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(54) GREASE COMPOSITION

(57) Provided is a grease composition containing a base oil (A) and a urea-based thickener (B), the base oil (A) containing a poly-α-olefin (PAO), the urea-based thickener (B) being one or more selected from diurea compounds represented by the general formula (b1): R^1-NHCONH-R^3-NHCONH-R^2(b1), when a content of the chain hydrocarbon group in R^1 and R^2 in the general formula (b1) is X molar equivalents and a content of the alicyclic hydrocarbon group in R^1 and R^2 in the general formula (b1) is Y molar equivalents, the grease composition satisfying the following Requirement (1) and having an increased cone penetration at a low temperature (-40°C): Requirement (1): having a X/Y ratio of 2/1 to 10/1.

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Description

Technical Field

[0001] The present invention relates to a grease composition.

Background Art

[0002] Grease compositions can achieve sealing more easily as compared with lubricating oils, and enable size reduction and weight reduction of a machine in which they are applied. Thus, grease compositions have heretofore been widely used for lubricating various sliding parts of automobiles, electrical appliances, industrial apparatuses, manufacturing machinery, and the like.

[0003] For example, in a wheel of an automobile, since a fluid lubricating oil composition cannot be used, a semi-solid grease composition is used as a lubricant.

[0004] Further, in a bearing and the like of a hub mounted on a wheel of an automobile, from the viewpoint of sealing properties (encapsulation property, leakage prevention property), a rubber member is also used. This means that, in such a part, since a metal member and a rubber member are in contact with each other, lubrication in metal-rubber sliding is required.

[0005] For example, PTL 1 discloses, with an object of reducing the coefficient of friction between a rubber member and a metal member, a grease composition in which a synthetic hydrocarbon oil and a urea-based compound as a thickener are used.

[0006] In addition, PTL 2 discloses a technique in which a grease composition containing a synthetic hydrocarbon oil and a urea-based compound is applied in a hub unit.

Citation List

Patent Literature

[0007]

PTL 1: JP 2021-123691A

PTL 2: JP 2021-102772A

Summary of Invention

Technical Problem

[0008] A grease composition for use in automobiles is used in a wide range of temperature from about -40°C which is an ambient temperature before starting an engine in winter to about 40°C which is an ambient temperature in summer. Thus, a grease composition is required to be applicable in a wide range of temperature condition from a high temperature environment to a low temperature environment. In addition, from the viewpoint of sealing properties (encapsulation property, leakage prevention property) in a bearing and the like, a grease composition is required to have an appropriate softness regardless of the varied temperature condition.

[0009] However, in the techniques of PTL 1 and PTL 2, a cone penetration, which is a measure of the softness of a grease composition, under a low temperature (-40°C) environment is not sufficiently studied.

[0010] Thus, the present invention has an object to provide a grease composition having an increased cone penetration at a low temperature (-40°C).

Solution to Problem

[0011] The present invention provides the following [1] to [2]:

[1] A grease composition containing a base oil (A) and a urea-based thickener (B),

the base oil (A) containing a poly-α-olefin (PAO),
the urea-based thickener (B) being one or more selected from diurea compounds represented by the following general formula (b1):

$$R^1\text{-NHCONH-}R^3\text{-NHCONH-}R^2 \qquad (b1)$$

in which R^1 and R^2 each independently represent a monovalent chain hydrocarbon group or alicyclic hydrocarbon group having 6 to 24 carbon atoms, R^1 and R^2 may be the same as or different from each other, and R^3 represents a divalent aromatic hydrocarbon group having 6 to 18 carbon atoms,
when a content of the chain hydrocarbon group in R^1 and R^2 in the general formula (b1) is X molar equivalents and a content of the alicyclic hydrocarbon group in R^1 and R^2 in the general formula (b1) is Y molar equivalents, the grease composition satisfying the following Requirement (1):

- Requirement (1): having a X/Y ratio of 2/1 to 10/1.

[2] A method for producing a grease composition, the method including a step of performing synthesis of a urea-based thickener (B) in a base oil (A),

the base oil (A) containing a poly-α-olefin (PAO),
the urea-based thickener (B) being one or more selected from diurea compounds represented by the following general formula (b1):

$$R^1\text{-NHCONH-}R^3\text{-NHCONH-}R^2 \qquad (b1)$$

in which R^1 and R^2 each independently represent a monovalent chain hydrocarbon group or alicyclic hydrocarbon group having 6 to 24 carbon atoms, R^1 and R^2 may be the same as or different from each other, and R^3 represents a divalent aromatic hydrocarbon group having 6 to 18 carbon atoms,
when a content of the chain hydrocarbon group in R^1 and R^2 in the general formula (b1) is X molar equivalents and a content of the alicyclic hydrocarbon group in R^1 and R^2 in the general formula (b 1) is Y molar equivalents, the synthesis being performed so that the grease composition satisfies the following Requirement (1):

- Requirement (1): having a X/Y ratio of 2/1 to 10/1.

Advantageous Effects of Invention

[0012] According to the present invention, it is possible to provide a grease composition having an increased cone penetration at a low temperature (-40°C).

Description of Embodiments

[0013] In this description, for preferred numerical ranges (for example, a range of a content or the like), lower limits and upper limits provided stepwise can be each independently combined. For example, a range in which a lower limit and an upper limit each independently selected from the statement "preferably 10 or more, more preferably 30 or more, further preferably 40 or more" as lower limits and the statement "preferably 90 or less, more preferably 80 or less, further preferably 70 or less" as upper limits are combined, such as "10 or more and 70 or less", "30 or more and 70 or less", or "40 or more and 80 or less", are combined can also be selected as a suitable range. Additionally, based on the same statement, a range that simply defines one of a lower limit and an upper limit, such as "40 or more" or "70 or less", can also be selected. Also, the same applies to a suitable range that can be selected from a statement of, for example, "preferably 10 or more and 90 or less, more preferably 30 or more and 80 or less, further preferably 40 or more and 70 or less" or "preferably 10 to 90, more preferably 30 to 80, further preferably 40 to 70". In this description, for a statement of a numerical range, for example, a statement "10 to 90" has the same meaning as "10 or more and 90 or less". Numerical values with "or more", "or less", "less than", "more than" for a statement of a numerical range can also be arbitrarily combined.
[0014] Note that, in this description, for example, "(meth)acrylate" is used as a term that represents both of "acrylate" and "methacrylate", and this also applies to other similar terms and similar expressions.

[Aspect of grease composition]

[0015] The grease composition of this embodiment is a grease composition containing a base oil (A) and a urea-based thickener (B),

the base oil (A) containing a poly-α-olefin (PAO),
the urea-based thickener (B) being one or more selected from diurea compounds represented by the following general formula (b1):

$$R^1\text{-NHCONH-}R^3\text{-NHCONH-}R^2 \qquad (b1)$$

[in the general formula (b1), R^1 and R^2 each independently represent a monovalent chain hydrocarbon group or alicyclic hydrocarbon group having 6 to 24 carbon atoms. R^1 and R^2 may be the same as or different from each other. R^3 represents a divalent aromatic hydrocarbon group having 6 to 18 carbon atoms.]
when the content of the chain hydrocarbon group in R^1 and R^2 in the general formula (b1) is X molar equivalents and the content of the alicyclic hydrocarbon group in R^1 and R^2 in the general formula (b1) is Y molar equivalents, the grease composition satisfying the following Requirement (1):

- Requirement (1): having a X/Y ratio of 2/1 to 10/1.

[0016] The present inventors have made intensive and extensive studies for solving the above problem. As a result, the present inventors have found that the above problem can be solved by adopting a chain hydrocarbon group or an alicyclic hydrocarbon group as a terminal functional group of a diurea compound used as a thickener and adjusting the ratio of the groups within a specific range, and thus the present invention has been completed.
[0017] In the following description, "base oil (A)" and "urea-based thickener (B)" are also referred to as "component (A)" and "component (B)", respectively.
[0018] In the grease composition of this embodiment, the total content of the component (A) and the component (B) based on the total amount (100% by mass) of the grease composition is preferably 60% by mass or more, more preferably 70% by mass or more, further preferably 80% by mass or more, furthermore preferably 90% by mass or more, and generally 100% by mass or less, preferably less than 100% by mass, more preferably 99% by mass or less, further preferably 98% by mass or less.
[0019] Note that the grease composition of this embodiment may contain a component other than the component (A) and the component (B) to the extent that the effect of the present invention is not impaired.
[0020] Components contained in the grease composition of this embodiment will be described below.

<Base oil (A)>

[0021] The grease composition of this embodiment contains a base oil (A).
[0022] Further, the base oil (A) contains a poly-α-olefin (hereinafter referred to as "PAO").
[0023] When the base oil (A) does not contain a PAO, the cone penetration at a low temperature (-40°C) is insufficient and the softness of the grease composition is insufficient.
[0024] Examples of the PAO include polybutene, polyisobutylene, a 1-decene oligomer, an ethylene-propylene copolymer, and hydrogenation products thereof.
[0025] One of the PAOs may be used alone or two or more thereof may be used in combination.
[0026] In the grease composition of this embodiment, the PAO has a 40°C kinematic viscosity of preferably 5 mm^2/s or more and 25 mm^2/s or less, more preferably 10 mm^2/s or more and 20 mm^2/s or less, further preferably 15 mm^2/s or more and 18 mm^2/s or less. When the 40°C kinematic viscosity of the PAO is 5 mm^2/s or more and 25 mm^2/s or less, the effect of the present invention is easier to be enhanced.
[0027] In the grease composition of this embodiment, the PAO has a viscosity index of preferably 90 or more, more preferably 100 or more, further preferably 110 or more. When the viscosity index of the PAO is 90 or more, the effect of the present invention is easier to be enhanced.
[0028] In the grease composition of this embodiment, the content of the PAO in the base oil (A) is, from the viewpoint of rubber compatibility, based on the total amount of the base oil (A), preferably 70% by mass or more, more preferably 80% by mass or more, further preferably 85% by mass or more.
[0029] In the grease composition of this embodiment, the base oil (A) may contain a base oil other than PAOs.
[0030] Examples of the other base oils include one or more selected from a mineral oil and a synthetic oil other than PAOs.
[0031] Examples of the mineral oil include an atmospheric residue obtained by distilling a crude oil, such as a paraffin base crude oil, an intermediate base crude oil, or a naphthene base crude oil under a normal pressure; a distillate obtained by distilling the atmospheric residue under a reduced pressure; and a mineral oil obtained by subjecting the distillate to one or more refining treatments, such as solvent deasphalting, solvent extraction, hydrogenation finishing, hydrocracking, severe hydrocracking, solvent dewaxing, catalytic dewaxing, and hydro-isomerizing dewaxing.

[0032] Examples of the synthetic oil other than PAOs include normal paraffin, isoparaffin, an aromatic oil, an ester oil, an ether oil, and a synthetic oil obtained by isomerizing a wax produced by a Fischer Toropsh method or the like (GTL wax). One of the synthetic oils may be used alone or two or more thereof may be used in combination.

[0033] Examples of the aromatic oil include alkylbenzenes, such as a monoalkylbenzene and a dialkylbenzene; and alkylnaphthalenes, such as a monoalkylnaphthalene, a dialkylnaphthalene, and a polyalkylnaphthalene.

[0034] Examples of the ester oil include diester oils, such as dibutyl sebacate, di-2-ethylhexyl sebacate, dioctyl adipate, diisodecyl adipate, ditridecyl adipate, ditridecyl glutarate, and methyl acetyl ricinolate; aromatic ester oils, such as trioctyl trimellitate, tridecyl trimellitate, and tetraoctyl pyromellitate; polyol ester oils, such as trimethylolpropane caprylate, trimethylolpropane pelargonate, pentaerythritol-2-ethylhexanoate, and pentaerythritol pelargonate; and complex ester oils, such as an oligoester of a polyhydric alcohol and a mixed fatty acid of a dibasic acid and a monobasic acid.

[0035] Examples of the ether oil include polyglycols, such as polyethylene glycol, polypropylene glycol, polyethylene glycol monoether, and polypropylene glycol monoether; phenyl ether oils, such as a monoalkyl triphenyl ether, an alkyl diphenyl ether, a dialkyl diphenyl ether, a pentaphenyl ether, a tetraphenyl ether, a monoalkyl tetraphenyl ether, and a dialkyl tetraphenyl ether.

[0036] When the base oil (A) contains said other base oil, from the viewpoint of enhancing the low temperature properties, the base oil (A) preferably contains an ester-based synthetic oil (A2) among the above other base oils.

[0037] When the base oil (A) contains the ester-based synthetic oil (A2), the 40°C kinematic viscosity of the ester-based synthetic oil (A2) is preferably 5 mm^2/s or more and 40 mm^2/s or less, more preferably 10 mm^2/s or more and 40 mm^2/s or less, further preferably 10 mm^2/s or more and 25 mm^2/s or less, furthermore preferably 10 mm^2/s or more and 20 mm^2/s or less, still further preferably 10 mm^2/s or more and 15 mm^2/s or less. When the 40°C kinematic viscosity of the ester-based synthetic oil (A2) is 5 mm^2/s or more and 40 mm^2/s or less, the effect of the present invention is easier to be enhanced.

[0038] When the base oil (A) contains the ester-based synthetic oil (A2), the viscosity index of the ester-based synthetic oil (A2) is preferably 90 or more, more preferably 100 or more, further preferably 110 or more. When the viscosity index of the ester-based synthetic oil (A2) is 90 or more, the effect of the present invention is easier to be enhanced.

[0039] When the base oil (A) contains the ester-based synthetic oil (A2), the content of the ester-based synthetic oil (A2) in the base oil (A) is, from the viewpoint of the rubber compatibility, based on the total amount of the base oil (A), preferably 1% by mass or more, more preferably 3% by mass or more, further preferably 5% by mass or more, and preferably 20% by mass or less, more preferably 18% by mass or less, further preferably 15% by mass or less.

[0040] Additionally, when the base oil (A) contains the ester-based synthetic oil (A2), the ratio of a hydrocarbon synthetic oil (A1) and the ester-based synthetic oil (A2) contained, [(A2)/(A1)], is preferably 0.01 to 0.5, more preferably 0.02 to 0.3, further preferably 0.03 to 0.2 by mass.

[0041] In the grease composition of this embodiment, the base oil (A) has a 40°C kinematic viscosity of preferably 5 mm^2/s or more, more preferably 10 mm^2/s or more, further preferably 15 mm^2/s or more. When the 40°C kinematic viscosity of the base oil (A) is 5 mm^2/s or more, the effect of the present invention is easier to be enhanced.

[0042] Further, in the grease composition of this embodiment, the 40°C kinematic viscosity of the base oil (A) is preferably 40 mm^2/s or less, more preferably 35 mm^2/s or less, further preferably 30 mm^2/s or less, furthermore preferably 20 mm^2/s or less, still further preferably 18.5 mm^2/s or less. When the 40°C kinematic viscosity of the base oil (A) is 40 mm^2/s or less, the effect of the present invention is easier to be enhanced.

[0043] The upper limits and the lower limits of the numerical range can be arbitrarily combined. Specifically, the 40°C kinematic viscosity of the base oil (A) is preferably 5 mm^2/s or more and 40 mm^2/s or less, more preferably 10 mm^2/s or more and 35 mm^2/s or less, further preferably 15 mm^2/s or more and 30 mm^2/s or less.

[0044] In the grease composition of this embodiment, the base oil (A) has a viscosity index of preferably 90 or more, more preferably 100 or more, further preferably 110 or more. When the viscosity index is 90 or more, the effect of the present invention is easier to be enhanced.

[0045] Note that, in this description, the 40°C kinematic viscosity and the viscosity index mean values measured or calculated according to JIS K2283:2000.

[0046] In the grease composition of this embodiment, the content of the base oil (A) based on the total amount (100% by mass) of the grease composition is preferably 60% by mass or more, more preferably 70% by mass or more, further preferably 75% by mass or more, furthermore preferably 80% by mass or more, and is preferably 97% by mass or less, more preferably 95% by mass or less, further preferably 93% by mass or less, furthermore preferably 90% by mass or less.

<Urea-based thickener (B)>

[0047] The grease composition of this embodiment contains a urea-based thickener (B).

[0048] The urea-based thickener (B) is one or more selected from diurea compounds represented by the following general formula (b1).

$$R^1\text{-NHCONH-}R^3\text{-NHCONH-}R^2 \qquad \text{(b1)}$$

[In the general formula (b1), R^1 and R^2 each independently represent a monovalent chain hydrocarbon group or alicyclic hydrocarbon group having 6 to 24 carbon atoms. R^1 and R^2 may be the same as or different from each other. R^3 represents a divalent aromatic hydrocarbon group having 6 to 18 carbon atoms.]

[0049] The number of carbons in the monovalent chain hydrocarbon group or alicyclic hydrocarbon group that can be selected as R^1 and R^2 in the general formula (b1) is 6 to 24, preferably 6 to 20, more preferably 6 to 18.

[0050] An example of the monovalent chain hydrocarbon group that can be selected as R^1 and R^2 is a saturated or unsaturated monovalent chain hydrocarbon group, and a saturated chain hydrocarbon group is preferred.

[0051] An example of the monovalent alicyclic hydrocarbon group that can be selected as R^1 and R^2 is a saturated or unsaturated monovalent alicyclic hydrocarbon group, and a saturated alicyclic hydrocarbon group is preferred.

[0052] A diurea compound containing a monovalent aromatic hydrocarbon group as the monovalent hydrocarbon group that can be selected as R^1 and R^2 in the general formula (b1) may also be contained.

[0053] When the content of the chain hydrocarbon group in R^1 and R^2 in the general formula (b1) is X molar equivalents and the content of the alicyclic hydrocarbon group therein is Y molar equivalents, the grease composition of this embodiment satisfies the following Requirement (1):

- Requirement (1): having a X/Y ratio of 2/1 to 10/1.

[0054] When the X/Y ratio is less than 2/1, a resulting value of the ratio of the unworked penetration at -40°C and the worked penetration at 25°C (the unworked penetration at -40°C to the worked penetration at 25°C) described later may be insufficient. In this case, such a grease composition has a lower unworked penetration at -40°C and is harder at a low temperature as compared with a grease composition having the same worked penetration at 25°C, and thus, the sealing properties as a grease composition at a low temperature may be insufficient.

[0055] Furthermore, when the X/Y ratio is more than 10/1, the worked penetration at 25°C may be too high. In this case, such a composition is very softer than a grease composition and thus, may require very high torque. In addition, the sealing properties as a grease composition at room temperature may be insufficient.

[0056] Here, from the viewpoints of the unworked penetration at -40°C, the worked penetration at 25°C, and the balance therebetween, the X/Y ratio defined in Requirement (1) is preferably 2/1 to 9/1, more preferably 7/3 to 9/1, further preferably 7/3 to 8/2.

[0057] Additionally, when the content of the chain hydrocarbon group in R^1 and R^2 in the general formula (b1) is X molar equivalents, the content of the alicyclic hydrocarbon group therein is Y molar equivalents, and the content of the aromatic hydrocarbon group therein is Z molar equivalents, from the viewpoint of facilitating enhancement of the effect of the present invention, the grease composition of this embodiment preferably satisfies the following requirement (2):

- Requirement (2): having a value of $[(X+Y)/(X+Y+Z)] \times 100$ of 90 or more (preferably 95 or more, more preferably 98 or more, further preferably 100).

[0058] Since the alicyclic hydrocarbon group, the chain hydrocarbon group, and the aromatic hydrocarbon group are groups selected as R^1 and R^2 in the general formula (b1), the sum of the values of X, Y, and Z is 2 molar equivalents per mole of the compound represented by the general formula (b1). Moreover, the values of Requirements (1) and (2) mean the average values based on the total amount of the compounds represented by the general formula (b1) contained in the grease composition.

[0059] By using a compound that satisfies the Requirement (1), preferably satisfies the Requirement (2), and is represented by the general formula (b 1), a grease composition superior in the unworked penetration at -40°C, the worked penetration at 25°C, and the balance therebetween is easier to be obtained.

[0060] Note that the values of X, Y, and Z can be calculated based on the molar equivalents of the amines used as raw materials.

[0061] An example of the monovalent saturated chain hydrocarbon group is a linear or branched alkyl group having 6 to 24 carbon atoms, and specific examples thereof include a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group, a tridecyl group, a tetradecyl group, a pentadecyl group, a hexadecyl group, a heptadecyl group, an octadecyl group (stearyl group), an octadecenyl group, a nonadecyl group, and an eicosyl group.

[0062] Note that the monovalent saturated chain hydrocarbon group may be linear or branched.

[0063] Among them, an octadecyl group (stearyl group) is preferred.

[0064] An example of the monovalent unsaturated chain hydrocarbon group include a linear or branched alkenyl group having 6 to 24 carbon atoms, and specific examples thereof include a hexenyl group, a heptenyl group, an octenyl group, a nonenyl group, a decenyl group, an undecenyl group, a dodecenyl group, a tridecenyl group, a tetradecenyl group, a pentadecenyl group, a hexadecenyl group, a heptadecenyl group, an octadecenyl group, a nonadecenyl group, an eicosenyl group, an oleyl group, a geranyl group, an farnesyl group, and a linoleyl group.

[0065] Note that the monovalent unsaturated chain hydrocarbon group may be linear or branched.

[0066] Examples of the monovalent saturated alicyclic hydrocarbon group include cycloalkyl groups, such as a cyclohexyl group, a cycloheptyl group, a cyclooctyl group, and a cyclononyl group; and cycloalkyl groups substituted with an alkyl group having 1 to 6 carbon atoms (preferably, a cyclohexyl group substituted with an alkyl group having 1 to 6 carbon atoms), such as a methylcyclohexyl group, a dimethylcyclohexyl group, an ethylcyclohexyl group, a diethylcyclohexyl group, a propylcyclohexyl group, an isopropylcyclohexyl group, a 1-methyl-propylcyclohexyl group, a butylcyclohexyl group, a pentylcyclohexyl group, a pentyl-methylcyclohexyl group, and a hexylcyclohexyl group.

[0067] Among them, a cyclohexyl group is preferred.

[0068] Examples of the monovalent unsaturated alicyclic hydrocarbon group include cycloalkenyl groups, such as a cyclohexenyl group, a cycloheptenyl group, and a cyclooctenyl group; and cycloalkenyl groups substituted with an alkyl group having 1 to 6 carbon atoms (preferably, a cyclohexenyl group substituted with an alkyl group having 1 to 6 carbon atoms), such as a methylcyclohexenyl group, a dimethylcyclohexenyl group, an ethycyclohexenyl group, a diethylcyclohexenyl group, and a propylcyclohexenyl group.

[0069] Examples of the monovalent aromatic hydrocarbon group include a phenyl group, a biphenyl group, a terphenyl group, a naphthyl group, a diphenylmethyl group, a diphenylethyl group, a diphenylpropyl group, a methylphenyl group, a dimethylphenyl group, an ethylphenyl group, and a propylphenyl group.

[0070] The number of carbons in the divalent aromatic hydrocarbon group that can be selected as R^3 in the general formula (b1) is 6 to 18, preferably 6 to 15, more preferably 6 to 13.

[0071] Examples of the divalent aromatic hydrocarbon group that is selected as R^3 include a phenylene group, a diphenylmethylene group, a diphenylethylene group, a diphenylpropylene group, a methylphenylene group, a dimethylphenylene group, and an ethylphenylene group.

[0072] Among them, a phenylene group, a diphenylmethylene group, a diphenylethylene group, or a diphenylpropylene group is preferred, and a diphenylmethylene group is more preferred.

[0073] In the grease composition of this embodiment, the content of the urea-based thickener (B) based on the total amount (100% by mass) of the grease composition is preferably 1.0 to 20.0% by mass, more preferably 3.0 to 19.0% by mass, further preferably 5.0 to 18.0% by mass, furthermore preferably 7.0 to 17.0% by mass, still further preferably 10.0% by mass to 16.0% by mass.

[0074] When the content of the component (B) is 1.0% by mass or more, the worked penetration of the resulting grease composition is easily adjusted within an appropriate range.

[0075] On the other hand, when the content of the component (B) is 20.0% by mass or less, the resulting grease composition can be adjusted to be soft, and thus, good lubrication is easily achieved and the unworked penetration at -40°C is easily appropriately adjusted.

<Acidic phosphate ester (C)>

[0076] The grease composition of this embodiment preferably contains an acidic phosphate ester (C).

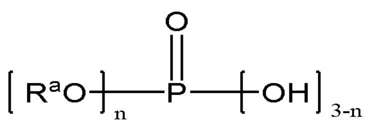
[0077] By incorporating the acidic phosphate ester (C) in the grease composition of this embodiment, a grease composition superior in reduction of friction can be achieved.

[0078] Examples of the acidic phosphate ester (C) include a monoaryl acid phosphate, a diaryl acid phosphate, a monoalkyl acid phosphate, a dialkyl acid phosphate, a monoalkenyl acid phosphate, and a dialkenyl acid phosphate.

[0079] The acidic phosphate ester (C) may be an amine salt.

[0080] Further, one of the acidic phosphate esters may be used alone or two or more thereof may be used in combination.

[0081] The acidic phosphate ester (C) is preferably a compound represented by the following general formula (c1).



(c1)

[0082] In the general formula (c1), n is 1 or 2. R^a's each independently represent an alkyl group having 1 to 18 (preferably 6 to 18) carbon atoms. The alkyl group is preferably linear or branched, more preferably branched.

[0083] When n is 2, more than one R^a may be the same as or different from each other.

[0084] Among the compounds represented by the general formula (c1), oleyl acid phosphate is preferred.

[0085] In the grease composition of this embodiment, the content of the acidic phosphate ester (C) is, from the viewpoint of reducing the friction, based on the total amount of the grease composition (100% by mass), preferably 0.5% by mass or more and 3.0% by mass or less, more preferably 0.8% by mass or more and 3.0% by mass or less, further preferably 1.0%

by mass or more and 3.0% by mass or less, furthermore preferably 1.0% by mass or more and 2.0% by mass or less, still further preferably 1.0% by mass or more and 1.5% by mass or less, still yet further preferably 1.0% by mass or more and 1.2% by mass or less.

[0086] From the viewpoint of reducing the friction, the ratio of the urea-based thickener (B) to the acidic phosphate ester (C) contained, [(B)/(C)], is preferably 1.0 to 25.0, more preferably 5.0 to 20.0, further preferably 10.0 to 18.0 by mass.

<Additive (D)>

[0087] The grease composition of this embodiment may contain an additive (D) which is to be added to a general grease, other than the component (B) and the component (C), to the extent that the effect of the present invention is not impaired.

[0088] Examples of the additive (D) include an antioxidant, a rust inhibitor, a solid lubricant, a detergent dispersant, a corrosion inhibitor, a metal deactivator, and a viscosity index improver.

[0089] One of the additives (D) may be used alone and two or more thereof may be used in combination.

[0090] An example of the antioxidant is a phenol-based antioxidant.

[0091] Examples of the rust inhibitor include a carboxylic acid-based rust inhibitor such as an alkenyl succinic acid polyhydric alcohol ester, zinc stearate, thiadiazole and derivatives thereof, and benzotriazole and derivatives thereof.

[0092] Examples of the solid lubricant include polyimide, PTFE, graphite, a metal oxide, boron nitride, and molybdenum disulfide.

[0093] Examples of the detergent dispersant include ash-free dispersants, such as succinimide and boron-based succinimide.

[0094] Examples of the corrosion inhibitor include a benzotriazole-based compound and a thiazole-based compound.

[0095] An example of the metal deactivator is a benzotriazole-based compound.

[0096] Examples of the viscosity index improver include polymers, such as a non-dispersant-type poly(meth)acrylate, a dispersant-type poly(meth)acrylate, a star polymer, an olefin copolymer (for example, an ethylene-propylene copolymer), a dispersant-type olefin copolymer, and a styrene copolymer (for example, a styrene-diene copolymer and a styrene-isoprene copolymer). Among them, a polymethacrylate and a star polymer are preferred.

[0097] One of the additives may be used alone or two or more thereof may be used in combination.

[Properties of grease composition]

<Worked penetration at 25°C>

[0098] The lower limit of the worked penetration at 25°C of the grease composition of this embodiment is, from the viewpoint of maintaining the torque reduction of the grease composition and the sealing properties and an appropriate softness of the grease composition at 25°C, preferably 210 or more, more preferably 240 or more, further preferably 250 or more.

[0099] The upper limit of the worked penetration at 25°C of the grease composition of this embodiment is, from the viewpoint of maintaining the torque reduction of the grease composition and the sealing properties and an appropriate softness of the grease composition at 25°C, preferably 300 or less, more preferably 290 or less, further preferably 270 or less.

[0100] The upper limits and the lower limits can be appropriately combined, and the worked penetration at 25°C is preferably 210 to 300, more preferably 240 to 300, further preferably 240 to 290, furthermore preferably 250 to 270.

[0101] In this description, the worked penetration at 25°C means a value measured at 25°C according to JIS K2220:2013 (Section 7).

<Unworked penetration at -40°C >

[0102] The lower limit of the unworked penetration at -40°C of the grease composition of this embodiment is, from the viewpoint of maintaining the torque reduction and an appropriate softness of the grease composition at -40°C, preferably 140 or more, more preferably 150 or more, further preferably 170 or more.

[0103] The upper limit of the unworked penetration at -40°C of the grease composition of this embodiment is, from the viewpoint of maintaining sealing properties and an appropriate softness of the grease composition at -40°C, preferably 200 or less, more preferably 190 or less.

[0104] The upper limits and the lower limits can be appropriately combined, and the unworked penetration at -40°C of the grease composition of this embodiment is, from the viewpoint of maintaining the torque reduction of the grease composition and the sealing properties and an appropriate softness of the grease composition at -40°C, preferably 140 to 200, more preferably 150 to 200, further preferably 170 to 200, furthermore preferably 170 to 190.

[0105] Note that, when the grease composition maintains an appropriate softness, occurrence of a void in the grease composition can be suppressed and thus, penetration of foreign matter from the void which results in deterioration in the sealing properties can be suppressed.

[0106] In this description, the unworked penetration at -40°C can be a value measured at - 40°C according to JIS K2220:2013 (Section 7). In addition, the unworked penetration at - 40°C is specifically a value measured by a method described in the section of Examples as provided later.

<Ratio of unworked penetration at -40°C to worked penetration at 25°C>

[0107] The lower limit of the ratio of the unworked penetration at -40°C to the worked penetration at 25°C [unworked penetration at -40°C / worked penetration at 25°C] of the grease composition of this embodiment is preferably 0.61 or more, more preferably 0.62 or more.

[0108] Additionally, the upper limit of the ratio of the unworked penetration at -40°C to the worked penetration at 25°C [unworked penetration at -40°C / worked penetration at 25°C] of the grease composition of this embodiment is preferably 0.80 or less, more preferably 0.75 or less.

[0109] The upper limits and the lower limits can be appropriately combined, and the grease composition of this embodiment has a ratio of the unworked penetration at -40°C to the worked penetration at 25°C [unworked penetration at -40°C / worked penetration at 25°C] of preferably 0.61 to 0.80, more preferably 0.61 to 0.75, further preferably 0.62 to 0.75.

[0110] When the ratio of the unworked penetration at -40°C to the worked penetration at 25°C is within the above range, such a grease composition is superior in the balance of the unworked penetration at -40°C and the worked penetration at 25°C, and thus, is also superior in the sealing properties as a grease composition at a low temperature.

[0111] In this description, the ratio of the unworked penetration at -40°C to the worked penetration at 25°C means a value calculated by a method described in the section of Examples provided later.

[0112] The kinematic friction of the grease composition of this embodiment can be measured, for example, by a method described in the section of Examples provided later.

[0113] The rubber compatibility of the grease composition of this embodiment can be measured, for example, by a method described in the section of Examples provided later.

[Method for producing grease composition]

[0114] The method for producing a grease composition of the present invention includes a step of performing synthesis of a urea-based thickener (B) in a base oil (A),

the base oil (A) containing a poly-α-olefin (PAO),
the urea-based thickener (B) being one or more selected from diurea compounds represented by the following general formula (b1):

$$R^1\text{-NHCONH-}R^3\text{-NHCONH-}R^2 \qquad \text{(b1)}$$

[in the general formula (b1), R^1 and R^2 each independently represent a monovalent chain hydrocarbon group or alicyclic hydrocarbon group having 6 to 24 carbon atoms. R^1 and R^2 may be the same as or different from each other. R^3 represents a divalent aromatic hydrocarbon group having 6 to 18 carbon atoms.]
when the content of the chain hydrocarbon group in R^1 and R^2 in the general formula (b1) is X molar equivalents and the content of the alicyclic hydrocarbon group in R^1 and R^2 in the general formula (b 1) is Y molar equivalents, the synthesis being performed so that the grease composition satisfies the following Requirement (1):

- Requirement (1): having a X/Y ratio of 2/1 to 10/1.

[0115] In an example of the synthetic method, the diurea compound represented by the general formula (b1) can be generally obtained by a reaction of a diisocyanate and a monoamine. The reaction is preferably performed in such a manner that a monoamine-containing base oil is obtained by blending a monoamine with the base oil (A) containing a PAO, followed by dissolution with heat, and while heating and stirring the monoamine-containing base oil, a base oil which is obtained by dissolving a diisocyanate in the base oil (A) containing a PAO is added thereto.

[0116] For example, when a diurea compound represented by the general formula (b1) is to be synthesized, a desired diurea compound can be synthesized by such a method as above in which a diisocyanate having a group corresponding to the divalent aromatic hydrocarbon group represented by R^3 in the general formula (b1) is used as the diisocyanate and an amine having a group corresponding to the monovalent chain hydrocarbon group or alicyclic hydrocarbon group represented by R^1 and R^2 is used as the monoamine.

[0117] As required, after the above step, another additive (D) may be blended with the base grease.

[Application of grease composition]

[0118] The grease composition of this embodiment is superior in the cone penetration at a low temperature (-40°C). Thus, the grease composition can be suitably used for lubrication of, for example, a sliding mechanism in which a metal material and a rubber material slide and which is required to have sealing properties even under a low temperature environment.

[0119] The metal material is not particularly limited, and examples thereof include various steels, such as a carbon steel and a stainless steel, various alloys, such as an aluminum alloy, and cupper. Note that the metal material may be replaced with a material having a high strength (for example, ceramic material).

[0120] The rubber material is not particularly limited, and examples thereof include an acrylonitrile-butadiene rubber (NBR), a hydrogenated nitrile rubber (H-NBR), a chloroprene rubber (CR), an ethylene-propylene-diene terpolymer (EPDM), a silicone rubber, a butyl rubber (IIR), a styrene butadiene rubber (SBR), a urethane rubber (U), a chlorosulfonated polyethylene (CSM), and a fluororubber (FKM). Among them, an acrylonitrile-butadiene rubber is preferred.

[0121] Examples of the fields of apparatuses in which the grease composition of the present invention can be suitably used include the field of bicycles, the field of automobiles, the field of business machines, the field of machine tools, the field of windmills, the field of construction, the field of agricultural machines, and the field of industrial robots.

[0122] Examples of the lubricating part in apparatuses in the field of automobiles in which the grease composition of the present invention can be suitably used include bearing parts in apparatuses, such as a radiator fun motor, a fan coupling, an alternator, an idler pulley, a hub unit, a hub bearing, a water pump, a power window, a wiper, an electrical power steering, a driving electrical motor flywheel, a ball joint, a wheel bearing, a spline part, and a constant velocity j oint; and bearing parts, gear parts, and sliding parts in apparatuses, such as a door lock, a door hinge, and a clutch booster.

[0123] More specific examples thereof include bearing parts of a hub unit, a hub bearing, an electrical power steering, a driving electrical motor flywheel, a ball joint, a wheel bearing, a spline part, a constant velocity joint, a clutch booster, a servomotor, a blade bearing, or a generator.

[0124] Examples of lubricating parts in apparatuses of the field of business machines in which the grease composition of the present invention can be suitably used include a fixing roll in an apparatus, such as a printer, a bearing and gear parts in an apparatus, such as polygon motor.

[0125] Examples of lubricating parts in apparatuses in the field of machine tools in which the grease composition of the present invention can be suitably used include bearing parts in a speed reducer of a spindle, a servomotor, a machining robot, or the like.

[0126] Examples of lubricating parts in apparatuses in the field of windmill in which the grease composition of the present invention can be suitably used include bearing parts in a blade bearing, a generator, and the like.

[0127] Examples of lubricating parts in apparatuses of the field of construction or agricultural machines in which the grease composition of the present invention can be suitably used include bearing parts, gear parts, and sliding parts in a ball joint, a spline part, and the like.

[Method for lubricating sliding mechanism]

[0128] The method for lubricating a sliding mechanism, applicable to the grease composition of the present invention is a method in which a sliding mechanism in which a metal material and a rubber material slide is lubricated by applying the grease composition of the present invention as described above.

[0129] According to this embodiment, the following [1] to [14] are provided.

[1] A grease composition containing a base oil (A) and a urea-based thickener (B),

the base oil (A) containing a poly-α-olefin (PAO),

the urea-based thickener (B) being one or more selected from diurea compounds represented by the following general formula (b1),

$$R^1\text{-NHCONH-}R^3\text{-NHCONH-}R^2 \qquad (b1)$$

[in the general formula (b1), R^1 and R^2 each independently represent a monovalent chain hydrocarbon group or alicyclic hydrocarbon group having 6 to 24 carbon atoms, R^1 and R^2 may be the same as or different from each other, and R^3 represents a divalent aromatic hydrocarbon group having 6 to 18 carbon atoms], when a content of the chain hydrocarbon group in R^1 and R^2 in the general formula (b1) is X molar equivalents and a content of the alicyclic hydrocarbon group in R^1 and R^2 in the general formula (b1) is Y molar equivalents, the grease composition satisfying the following Requirement (1):

- Requirement (1): having a X/Y ratio of 2/1 to 10/1.

[2] The grease composition according to [1], in which the chain hydrocarbon group in R^1 and R^2 in the general formula (b1) is a saturated chain hydrocarbon group.
[3] The grease composition according to [1] or [2], in which the alicyclic hydrocarbon group in R^1 and R^2 in the general formula (b1) is a saturated alicyclic hydrocarbon group.
[4] The grease composition according to any one of [1] to [3], in which the grease composition has a worked penetration at 25°C of 240 to 300.
[5] The grease composition according to any one of [1] to [4], in which the grease composition has an unworked penetration at -40°C of 150 or more.
[6] The grease composition according to any one of [1] to [5], in which the base oil (A) has a 40°C kinematic viscosity of 10 mm^2/s or more and 40 mm^2/s or less.
[7] The grease composition according to any one of [1] to [6], in which the base oil (A) further contains an ester-based synthetic oil (A2).
[8] The grease composition according to [7], in which the ester-based synthetic oil (A2) is contained in an amount of 20% by mass or less based on a total amount of the base oil (A).
[9] The grease composition according to [7] or [8], in which the ester-based synthetic oil (A2) has a 40°C kinematic viscosity of 10 mm^2/s or more and 40 mm^2/s or less.
[10] The grease composition according to any one of [1] to [9], in which the grease composition further contains an acidic phosphate ester (C).
[11] The grease composition according to [10], in which the acidic phosphate ester (C) is contained in an amount of 1.0% by mass to 3.0% by mass based on a total amount of the grease composition.
[12] The grease composition according to any one of [1] to [11], in which the grease composition is used for lubricating a sliding mechanism in which a metal material and a rubber material slide.
[13] A method of lubrication, the method including lubricating, with the grease composition according to any one of [1] to [11], a sliding mechanism in which a metal material and a rubber material slide.
[14] A method for producing a grease composition, the method including a step of performing synthesis of a urea-based thickener (B) in a base oil (A),

the base oil (A) containing a poly-α-olefin (PAO),
the urea-based thickener (B) being one or more selected from diurea compounds represented by the following general formula (b1),

$$R^1\text{-NHCONH-}R^3\text{-NHCONH-}R^2 \qquad \text{(b1)}$$

[in the general formula (b1), R^1 and R^2 each independently represent a monovalent chain hydrocarbon group or alicyclic hydrocarbon group having 6 to 24 carbon atoms, R^1 and R^2 may be the same as or different from each other, and R^3 represents a divalent aromatic hydrocarbon group having 6 to 18 carbon atoms],
when a content of the chain hydrocarbon group in R^1 and R^2 in the general formula (b1) is X molar equivalents and a content of the alicyclic hydrocarbon group in R^1 and R^2 in the general formula (b 1) is Y molar equivalents, the synthesis being performed so that the grease composition satisfies the following Requirement (1).

- Requirement (1): having a X/Y ratio of 2/1 to 10/1.

Examples

[0130] The present invention will be described more specifically with reference to the following examples. However, the present invention is not to be limited to the following examples.

[Examples 1 to 16 and Comparative Examples 1 to 5]

[0131] Grease compositions of Examples 1 to 16 and Comparative Examples 1 to 5 were prepared by methods described below and were subjected to evaluations as described later.

[0132] Note that the 40°C kinematic viscosities and the viscosity indexes of the base oils (A) used in preparation of the grease compositions were measured or calculated according to JIS K2283:2000.

<Examples 1 to 3>

[0133] In Examples 1 to 3, a grease composition containing a urea-based thickener (B1) was prepared.
[0134] The urea-based thickener (B1) corresponds to a compound represented by the general formula (b1) in which R^1 and R^2 are a stearyl group or a cyclohexyl group and R^3 is a diphenylmethylene group.
[0135] The molar ratio of stearyl amine and cyclohexyl amine used as raw materials (stearyl amine / cyclohexyl amine) is 7/3.

(Example 1)

[0136] A poly-α-olefin (PAO) (40°C kinematic viscosity: 17.5 mm^2/s, viscosity index: 120) was used as the base oil (A1).
[0137] To 349.75 g of the base oil (A1) heated to 75°C, 73.27 g of diphenylmethane-4,4'-doisocyanate (MDI) was added to prepare a solution α.
[0138] Further, to 500 g of the base oil (A1) which was separately provided and was heated to 70°C, 30.98 g of stearyl amine and 46.00 g of cyclohexyl amine were added to prepare a solution β.
[0139] Then, while stirring the solution β heated to 75°C, the solution α heated to 75°C was added thereto. While rotating a stirring blade to continue stirring, the temperature was increased to 160°C and was held for 1 hour, thus preparing a grease composition of Example 1 containing 15.0 % by mass of the urea-based thickener (B1).

(Example 2)

[0140] To 90 g of the grease composition of Example 1, 10 g of the base oil (A1) was added and was mixed, thus preparing a grease composition of Example 2 containing 13.5% by mass of the urea-based thickener (B1).

(Example 3)

[0141] To 80 g of the grease composition of Example 1, 20 g of the base oil (A1) was added and mixed, thus preparing a grease composition of Example 3 containing 12.0% by mass of the urea-based thickener (B1).

<Examples 4 to 6>

[0142] In Example 4 to 6, grease compositions containing a urea-based thickener (B2) were prepared.
[0143] The urea-based thickener (B2) corresponds to a compound represented by the general formula (b1) in which R^1 and R^2 are a stearyl group or a cyclohexyl group and R^3 is a diphenylmethylene group.
[0144] Further, the molar ratio of stearyl amine and cyclohexyl amine used as raw materials (stearyl amine / cyclohexyl amine) is 7.5/2.5.

(Example 4)

[0145] A grease composition of Example 4 containing 15.0% by mass of the urea-based thickener (B2) was prepared in the same manner as in Example 1 except for changing the contents of the components in the grease composition of Example 1 as follows.

- Base oil (A1): 849.70 g
- Diphenylmethane-4,4'-diisocyanate (MDI): 54.03 g
- Stearyl amine: 85.67 g
- Cyclohexyl amine: 10.60 g

(Example 5)

[0146] To 90 g of the grease composition of Example 4, 10 g of the base oil (A1) was added and mixed, thus preparing a grease composition of Example 5 containing 13.5% by mass of the urea-based thickener (B2).

(Example 6)

[0147] To 80 g of the grease composition of Example 4, 20 g of the base oil (A1) was added and mixed, thus preparing a grease composition of Example 6 containing 12.0% by mass of the urea-based thickener (B2).

<Examples 7 to 11>

[0148] In Example 7 to 11, grease compositions containing a urea-based thickener (B3) were prepared.
[0149] The urea-based thickener (B3) corresponds to a compound represented by the general formula (b1) in which R^1 and R^2 are a stearyl group or a cyclohexyl group and R^3 is a diphenylmethylene group.
[0150] Further, the molar ratio of stearyl amine and cyclohexyl amine used as raw materials (stearyl amine / cyclohexyl amine) is 8/2.

(Example 7)

[0151] A grease composition of Example 7 containing 15.0% by mass of the urea-based thickener (B3) was prepared in the same manner as in Example 1 except for changing the contents of the components in the grease composition of Example 1 as follows.

- Base oil (A1): 850.29 g
- Diphenylmethane-4,4'-diisocyanate (MDI): 52.57 g
- Stearyl amine: 88.90 g
- Cyclohexyl amine: 8.25 g

(Example 8)

[0152] To 90 g of the grease composition of Example 7, 10 g of the base oil (A1) was added and mixed, thus preparing a grease composition of Example 8 containing 13.5% by mass of the urea-based thickener (B3).

(Example 9)

[0153] To 80 g of the grease composition of Example 7, 5 g of the base oil (A1) and 5 g of a diester (40°C kinematic viscosity: 11.6 mm^2/s, viscosity index: 153) as the base oil (A2) were added and mixed, thus preparing a grease composition of Example 9 containing 13.5% by mass of the urea-based thickener (B3).

(Example 10)

[0154] To 80 g of the grease composition of Example 7, 10 g of a diester (40°C kinematic viscosity: 11.6 mm^2/s, viscosity index: 153) as the base oil (A2) was added and mixed, thus preparing a grease composition of Example 10 containing 13.5% by mass of the urea-based thickener (B3).

(Example 11)

[0155] To 80 g of the grease composition of Example 7, 20 g of the base oil (A1) was added and mixed, thus preparing a grease composition of Example 11 containing 12.0% by mass of the urea-based thickener (B3).

<Examples 12 to 16>

[0156] In Examples 12 to 16, grease compositions containing a urea-based thickener (B4) were prepared.
[0157] The urea-based thickener (B4) corresponds to a compound represented by the general formula (b1) in which R^1 and R^2 are a stearyl group or a cyclohexyl group and R^3 is a diphenylmethylene group.
[0158] Further, the molar ratio of stearyl amine and cyclohexyl amine used as raw materials (stearyl amine / cyclohexyl amine) is 9/1.

(Example 12)

[0159] A grease composition of Example 12 containing 15.0% by mass of the urea-based thickener (B4) was prepared in the same manner as in Example 1 except for changing the contents of the components in the grease composition of

Example 1 as follows.

- Base oil (A1): 849.95 g
- Diphenylmethane-4,4'-diisocyanate (MDI): 50.34 g
- Stearyl amine: 95.77 g
- Cyclohexyl amine: 3.95 g

(Example 13)

[0160] To 90 g of the grease composition of Example 12, 10 g of the base oil (A1) was added and mixed, thus preparing a grease composition of Example 13 containing 13.5% by mass of the urea-based thickener (B4).

(Example 14)

[0161] To 90 g of the grease composition of Example 12, 5 g of the base oil (A1) and 5 g of a diester (40°C kinematic viscosity: 11.6 mm^2/s, viscosity index: 153) as the base oil (A2) were added and mixed, thus preparing a grease composition of Example 14 containing 13.5% by mass of the urea-based thickener (B4).

(Example 15)

[0162] To 90 g of the grease composition of Example 12, 10 g of a diester (40°C kinematic viscosity: 11.6 mm^2/s, viscosity index: 153) as the base oil (A2) was added and mixed, thus preparing a grease composition of Example 15 containing 13.5% by mass of the urea-based thickener (B4).

(Example 16)

[0163] To 80 g of the grease composition of Example 12, 20 g of the base oil (A1) was added and mixed, thus preparing a grease composition of Example 16 containing 12.0% by mass of the urea-based thickener (B4).

<Comparative Examples 1 to 2>

[0164] In Comparative Examples 1 to 2, grease compositions containing a urea-based thickener (B5) were prepared.
[0165] The urea-based thickener (B5) corresponds to a compound represented by the general formula (b1) in which R^1 and R^2 are a stearyl group or a cyclohexyl group and R^3 is a diphenylmethylene group.
[0166] Further, the molar ratio of stearyl amine and cyclohexyl amine used as raw materials (stearyl amine / cyclohexyl amine) is 6/4.

(Comparative Example 1)

[0167] A grease composition of Comparative Example 1 containing 13.5% by mass of the urea-based thickener (B5) was prepared in the same manner as in Example 1 except for changing the contents of the components in the grease composition of Example 1 as follows.

- Base oil (A1): 849.86 g
- Diphenylmethane-4,4'-diisocyanate (MDI): 58.14 g
- Stearyl amine: 73.75 g
- Cyclohexyl amine: 18.25 g

(Comparative Example 2)

[0168] To 90 g of the grease composition of Comparative Example 1, 10 g of the base oil (A1) was added and mixed, thus preparing a grease composition of Comparative Example 2 containing 12.0% by mass of the urea-based thickener (B5).

<Comparative Examples 3 to 5>

[0169] In Comparative Examples 3 to 5, grease compositions containing a urea-based thickener (B6) were prepared.
[0170] The urea-based thickener (B6) corresponds to a compound represented by the general formula (b1) in which R^1 and R^2 are a stearyl group or a cyclohexyl group and R^3 is a diphenylmethylene group.

[0171] Further, the molar ratio of stearyl amine and cyclohexyl amine used as raw materials (stearyl amine / cyclohexyl amine) is 9.5/0.5.

(Comparative Example 3)

[0172] A grease composition of Comparative Example 3 containing 15.0% by mass of the urea-based thickener (B6) was prepared in the same manner as in Example 1 except for changing the contents of the components in the grease composition of Example 1 as follows.

- Base oil (A1): 850.10 g
- Diphenylmethane-4,4'-diisocyanate (MDI): 49.19 g
- Stearyl amine: 98.79 g
- Cyclohexyl amine: 1.93 g

(Comparative Example 4)

[0173] To 90 g of the grease composition of Comparative Example 3, 10 g of the base oil (A1) was added and mixed, thus preparing a grease composition of Comparative Example 4 containing 13.5% by mass of the urea-based thickener (B6).

(Comparative Example 5)

[0174] To 80 g of the grease composition of Comparative Example 3, 20 g of the base oil (A1) was added and mixed, thus preparing a grease composition of Comparative Example 5 containing 12.0% by mass of the urea-based thickener (B6).

<Evaluation 1: measurement of worked penetration at 25°C>

[0175] The worked penetrations of the grease compositions of Examples 1 to 16 and Comparative Examples 1 to 5 were measured at 25°C according to JIS K2220:2013 (Section 7).

[0176] Note that a worked penetration at 25°C within 210 to 300 was considered as acceptable.

<Evaluation 2: measurement of unworked penetration at -40°C>

[0177] The unworked penetrations of the grease compositions of Examples 1 to 16 and Comparative Examples 1 to 5 were measured at -40°C according to JIS K2220:2013 (Section 7).

[0178] Specifically, each of grease compositions of Examples 1 to 16 and Comparative Examples 1 to 5 which was not stirred and a conical needle were allowed to stand in a -40°C thermostat for 2 hours. Then, the conical needle was dropped into the grease composition immediately without mixing the grease composition. The depth that the conical needle sank into the grease composition was measured, and the depth was decupled to thus determine the unworked penetration at -40°C.

[0179] Note that an unworked penetration at -40°C within 140 to 200 was considered as acceptable.

<Evaluation 3: calculation of ratio of unworked penetration at -40°C to worked penetration at 25°C>

[0180] For each of the grease compositions of Examples 1 to 16 and Comparative Examples 1 to 5, the ratio [unworked penetration at -40°C / worked penetration at 25°C] was calculated by dividing the unworked penetration at -40°C determined in Evaluation 2 by the worked penetration at 25°C determined in Evaluation 1.

[0181] Note that a value of the [unworked penetration at -40°C / worked penetration at 25°C] within 0.61 to 0.80 was considered as acceptable.

[0182] The results are shown in Tables 1 to 4.

Table 1

Component (unit)				Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Grease composition	Base oil (A)	Base oil (A1)	% by mass	85.0	86.5	88.0	85.0	86.5	88.0
		Base oil (A2)	% by mass	-	-	-	-	-	-
	Urea-based thickener (B)	Urea-based thickener (B1)	% by mass	15.0	13.5	12.0	-	-	-
		Urea-based thickener (B2)	% by mass	-	-	-	15.0	13.5	12.0
		Urea-based thickener (B3)	% by mass	-	-	-	-	-	-
		Urea-based thickener (B4)	% by mass	-	-	-	-	-	-
		Urea-based thickener (B5)	% by mass	-	-	-	-	-	-
		Urea-based thickener (B6)	% by mass	-	-	-	-	-	-
Total			% by mass	100.0	100.0	100.0	100.0	100.0	100.0
Urea-based thickener (B)	Chain hydrocarbon group (X)	Stearyl amine	% by mole	7.0	7.0	7.0	7.5	7.5	7.5
	Alicyclic hydrocarbon group (Y)	Cyclohexyl amine	% by mole	3.0	3.0	3.0	2.5	2.5	2.5
	Total		% by mole	10.0	10.0	10.0	10.0	10.0	10.0
Ratio	[(A2)/(A1)]		-	-	-	-	-	-	-
	(X/Y)		-	2.3	2.3	2.3	3.0	3.0	3.0
Property values	Base oil (A) (Mixed base oil)	40°C Kinematic viscosity	mm^2/s	17.5	17.5	17.5	17.5	17.5	17.5
		Viscosity index	-	120	120	120	120	120	120
Results of Evaluations	Worked penetration at 25°C		-	228	251	278	213	230	248
	Unworked penetration at -40°C		-	148	155	178	141	161	174
	[Unworked penetration at -40°C / worked penetration at 25°C]		-	0.65	0.62	0.64	0.66	0.70	0.70

Table 2

<table>
<tr><td colspan="4" rowspan="2">Component (unit)</td><td colspan="6">Examples</td></tr>
<tr><td>7</td><td>8</td><td>9</td><td>10</td><td>11</td><td>12</td></tr>
<tr><td rowspan="8">Grease composition</td><td rowspan="2">Base oil (A)</td><td>Base oil (A1)</td><td>% by mass</td><td>85.0</td><td>86.5</td><td>81.5</td><td>76.5</td><td>88.0</td><td>85.0</td></tr>
<tr><td>Base oil (A2)</td><td>% by mass</td><td>-</td><td>-</td><td>5.0</td><td>10.0</td><td>-</td><td>-</td></tr>
<tr><td rowspan="6">Urea-based thickener (B)</td><td>Urea-based thickener (B1)</td><td>% by mass</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Urea-based thickener (B2)</td><td>% by mass</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Urea-based thickener (B3)</td><td>% by mass</td><td>15.0</td><td>13.5</td><td>13.5</td><td>13.5</td><td>12.0</td><td>-</td></tr>
<tr><td>Urea-based thickener (B4)</td><td>% by mass</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td><td>15.0</td></tr>
<tr><td>Urea-based thickener (B5)</td><td>% by mass</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Urea-based thickener (B6)</td><td>% by mass</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td colspan="3">Total</td><td>% by mass</td><td>100.0</td><td>100.0</td><td>100.0</td><td>100.0</td><td>100.0</td><td>100.0</td></tr>
<tr><td rowspan="3">Urea-based thickener (B)</td><td>Chain hydrocarbon group (X)</td><td>Stearyl amine</td><td>% by mole</td><td>8.0</td><td>8.0</td><td>8.0</td><td>8.0</td><td>8.0</td><td>9.0</td></tr>
<tr><td>Alicyclic hydrocarbon group (Y)</td><td>Cyclohexyl amine</td><td>% by mole</td><td>2.0</td><td>2.0</td><td>2.0</td><td>2.0</td><td>2.0</td><td>1.0</td></tr>
<tr><td colspan="2">Total</td><td>% by mole</td><td>10.0</td><td>10.0</td><td>10.0</td><td>10.0</td><td>10.0</td><td>10.0</td></tr>
<tr><td rowspan="2">Ratio</td><td colspan="2">[(A2)/(A1)]</td><td>-</td><td>-</td><td>-</td><td>0.06</td><td>0.13</td><td>-</td><td>-</td></tr>
<tr><td colspan="2">(X/Y)</td><td>-</td><td>4.0</td><td>4.0</td><td>4.0</td><td>4.0</td><td>4.0</td><td>9.0</td></tr>
<tr><td rowspan="2">Property values</td><td rowspan="2">Base oil (A) (mixed base oil)</td><td>40°C Kinematic viscosity</td><td>mm^2/s</td><td>17.5</td><td>17.5</td><td>16.8</td><td>16.2</td><td>17.5</td><td>17.5</td></tr>
<tr><td>Viscosity index</td><td>-</td><td>120</td><td>120</td><td>126</td><td>128</td><td>120</td><td>120</td></tr>
<tr><td rowspan="3">Results of Evaluations</td><td colspan="2">Worked penetration at 25°C</td><td>-</td><td>249</td><td>264</td><td>251</td><td>250</td><td>295</td><td>241</td></tr>
<tr><td colspan="2">Unworked penetration at -40°C</td><td>-</td><td>177</td><td>179</td><td>178</td><td>180</td><td>188</td><td>169</td></tr>
<tr><td colspan="2">[Unworked penetration at -40°C / worked penetration at 25°C]</td><td>-</td><td>0.71</td><td>0.68</td><td>0.71</td><td>0.72</td><td>0.64</td><td>0.70</td></tr>
</table>

Table 3

Component (unit)				Examples			
				13	14	15	16
Grease composition	Base oil (A)	Base oil (A1)	% by mass	86.5	81.5	76.5	88.0
		Base oil (A2)	% by mass	-	5.0	10.0	-
	Urea-based thickener (B)	Urea-based thickener (B1)	% by mass	-	-	-	-
		Urea-based thickener (B2)	% by mass	-	-	-	-
		Urea-based thickener (B3)	% by mass	-	-	-	-
		Urea-based thickener (B4)	% by mass	13.5	13.5	13.5	12.0
		Urea-based thickener (B5)	% by mass	-	-	-	-
		Urea-based thickener (B6)	% by mass	-	-	-	-
Total			% by mass	100.0	100.0	100.0	100.0
Urea-based thickener (B)	Chain hydrocarbon group (X)	Stearyl amine	% by mole	9.0	9.0	9.0	9.0
	Alicyclic hydrocarbon group (Y)	Cyclohexyl amine	% by mole	1.0	1.0	1.0	1.0
	Total		% by mole	10.0	10.0	10.0	10.0
Ratio	[(A2)/(A1)]		-	-	0.06	0.13	-
	(X/Y)		-	9.0	9.0	9.0	9.0
Property values	Base oil (A) (mixed base oil)	40°C Kinematic viscosity	mm2/s	17.5	16.8	16.2	17.5
		Viscosity index	-	120	126	128	120
Results of Evaluations	Worked penetration at 25°C		-	263	270	266	284
	Unworked penetration at -40°C		-	183	183	180	192
	[Unworked penetration at -40°C / worked penetration at 25°C]		-	0.70	0.68	0.68	0.68

Table 4

Component (unit)				Comparative Example				
				1	2	3	4	5
Grease composition	Base oil (A)	Base oil (A1)	% by mass	86.5	88.0	85.0	86.5	88.0
		Base oil (A2)	% by mass	-	-	-	-	-
	Urea-based thickener (B)	Urea-based thickener (B1)	% by mass	-	-	-	-	-
		Urea-based thickener (B2)	% by mass	-	-	-	-	-
		Urea-based thickener (B3)	% by mass	-	-	-	-	-
		Urea-based thickener (B4)	% by mass	-	-	-	-	-
		Urea-based thickener (B5)	% by mass	13.5	12.0	-	-	-
		Urea-based thickener (B6)	% by mass	-	-	15.0	13.5	12.0
Total			% by mass	100.0	100.0	100.0	100.0	100.0
Urea-based thickener (B)	Chain hydrocarbon group (X)	Stearyl amine	% by mole	6.0	6.0	9.5	9.5	9.5
	Alicyclic hydrocarbon group (Y)	Cyclohexyl amine	% by mole	4.0	4.0	0.5	0.5	0.5
	Total		% by mole	10.0	10.0	10.0	10.0	10.0
Ratio	[(A2)/(A1)]		-	-	-	-	-	-
	(X/Y)		-	1.5	1.5	19.0	19.0	19.0
Property values	Base oil (A) (mixed base oil)	40°C kinematic viscosity	mm^2/s	17.5	17.5	17.5	17.5	17.5
		Viscosity index	-	120	120	120	120	120
Results of Evaluations	Worked penetration at 25°C		-	268	276	304	338	346
	Unworked penetration at -40°C		-	157	163	205	214	220
	[Unworked penetration at -40°C / worked penetration at 25°C]		-	0.59	0.59	0.67	0.63	0.64

[0183] As shown in Tables 1 to 3, the grease compositions of Examples 1 to 16 in which the X/Y ratio defined in Requirement (1) fell within the range of 2/1 to 10/1 provided suitable results of the worked penetration at 25°C, the unworked penetration at -40°C, and the ratio of the unworked penetration at -40°C to the worked penetration at 25°C.

[0184] On the other hand, as shown in Table 4, the grease compositions of Comparative Examples 1 to 2 in which the X/Y ratio defined in Requirement (1) was less than 2/1 provided a result in which the ratio of the unworked penetration at -40°C to the worked penetration at 25°C was less than 0.61 and thus, the unworked penetration at -40°C was insufficient relative to the worked penetration at 25°C. This result suggests that such grease compositions have a lower unworked penetration at -40°C and are thus harder at a low temperature than a grease composition that has the same worked penetration at 25°C so that the sealing properties as a grease composition at a low temperature are possibly insufficient.

[0185] Additionally, as shown in Table 4, the grease compositions of Comparative Examples 3 to 5 in which the X/Y ratio defined in Requirement (1) was more than 10/1 provided a result in which the worked penetration at 25°C was more than 300. This result suggests that such grease compositions are considerably softer as compared with the grease compositions of Examples, and thus, require very high torque. The result also suggests that the sealing properties as a grease composition at a normal temperature is possibly insufficient.

<Evaluation 4: evaluation of kinematic friction>

[0186] As shown in Table 5, to the grease composition of Example 8, an acidic phosphate ester (C1) was added and mixed, thus preparing a grease composition containing the acidic phosphate ester (C1) (Example 17).

[0187] Then, for the grease compositions of Example 8 and Example 17, using a ball-on-plate-style Bowden-type reciprocating kinematic friction tester (manufactured by Seimitsu Industrial Co., Ltd.), a kinematic friction between metal and rubber was measured based on the friction in 10 reciprocations before completion of the test under the following testing conditions.

- Testing conditions -

[0188]

- Load: 1 kgf
- Number of reciprocations: 20
- Stroke: 10.0 mm
- Speed: 3.0 mm/sec.
- Temperature: 80°C
- Friction material on ball side: a rubber (material: acrylonitrile-butadiene rubber (NBR), molded to be integrated with a metal ball having a diameter of 12.7 mm)
- Friction material on plate side: a metal plate (material: SPCC, 50 mm × 1,000 mm × 5 mm) on which 1 to 2 mL of a grease composition was applied into a uniform thickness.

[0189] The results are shown in Table 5.

Table 5

Component (unit)				Example	
				8	17
Grease composition	Base oil (A)	Base oil (A1)	% by mass	86.5	84.2
	Urea-based thickener (B)	Urea-based thickener (B3)	% by mass	13.5	14.8
	Acidic phosphate ester (C)	Acidic phosphate ester (C1)	% by mass	-	1.0
Total			% by mass	100.0	100.0
Urea-based thickener (B)	Chain hydrocarbon group (X)	Stearyl amine	% by mole	8.0	8.0
	Alicyclic hydrocarbon group (Y)	Cyclohexyl amine	% by mole	2.0	2.0
	Total		% by mole	10.0	10.0
Ratio	[(B)/(C)]		-	-	14.8
	(X/Y)		-	4.0	4.0
Property values	Base oil (A) (mixed base oil)	40°C Kinematic viscosity	mm^2/s	17.5	17.5
		Viscosity index	-	120	120
Results of Evaluations	Worked penetration at 25°C		-	264	259
	Unworked penetration at -40°C		-	179	176
	[Unworked penetration at -40°C / worked penetration at 25°C]		-	0.68	0.68
Results of Evaluations	Kinematic friction		N	0.67	0.42

[0190] Table 5 shows a result that Example 17 in which the acidic phosphate ester (C1) was added had a lower kinematic friction than that of Example 8. It has been found from this result that incorporation of the acidic phosphate ester (C1) leads to a good reduction in the friction.
[0191] Note that the components contained in Example 17 are as follows.

- Base oil (A1): poly-α-olefin (PAO) (40°C kinematic viscosity: 17.5 mm^2/s, viscosity index: 120)
- Urea-based thickener (B3): the same as in Example 8
- Acidic phosphate ester (C1): oleyl acid phosphate (content of phosphorus atoms: 6.3% by mass)

<Evaluation 5: rubber compatibility test>

[0192] As shown in Table 6, to the grease composition of Example 8, the acidic phosphate ester (C1) and additives (D) were added and mixed, thus preparing a grease composition containing the acidic phosphate ester (C1) (Example 18).
[0193] For the grease composition of Example 18, a rubber compatibility test (type of rubber: acrylonitrile-butadiene rubber (NBR)) was performed according to JIS K 6258 to measure the volume change (%), the mass change (%), and the consistency change (%).
[0194] Note that a volume change (%) of 0 or more and 15 or less, a mass change (%) of 0 or more and 15 or less, and a consistency change (%) of -15 or more and 0 or less were considered as acceptable.
[0195] The results are shown in Table 6.

Table 6

Component (unit)				Example
				18
Grease composition	Base oil (A)	Base oil (A1)	% by mass	83.0
	Urea-based thickener (B)	Urea-based thickener (B3)	% by mass	14.8
	Acidic phosphate ester (C)	Acidic phosphate ester (C1)	% by mass	1.0
	Additive (D)	Phenol-based antioxidant	% by mass	1.0
		Carboxylic acid-based rust inhibitor	% by mass	0.2
Total			% by mass	100.0
Urea-based thickener (B)	Chain hydrocarbon group (X)	Stearyl amine	% by mole	8.0
	Alicyclic hydrocarbon group (Y)	Cyclohexyl amine	% by mole	2.0
	Total		% by mole	10.0
Ratio	[(B)/(C)]		-	14.8
	(X/Y)		-	4.0
Property values	Base oil (A) (mixed base oil)	40°C Kinematic viscosity	mm^2/s	17.5
		Viscosity index	-	120
Results of Evaluations	Worked penetration at 25°C		-	259
	Unworked Penetration At -40°C		-	176
	[Unworked penetration at -40°C / worked penetration at 25°C]		-	0.68
	Rubber compatibility test	Volume change	%	10
		Mass change	%	8
		consistency change	%	-11

[0196] Table 6 shows a result that the grease composition of Example 18 had a compatibility to a rubber.
[0197] Note that the components contained in Example 18 were as follows.

- Base oil (A1): poly-α-olefin (PAO) (40°C kinematic viscosity: 17.5 mm^2/s, viscosity index: 120)

- Urea-based thickener (B3): the same as in Example 8
- Acidic phosphate ester (C1): oleyl acid phosphate (content of phosphorus atoms: 6.3% by mass)
- Additive (D): phenol-based antioxidant, carboxylic acid-based rust inhibitor

Claims

1. A grease composition comprising a base oil (A) and a urea-based thickener (B),

the base oil (A) comprising a poly-α-olefin (PAO),
the urea-based thickener (B) being one or more selected from diurea compounds represented by the following general formula (b1):

$$R^1\text{-NHCONH-}R^3\text{-NHCONH-}R^2 \quad \text{(b1)}$$

wherein R^1 and R^2 each independently represent a monovalent chain hydrocarbon group or alicyclic hydrocarbon group having 6 to 24 carbon atoms, R^1 and R^2 may be the same as or different from each other, and R^3 represents a divalent aromatic hydrocarbon group having 6 to 18 carbon atoms,
when a content of the chain hydrocarbon group in R^1 and R^2 in the general formula (b1) is X molar equivalents and a content of the alicyclic hydrocarbon group in R^1 and R^2 in the general formula (b1) is Y molar equivalents, the grease composition satisfying the following Requirement (1):

• Requirement (1): having a X/Y ratio of 2/1 to 10/1.

2. The grease composition according to claim 1, wherein the chain hydrocarbon group in R^1 and R^2 in the general formula (b1) is a saturated chain hydrocarbon group.

3. The grease composition according to claim 1 or 2, wherein the alicyclic hydrocarbon group in R^1 and R^2 in the general formula (b1) is a saturated alicyclic hydrocarbon group.

4. The grease composition according to any one of claims 1 to 3, wherein the grease composition has a worked penetration at 25°C of 240 to 300.

5. The grease composition according to any one of claims 1 to 4, wherein the grease composition has an unworked penetration at -40°C of 150 or more.

6. The grease composition according to any one of claims 1 to 5, wherein the base oil (A) has a 40°C kinematic viscosity of 10 mm^2/s or more and 40 mm^2/s or less.

7. The grease composition according to any one of claims 1 to 6, wherein the base oil (A) further comprises an ester-based synthetic oil (A2).

8. The grease composition according to claim 7, wherein the ester-based synthetic oil (A2) is comprised in an amount of 20% by mass or less based on a total amount of the base oil (A).

9. The grease composition according to claim 7 or 8, wherein the ester-based synthetic oil (A2) has a 40°C kinematic viscosity of 10 mm^2/s or more and 40 mm^2/s or less.

10. The grease composition according to any one of claims 1 to 9, wherein the grease composition further comprises an acidic phosphate ester (C).

11. The grease composition according to claim 10, wherein the acidic phosphate ester (C) is comprised in an amount of 1.0% by mass to 3.0% by mass based on a total amount of the grease composition.

12. The grease composition according to any one of claims 1 to 11, wherein the grease composition is used for lubricating a sliding mechanism in which a metal material and a rubber material slide.

13. A method of lubrication, the method comprising lubricating, with the grease composition according to any one of claims 1 to 11, a sliding mechanism in which a metal material and a rubber material slide.

14. A method for producing a grease composition, the method comprising a step of performing synthesis of a urea-based thickener (B) in a base oil (A),

the base oil (A) comprising a poly-α-olefin (PAO),
the urea-based thickener (B) being one or more selected from diurea compounds represented by the following general formula (b1):

$$R^1\text{-NHCONH-}R^3\text{-NHCONH-}R^2 \quad \text{(b1)}$$

wherein R^1 and R^2 each independently represent a monovalent chain hydrocarbon group or alicyclic hydrocarbon group having 6 to 24 carbon atoms, R^1 and R^2 may be the same as or different from each other, and R^3 represents a divalent aromatic hydrocarbon group having 6 to 18 carbon atoms,
when a content of the chain hydrocarbon group in R^1 and R^2 in the general formula (b1) is X molar equivalents and a content of the alicyclic hydrocarbon group in R^1 and R^2 in the general formula (b 1) is Y molar equivalents, the synthesis being performed so that the grease composition satisfies the following Requirement (1):

- Requirement (1): having a X/Y ratio of 2/1 to 10/1.

INTERNATIONAL SEARCH REPORT

International application No. **PCT/JP2023/013419**

A. CLASSIFICATION OF SUBJECT MATTER

C10M 169/02(2006.01)i; *C10M 105/32*(2006.01)n; *C10M 107/02*(2006.01)n; *C10M 137/04*(2006.01)n; *C10N 20/02*(2006.01)n; *C10N 30/08*(2006.01)n; *C10N 40/02*(2006.01)n; *C10N 40/04*(2006.01)n; *C10N 50/10*(2006.01)n
FI: C10M169/02; C10M107/02; C10M105/32; C10M137/04; C10N50:10; C10N20:02; C10N30:08; C10N40:02; C10N40:04

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)

C10M169/02; C10N20/02; C10N30/08; C10N40/02; C10N40/04; C10N50/10; C10M105/32; C10M107/02; C10M137/04

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2023
Registered utility model specifications of Japan 1996-2023
Published registered utility model applications of Japan 1994-2023

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 2013/125510 A1 (IDEMITSU KOSAN CO., LTD.) 29 August 2013 (2013-08-29) claims, examples 3-5	1-14
X	JP 9-59661 A (NSK LTD.) 04 March 1997 (1997-03-04) claims, examples 2, 5, comparative example 6	1-14
X	JP 2009-197162 A (KYODO YUSHI CO., LTD.) 03 September 2009 (2009-09-03) comparative example 6	1-14
X	JP 2005-105025 A (NSK LTD.) 21 April 2005 (2005-04-21) examples 1-6, comparative example 1	1-14
X	JP 2005-105026 A (NSK LTD.) 21 April 2005 (2005-04-21) examples 2, 5	1-14
X	JP 2004-224823 A (NSK LTD.) 12 August 2004 (2004-08-12) claims, example 1	1-14

☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 June 2023	**20 June 2023**

Name and mailing address of the ISA/JP	Authorized officer
Japan Patent Office (ISA/JP) **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/013419

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2021-46557 A (MINEBEAMITSUMI INC.) 25 March 2021 (2021-03-25) claims, examples 1-11, 3-9	1-14
X	JP 2016-50234 A (KYODO YUSHI CO., LTD.) 11 April 2016 (2016-04-11) claims, example 5, comparative example 5	1-14
X	JP 2008-239687 A (KYODO YUSHI CO., LTD.) 09 October 2008 (2008-10-09) claims, example 1	1-14

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/013419

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO 2013/125510 A1	29 August 2013	US 2015/0045273 A1 examples 3-5, claims EP 2821465 A1 CN 104169404 A KR 10-2014-0127241 A TW 201336983 A	
JP 9-59661 A	04 March 1997	(Family: none)	
JP 2009-197162 A	03 September 2009	WO 2009/104790 A1 EP 2264132 A1 comp. example 6 KR 10-2010-0103809 A CN 101952401 A	
JP 2005-105025 A	21 April 2005	(Family: none)	
JP 2005-105026 A	21 April 2005	(Family: none)	
JP 2004-224823 A	12 August 2004	(Family: none)	
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JP 2016-50234 A	11 April 2016	US 2017/0275558 A1 example 5, comparative example 5, claims WO 2016/031998 A1 EP 3187572 A1 CN 106795450 A	
JP 2008-239687 A	09 October 2008	US 2010/0087344 A1 example 1, claims WO 2008/117819 A1 CN 101646759 A	

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2021123691 A **[0007]**
- JP 2021102772 A **[0007]**