A1	1-9
X	JP 2006-002018 A (NTN Corp.), 05 January 2006 (05.01.2006), claims; paragraphs [0008] to [0012], [0017]; examples & US 2005/0282640 A1 & EP 1607648 A2	1-9
X	JP 60-031598 A (Daihatsu Motor Co., Ltd.), 18 February 1985 (18.02.1985), claims; examples (Family: none)	1-6, 9



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"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

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"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
13 April, 2011 (13.04.11)

Date of mailing of the international search report
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Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2011/057462

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	JP 3-128994 A (Nippon Koyu Ltd.), 31 May 1991 (31.05.1991), claims; examples (Family: none)	1, 3-9
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X Y	Akihiko YANO et al., "Evaluation of Fretting Protection Property of Lubricating Grease Applied to Thrust Ball Bearing", Journal of Japanese Society of Tribologists, 2009, 54(1), pages 64 to 72	1-9 10
Y	JP 2006-161624 A (NTN Corp.), 22 June 2006 (22.06.2006), claims; examples & US 2007/0154128 A1 & EP 1719812 A1 & WO 2005/075610 A1	10
P, X	WO 2010/150726 A1 (Idemitsu Kosan Co., Ltd.), 29 December 2010 (29.12.2010), claims; examples (Family: none)	1-10
P, X	JP 2010-248442 A (Kyodo Yushi Co., Ltd.), 04 November 2010 (04.11.2010), claims; examples (Family: none)	1-10

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REFERENCES CITED IN THE DESCRIPTION

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- JP 2008038088 A [0003]
- JP 2007063423 A [0003]
- JP 7133234 A [0053]
- JP 3131612 A [0053]

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- 「Fretting Wear Resistant Characteristic of Lithium Soap Grease in Oscillating Thrust Ball Bearing」. *Tribologist*, 1997, vol. 42 (6), 492 [0004]