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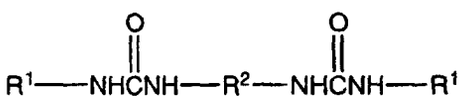
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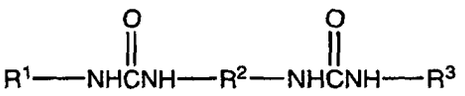
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(54) GREASE COMPOSITION

(57) A grease composition containing a lubricant base oil, diurea compounds represented by the following general formulas (1) to (3), and an organic molybdenum compound; wherein respective contents of the diurea compounds represented by the following general formulas (1) to (3) satisfy conditions defined by the following expressions (4) and (5); and wherein the organic molybdenum compound is contained by 0.1 to 20 mass% based on the total amount of the grease composition:

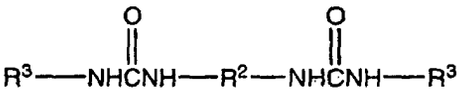


(1)



(2)

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(3)

where R^1 is a hydrocarbon group containing an aromatic ring, R^2 is a divalent hydrocarbon group, and R^3 is a hydrocarbon group containing an aliphatic ring;

$$5 \leq W_1 + W_2 + W_3 \leq 30 \quad (4)$$

$$0.1 \leq (W_1 + 0.5 \times W_2)/(W_1 + W_2 + W_3) \leq 1.0 \quad (5)$$

where W_1, W_2, and W_3 are respective contents (mass%) of the diurea compounds represented by general formulas (1) to (3) based on the total amount of the grease composition.

Description

Technical Field

[0001] The present invention relates to a grease composition; and, more specifically, to a grease composition favorably used in a constant velocity joint, a bearing for a continuously variable transmission, a bearing for both a car and a railway vehicle, etc.

Background Art

[0002] Various mechanical elements where metals contact with each other, such as constant velocity joints for a shaft transmitting a driving force from a transmission of a car to its tires, bearings for continuously variable transmissions of cars and the like, and axle bearings for cars and railway vehicles are filled with grease acting as a lubricant.

[0003] The grease used in these various mechanical elements is required to suppress the temperature rise in its early stage of use from the viewpoint of extending life in particular, and reduce the friction from the viewpoints of extending life and saving energy.

[0004] As a method of suppressing the temperature rise, the kinetic viscosity of a base oil of grease has been lowered in general. As a method of reducing the friction, the use of various additives such as organic molybdenum compounds and organic zinc compounds has been known.

Disclosure of the Invention

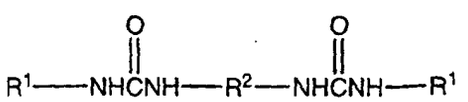
[0005] However, it has been quite difficult for the above-mentioned conventional methods to suppress the temperature rise in the early stage of use and reduce the friction at the same time. For example, when the kinetic viscosity of the base oil is lowered in order to suppress the temperature rise in the early stage of use, the oil film thickness decreases so that metals are more likely to contact with each other, whereby the friction/wear tends to increase. Further, there is a fear of the life shortening at a high temperature.

[0006] Also, under recent circumstances where load has been increasing as various mechanical elements such as constant velocity joints, bearings for continuously variable transmissions, and axle bearings for cars and railway vehicles have been attaining higher performances and lighter weights, properties demanded for the grease to suppress the temperature rise in the early stage of use and lower the friction have been increasing.

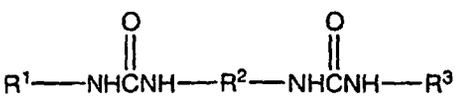
[0007] In view of the above-mentioned problem of the prior art, it is an object of the present invention to provide a grease composition which can realize, at a high level, the suppression of the temperature rise in the early stage of use and the reduction of the friction.

[0008] The inventors conducted diligent studies in order to achieve the above-mentioned object and, as a result, have found that a grease composition in which specific diurea and organic molybdenum compounds are compounded at respective predetermined compounding ratios in a lubricant base oil can suppress the temperature rise in constant velocity joints, bearings for continuously variable transmissions, axle bearings for cars and railway vehicles, and the like in their early stage of use and lower the friction therein, thereby completing the present invention.

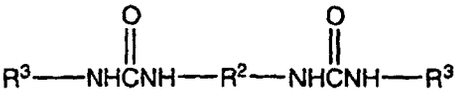
[0009] Namely, the grease composition in accordance with the present invention is one containing a lubricant base oil, diurea compounds represented by the following general formulas (1) to (3), and an organic molybdenum compound; wherein respective contents of the diurea compounds represented by the following general formulas (1) to (3) satisfy conditions defined by the following expressions (4) and (5); and wherein the organic molybdenum compound is contained by 0.1 to 20 mass% based on the total amount of'the grease composition:



(1)



(2)



(3)

where R^1 is a hydrocarbon group containing an aromatic ring, R^2 is a divalent hydrocarbon group, and R^3 is a hydrocarbon group containing an aliphatic ring;

$$5 \leq W_1 + W_2 + W_3 \leq 30 \quad (4)$$

$$0.1 \leq (W_1 + 0.5 \times W_2)/(W_1 + W_2 + W_3) \leq 1.0 \quad (5)$$

where W_1, W_2, and W_3 are respective contents (each expressed by the unit of mass%) of the diurea compounds represented by general formulas (1) to (3) based on the total amount of the grease composition.

Brief Description of the Drawings

[0010] Figs. 1A and 1B are perspective and top plan views showing a test piece used in a friction test, respectively.

Best Modes for Carrying Out the Invention

[0011] In the following, preferred embodiments of the present invention will be explained in detail.

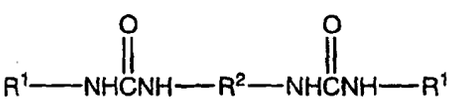
[0012] Examples of the lubricant base oil used in the grease composition of the present invention are mineral oils and/or synthetic oils.

[0013] Examples of the mineral oils are those obtained by a method usually carried out in a lubricant manufacturing process in a petroleum refining industry, more specifically, those obtained when a lubricant fraction yielded by distilling a crude oil under normal pressure and under reduced pressure is refined by carrying out at least one of processes of solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, contact dewaxing, hydro-refining, washing with sulfuric acid, clay treatment, etc.

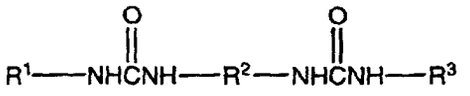
[0014] Specific examples of the synthetic oils include poly α-olefins such as polybutene, 1-octene oligomer, and 1-decene oligomer or their hydrogenated products; diesters such as ditridecyl glutarate, di(2-ethylhexyl) adipate, diisodecyl adipate, ditridecyl adipate, and di (3-ethylhexyl) sebacate; polyol esters such as trimethylolpropane caprylate, trimethylolpropane pelargonate, pentaerythritol 2-ethylhexanoate, and pentaerythritol pelargonate; aromatic ester oils such as trioctyl trimellitate, tridecyl trimellitate, and tetraoctyl pyromellitate; complex esters which are esters formed by a mixed fatty acid of a dibasic acid and a monobasic acid, and a polyhydric alcohol; alkyl' naphthalene; alkyl benzene; polyoxyalkylene glycol; polyphenyl ether; dialkyldiphenyl ether; silicone oil; and their mixtures.

[0015] The kinetic viscosity of the lubricant base oil at 100°C is preferably 2 to 40 mm^2/s, more preferably 3 to 20 mm^2/s. The viscosity index of the base oil is preferably at least 90, more preferably at least 100.

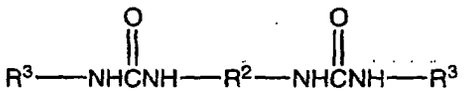
[0016] In the present invention, diurea compounds represented by the following general formulas (1) to (3) are added as a thickener to the lubricant base oil:



(1)



(2)

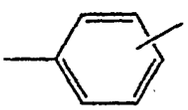


(3)

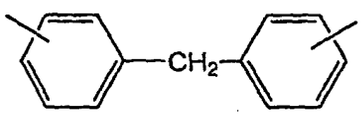
[0017] In the above-mentioned formulas (1) to (3), R^1 is a hydrocarbon group containing an aromatic ring. Examples of such a group include phenyl group, naphthyl group, alkylaryl groups in which at least one alkyl group is added to these groups as a substituent, and arylalkyl groups in which aryl groups such as phenyl and naphthyl groups are added to alkyl groups as substituents.

[0018] Though the number of carbons in the hydrocarbon group containing an aromatic ring represented by R^1 is not limited in particular, one with a carbon number of 7 to 12 is preferably used. Specific examples of the hydrocarbon group containing an aromatic ring with such a carbon number include toluyl group, xylyl group, β-phenacyl group, t-butylphenyl group, dodecylphenyl group, benzyl group, and methylbenzyl group.

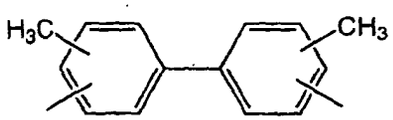
[0019] R^2 in general formulas (1) to (3) is a divalent hydrocarbon group (preferably with a carbon number of 6 to 20, a carbon number of 6 to 15 in particular). Examples of such a hydrocarbon group include linear or branched alkylene groups, linear or branched alkenylene groups, cycloalkylene groups, and aromatic groups. Among them, ethylene group, 2,2-dimethyl-4-methylhexylene group, and groups represented by the following formulas (6) to (14) are preferred, the groups represented by the formulas (7) and (9) in particular:



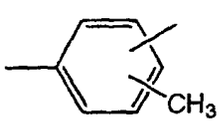
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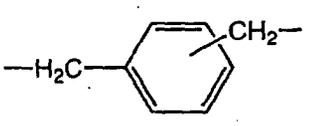
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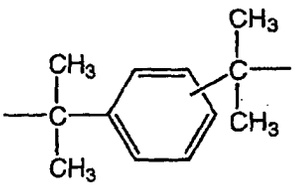
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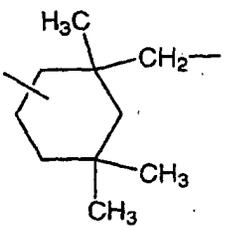
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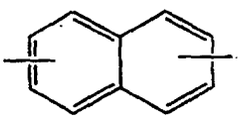
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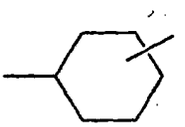
(11)



(12)



(13)



(14)

[0020] In general formulas (2) and (3), R^3 is a hydrocarbon group containing an aliphatic ring. Though the number of carbons contained in the hydrocarbon group containing an aliphatic ring represented by R^3 is not restricted in particular, one with a carbon number of 7 to 12 is preferably used.

[0021] As the hydrocarbon group containing an aliphatic ring represented by R^3, cyclohexyl group or alkylcyclohexyl group is preferably used. Specific examples include methylcyclohexyl group, dimethylcyclohexyl group, ethylcyclohexyl group, diethylcyclohexyl group, propylcyclohexyl group, isopropylcyclohexyl group, 1-methyl-3-propylcyclohexyl group, butylcyclohexyl group, pentylcyclohexyl group, pentylmethylcyclohexyl group, and hexylcyclohexyl group, among which cyclohexyl group, methylcyclohexyl group, dimethylcyclohexyl group, and ethylcyclohexyl group are more preferable.

[0022] The respective contents of the diurea compounds represented by general formulas (1) to (3) are required to satisfy the conditions represented by the following expressions (4) and (5):

$$5 \leq W_1 + W_2 + W_3 \leq 30 \quad (4)$$

$$0.1 \leq (W_1 + 0.5 \times W_2)/(W_1 + W_2 + W_3) \leq 1.0 \quad (5)$$

where W_1, W_2, and W_3 are respective contents (each expressed by the unit of mass%) of the diurea compounds represented by general formulas (1) to (3) based on the total amount of the grease composition.

[0023] As expression (4) shows, the sum $W_1+W_2+W_3$ of contents of the diurea compounds represented by general formulas (1) to (3) is 5 to 30 mass% based on the total amount of the grease composition. When the sum $W_1+W_2+W_3$ is less than 5 mass%, the effect of the thickener is so weak that the composition fails to become sufficiently greasy. For the same reason, $W_1+W_2+W_3$ is preferably at least 10 mass%. When $W_1+W_2+W_3$ exceeds 30 mass%, the composition becomes too hard as a grease, thereby failing to exhibit a sufficient lubricating property. For the same reason, $W_1+W_2+W_3$ is preferably 20 mass% or less.

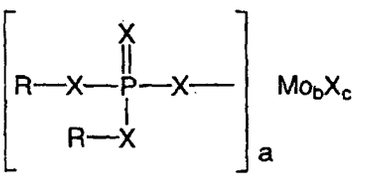
[0024] When $(W_1+0.5\times W_2)/ (W_1+W_2+W_3)$ in expression (5) is less than 0.1, the effect of suppressing the temperature rise in the early stage of use becomes weaker. For the same reason, $(W_1+0.5\times W_2)/(W_1+W_2+W_3)$ is preferably at least 0.2, more preferably at least 0.3, further preferably at least 0.4. Similarly, from the viewpoint of the effect of suppressing the temperature rise in the early stage of use, $(W_1+0.5\times W_2)/(W_1+W_2+W_3)$ is preferably not greater than 0.7, more preferably less than 0.55, further preferably less than 0.5.

[0025] Though urea type thickeners apt to become harder as time passes in general, the grease composition of the present invention is relatively less likely to harden. For making it further less likely to harden, $(W_1+0.5\times W_2)/(W_1+W_2+W_3)$ is preferably at least 0.3, more preferably at least 0.35, further preferably at least 0.4, at least 0.45 in particular.

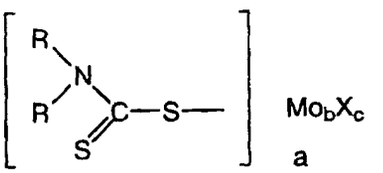
[0026] For example, these diurea compounds are obtained when a diisocyanate represented by the general formula of OCN-R^2-NCO and an amine represented by the general formula of R^1-NH_2 and/or R^3-NH_2 are caused to react against each other at a temperature of 10° to 200°C in the base oil. Here, R^1, R^2, and R^3 correspond to those of (1) to (3), respectively.

[0027] When the value of $(W_1+0.5\times W_2)/ (W_1+W_2+W_3)$ in expression (5) is not 1, the diurea compounds may be a mixture of a reaction product of diisocyanate and the amine represented by R^1-NH_2, and a reaction product of diisocyanate and the amine represented by R^3-NH_2; or a reaction product of diisocyanate and a mixture of the amine represented by R^1-NH_2 and the amine represented by R^3-NH_2.

[0028] The grease composition of the present invention further contains an organic molybdenum compound in addition to the above-mentioned lubricant base oil and diurea compounds. Examples of the organic molybdenum compound include a phosphate or thiophosphate ester derivative represented by the following general formula. (15) and a dithiocarbamate ester derivative represented by the following general formula (16):



(15)



(16)

[0029] In general formulas (15) and (16), R may be identical or different, each representing a hydrocarbon group with a carbon number of at least 1; c pieces of X may be identical or different, each representing an oxygen atom or sulfur atom; and each of a, b, and c represents an integer of 1 to 6.

[0030] Examples of the hydrocarbon group represented by R in the above-mentioned formulas (15) and (16) include

alkyl groups with a carbon number of 1 to 24, cycloalkyl groups with a carbon number of 5 to 7, alkylcycloalkyl groups with a carbon number of 6 to 11, aryl groups with a carbon number of 6 to 18, alkylaryl groups with a carbon number of 7 to 24, and arylalkyl groups with a carbon number of 7 to 12.

[0031] Specific examples of the above-mentioned alkyl groups include methyl group, ethyl group, propyl group (including all the branched isomers thereof), pentyl group (including all the branched isomers thereof), hexyl group (including all the branched isomers thereof), heptyl group (including all the branched isomers thereof), octyl group (including all the branched isomers thereof), nonyl group (including all the branched isomers thereof), decyl group (including all the branched isomers thereof), undecyl group (including all the branched isomers thereof), dodecyl group (including all the branched isomers thereof), tridecyl group (including all the branched isomers thereof), tetradecyl group (including all the branched isomers thereof), pentadecyl group (including all the branched isomers thereof), hexadecyl group (including all the branched isomers thereof), heptadecyl group (including all the branched isomers thereof), octadecyl group (including all the branched isomers thereof), nonadecyl group (including all the branched isomers thereof), icosyl group (including all the branched isomers thereof), henicosyl group (including all the branched isomers thereof), docosyl group (including all the branched isomers thereof), tricosyl group (including all the branched isomers thereof), and tetracosyl group (including all the branched isomers thereof).

[0032] Specific examples of the above-mentioned cycloalkyl groups include cyclopentyl group, cyclohexyl group, and cycloheptyl group.

[0033] Specific examples of the above-mentioned alkylcycloalkyl groups include methylcyclopentyl group (including all the substituted isomers thereof), ethylcyclopentyl group (including all the substituted isomers thereof), dimethylcyclopentyl group (including all the substituted isomers thereof), propylcyclopentyl group (including all the branched isomers and substituted isomers thereof), methylethylcyclopentyl group (including all the substituted isomers thereof), trimethylcyclopentyl group (including all the substituted isomers thereof), butylcyclopentyl group (including all the branched isomers and substituted isomers thereof), methylpropylcyclopentyl group (including all the branched isomers and substituted isomers thereof), diethylcyclopentyl group (including all the substituted isomers thereof), dimethylcyclopentyl group (including all the substituted isomers thereof), methylcyclohexyl group (including all the substituted isomers thereof), ethylcyclohexyl group (including all the substituted isomers thereof), dimethylcyclohexyl group (including all the substituted isomers thereof), propylcyclohexyl group (including all the branched isomers and substituted' isomers thereof), methylethylcyclohexyl group (including all the substituted isomers thereof), trimethylcyclohexyl group (including all the substituted isomers thereof), butylcyclohexyl group (including all the branched isomers and substituted isomers thereof), methylpropylcyclohexyl group (including all the branched isomers and substituted isomers thereof), diethylcyclohexyl group (including all the substituted isomers thereof), dimethylethylcyclohexyl group (including all the substituted isomers thereof), methylcycloheptyl group (including all the substituted isomers thereof), ethylcycloheptyl group (including all the substituted isomers thereof), dimethylcycloheptyl group (including all the substituted isomers thereof), propylcycloheptyl group (including all the substituted isomers thereof), methylethylcycloheptyl group (including all the substituted isomers thereof), trimethylcycloheptyl group (including all the substituted isomers thereof), butylcycloheptyl group (including all the branched isomers and substituted isomers thereof), methylpropylcycloheptyl group (including all the branched isomers and substituted isomers thereof), diethylcycloheptyl group (including all the substituted isomers thereof), and dimethylethylcycloheptyl group (including all the substituted isomers thereof).

[0034] Specific examples of the above-mentioned aryl groups include phenyl group and naphthyl group.

[0035] Specific examples of the above-mentioned alkylaryl groups include tolyl group (including all the substituted isomers thereof), xylyl group (including all the substituted isomers thereof), ethylphenyl group (including all the substituted isomers thereof), propylphenyl group (including all the branched isomers and substituted isomers thereof), methylethylphenyl group (including all the substituted isomers thereof), trimethylphenyl group (including all the substituted isomers thereof), butylphenyl group (including all the branched isomers and substituted isomers thereof), methylpropylphenyl group (including all the branched isomers and substituted isomers thereof), diethylphenyl group (including all the substituted isomers thereof), dimethylethylphenyl group (including all the substituted isomers thereof), pentylphenyl group (including all the branched isomers and substituted isomers thereof), hexylphenyl group (including all the branched isomers and substituted isomers thereof), heptylphenyl group (including all the branched isomers and substituted isomers thereof), octylphenyl group (including all the branched isomers and substituted isomers thereof), nonylphenyl group (including all the branched isomers and substituted isomers thereof), decylphenyl group (including all the branched isomers and substituted isomers thereof), undecylphenyl group (including all the branched isomers and substituted isomers thereof), dodecylphenyl group (including all the branched isomers and substituted isomers thereof), tridecylphenyl group (including all the branched isomers and substituted isomers thereof), tetradecylphenyl group (including all the branched isomers and substituted isomers thereof), pentadecylphenyl group (including all the branched isomers and substituted isomers thereof), hexadecylphenyl group (including all the branched isomers and substituted isomers thereof), heptadecylphenyl group (including all the branched isomers and substituted isomers thereof), and octadecylphenyl group (including all the branched isomers and substituted isomers thereof).

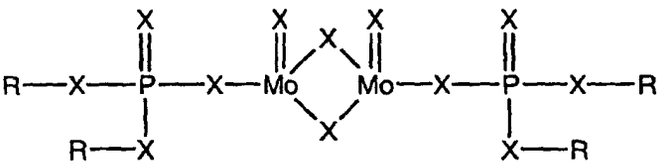
[0036] Examples of the arylalkyl groups include benzyl group, phenethyl group, phenylpropyl group (including all the

branched isomers thereof), and phenylbutyl group (including all the branched isomers and substituted isomers thereof).

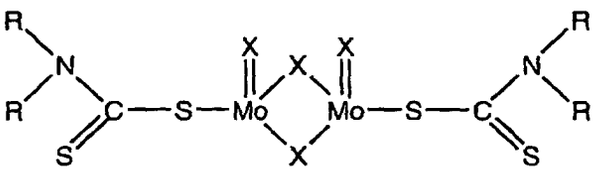
[0037] Specific examples of the compounds represented by the above-mentioned general formulas (15) and (16) include molybdenum phosphate, molybdenum thiophosphate, molybdenum dithiophosphate, and molybdenum dithiocarbamate.

[0038] The phosphate or thiophosphate ester derivative represented by the above-mentioned formula (15) and the dithiocarbamate ester derivative represented by the above-mentioned formula (16) are compounds usually obtained by causing a phosphate ester, a thiophosphate ester, or a dithiocarbamate ester to react with an inorganic molybdenum compound (molybdenum trioxide, molybdenum oxide, salts thereof, etc.) together with a sulfur source if necessary.

[0039] Since molybdenum can take various valences, the compounds obtained by the above-mentioned reaction are usually mixtures. Among them, the most typical compounds are those represented by the following compounds (17) and (18):



(17)



(18)

[0040] As the organic molybdenum compound in the present invention, the respective compounds represented by the above-mentioned general formulas (15) and (16) may be used separately or in a mixture. For use in bearing grease, the compound represented by the above-mentioned general formula (16) is more preferable because of its better thermal stability.

[0041] The content of the organic molybdenum compound in the present invention is at least 0.1 mass%, preferably at least 0.5 mass%, based on the total amount of the grease composition. On the other hand, the content is not greater than 20 mass%, preferably not greater than 10 mass%. The friction reducing effect of the grease is insufficient when the content of the organic molybdenum compound is less than 0.1 mass%, whereas the friction reducing effect cannot be obtained in proportion to the amount of addition when the content exceeds 20 mass%.

[0042] For improving the resistance to fretting, it will be preferred if at least one species of compound selected from the group consisting of paraffin oxides and phosphorus compounds is added to the grease composition of the present invention. When these compounds are added, a higher level of resistance to fretting can be achieved over a long period in a constant velocity joint in which micromotion wear (fretting) is likely to become problematic upon minute reciprocation in particular.

[0043] Examples of the paraffin oxides used in the present invention include paraffin oxide, salts of paraffin oxide, and esters of paraffin oxide. Examples of paraffin oxide mentioned here include those obtained by oxidizing petroleum waxes such as paraffin wax, microcrystalline wax, and slack wax, or a synthetic wax such as polyolefin wax. Examples of the salts of paraffin oxide include alkali metal salts, alkaline earth metal salts, and amine salts of paraffin oxide. Examples of the esters of paraffin oxide include esters formed between an alcohol (most preferably methanol) having a carbon number of 1 to 24 (preferably 1 to 12, more preferably 1 to 6) and paraffin oxide. The paraffin oxides used in the present invention may have any properties. However, from the viewpoint of the resistance to fretting, their melting point is preferably at least 25°C, more preferably 30°C, but preferably not higher than 110°C, more preferably not higher than 70°C. The total acid number is preferably at least 0.2 mgKOH/g, more preferably at least 1 mgKOH/g, but preferably not greater than 65 mgKOH/g, more preferably not greater than 40 mgKOH/g.

[0044] Specific examples of the phosphorus compounds include phosphate esters, acid phosphate esters, amine salts of acid phosphate esters, chlorinated phosphate esters, phosphite esters, and thiophosphate esters. These phosphorus compounds are esters formed between phosphoric acid, phosphorous acid, or thiophosphoric acid and an alkanol or polyether alcohol, or their derivatives.

[0045] More specific examples of phosphate esters include tributyl phosphate, tripentyl phosphate, trihexyl phos-

phate, triheptyl phosphate, trioctyl phosphate, trinonyl phosphate, tridecyl phosphate, triundecyl phosphate, tridodecyl phosphate, tritridecyl phosphate, tritetradecyl phosphate, tripentadecyl phosphate, trihexadecyl phosphate, triheptadecyl phosphate, trioctadecyl phosphate, trioleyl phosphate, triphenyl phosphate, tricresyl phosphate, trixylenyl phosphate, cresyldiphenyl phosphate, and xylenyldiphenyl phosphate.

[0046] Examples of the acid phosphate esters include monobutyl acid phosphate, monopentyl acid phosphate, monohexyl acid phosphate, monoheptyl acid phosphate, monooctyl acid phosphate, monononyl acid phosphate, monodecyl acid phosphate, monoundecyl acid phosphate, monododecyl acid phosphate, monotridecyl acid phosphate, monotetradecyl acid phosphate, monopentadecyl acid phosphate, monohexadecyl acid phosphate, monoheptadecyl acid phosphate, monooctadecyl acid phosphate, monooleyl acid phosphate, dibutyl acid phosphate, dipentyl acid phosphate, dihexyl acid phosphate, diheptyl acid phosphate, dioctyl acid phosphate, dinonyl acid phosphate, didecyl acid phosphate, diundecyl acid phosphate, didodecyl acid phosphate, ditridecyl acid phosphate, ditetradecyl acid phosphate, dipentadecyl acid phosphate, dihexadecyl acid phosphate, diheptadecyl acid phosphate, dioctadecyl acid phosphate, and dioleyl acid phosphate.

[0047] Examples of the amine salts of acid phosphate esters include salts formed between the acid phosphate esters and amines such as methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, heptylamine, octylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, dipentylamine, dihexylamine, diheptylamine, dioctylamine, trimethylamine, triethylamine, tripropylamine, tributylamine, tripentylamine, trihexylamine, triheptylamine, and trioctylamine.

[0048] Examples of the chlorinated phosphate esters include tris(dichloropropyl)phosphate, tris(chloroethyl)phosphate, tris(chlorophenyl)phosphate, and polyoxyalkylene bis[di(chloroalkyl)]phosphate.

[0049] Examples of the phosphite esters include phosphite diesters such as dibutyl hydrogen phosphite, dipentyl hydrogen phosphite, dihexyl hydrogen phosphite, diheptyl hydrogen phosphite, dioctyl hydrogen phosphite, dinonyl hydrogen phosphite, didecyl hydrogen phosphite, diundecyl hydrogen phosphite, didodecyl hydrogen phosphite, dioleyl hydrogen phosphite, diphenyl hydrogen phosphite, and dicresyl hydrogen phosphite; and phosphite triesters such as tributyl phosphite, tripentyl phosphite, trihexyl phosphite, triheptyl phosphite, trioctyl phosphite, trinonyl phosphite, tridecyl phosphite, triundecyl phosphite, tridodecyl phosphite, trioleyl phosphite, triphenyl phosphite, and tricresyl phosphite.

[0050] Examples of phosphorothionate include tributyl phosphorothionate, tripentyl phosphorothionate, trihexyl phosphorothionate, triheptyl phosphorothionate, trioctyl phosphorothionate, trinonyl phosphorothionate, tridecyl phosphorothionate, triundecyl phosphorothionate, tridodecyl phosphorothionate, tritridecyl phosphorothionate, tritetradecyl phosphorothionate, tripentadecyl phosphorothionate, trihexadecyl phosphorothionate, triheptadecyl phosphorothionate, trioctadecyl phosphorothionate, trioleyl phosphorothionate, triphenyl phosphorothionate, tricresyl phosphorothionate, trixylenyl phosphorothionate, cresyldiphenyl phosphorothionate, xylenyldiphenyl phosphorothionate, tris(n-propylphenyl)phosphorothionate, tris(isopropylphenyl)phosphorothionate, tris(n-butylphenyl)phosphorothionate, tris(isobutylphenyl)phosphorothionate, tris(s-butylphenyl)phosphorothionate, and tris(t-butylphenyl)phosphorothionate.

[0051] The above-mentioned phosphorus compounds may be used one by one or in a mixture of two or more.

[0052] Among them, because of better resistance to fretting, phosphite esters are preferable, phosphite diesters are more preferable, and diphenyl hydrogen phosphite is further preferable.

[0053] The content of at least one compound selected from the group consisting of the paraffin oxides and phosphorus compounds is preferably at least 0.5 mass%, more preferably at least 1.0 mass%, based on the total amount of the grease composition. When the content is less than 0.5 mass%, the resistance to fretting tends to become insufficient in the grease. On the other hand, the content is preferably not greater than 15 mass%, more preferably 10 mass%. When the content exceeds 15 mass%, the resistance to fretting cannot be obtained in proportion to the amount of addition.

[0054] For further improving the resistance to fretting, $(W_1+0.5\times W_2)/(W_1+W_2+W_3)$ in expression (5) is preferably at least 0.3, more preferably at least 0.35, further preferably at least 0.4, furthermore preferably at least 0.45, but is preferably not greater than 0.7, more preferably not greater than 0.6, further preferably less than 0.5.

[0055] For improving performances, the grease composition of the present invention can further contain solid lubricants, extreme pressure agents, antioxidants, oily agents, antirusts, viscosity index improvers, etc. when necessary as long as its properties do not deteriorate.

[0056] Specific examples of the solid lubricants include graphite, graphite fluoride, polytetrafluoroethylene, molybdenum disulfide, antimony sulfide, and alkali (earth) metal borates.

[0057] Specific examples of the extreme pressure agents include organic zinc compounds such as zinc dialkyldithiophosphate and zinc diaryldithiophosphate; and sulfur-containing compounds such as dihydrocarbyl polysulfide, sulfide esters, thiazole compounds, and thiadiazole compounds.

[0058] Specific examples of the antioxidants include phenol type compounds such as 2,6-di-t-butylphenol and 2,6-di-t-butyl-p-cresol; amine type compounds such as dialkyldiphenylamine, phenyl-α-naphthylamine, and p-alkylphenyl-α-naphthylamine; sulfur type compounds; and phenothiazine type compounds.

[0059] Specific examples of the oily agents include amines such as laurylamine, myristylamine, palmitylamine, stearylamine, and oleylamine; higher alcohols such as lauryl alcohol, myristyl alcohol, palmityl alcohol, stearyl alcohol, and oleyl alcohol; higher fatty acids such as lauric acid, myristic acid, palmitic acid, stearic acid, and oleic acid; fatty acid esters such as methyl laurate, methyl myristate, methyl palmitate, methyl stearate, and methyl oleate; amides such as laurylamide, myristylamide, palmitylamide, stearylamide, and oleylamide; and fats and oils.

[0060] Specific examples of the antirusts include metal soaps; polyhydric alcohol partial esters such as sorbitan fatty acid esters; amines; phosphoric acid; and phosphates.

[0061] Specific examples of the viscosity index improvers include polymethacrylate, polyisobutylene, and polystyrene.

[0062] The grease composition of the present invention can be prepared, for example, by mixing and stirring the diurea compounds represented by general formulas (1) to (3) and an organic molybdenum compound, together with other additives if necessary, with a lubricant base oil; and passing thus obtained mixture through a roll mill or the like. The grease composition can also be made by adding the material components of the diurea compounds represented by general formulas (1) to (3) to the lubricant base oil beforehand; melting them together; stirring and mixing them so as to prepare the diurea compounds; then mixing and stirring them with the organic molybdenum compound, together with other additives if necessary; and passing thus obtained mixture through a roll mill or the like.

[0063] The grease composition of the present invention is excellent in suppressing temperature rises and reducing friction, and thus is useful as a grease for various gears of constant velocity joints, constant velocity gears, and transmission gears, and various bearings such as ball bearings and roller bearings, and is favorably used in constant velocity joints, bearings for continuously variable transmissions, gears and bearings for ironmaking equipment, axle bearings for cars/railway vehicles, etc. in particular.

Examples

[0064] In the following, details of the present invention will be explained more specifically with reference to examples and comparative examples. However, the following examples do not restrict the present invention at all.

Examples 1 to 7 and Comparative Examples 1 to 5

[0065] Using poly-α-olefin (having a kinetic viscosity of 48 mm^2/s at 40°C) as a lubricant base oil, diphenylmethane-4,4'-diisocyanate (MDI) was dissolved into the base oil by heating, and monoamines listed in Tables 1 and 2, each dissolved in the base oil, were added thereto. Various additives listed in the following were added to thus generated gel-like materials, so as to yield the compositions shown in Tables 1 and 2, and after stirring, the resulting mixtures were passed through a roll mill, so as to yield the grease compositions of Examples 1 to 7 and Comparative Examples 1 to 5. The values of $W_1+W_2+W_3$ and $(W_1+0.5\times W_2)/(W_1+W_2+W_3)$ in thus obtained grease compositions are shown in Tables 1 and 2. In Table 2, the cells for $W_1+W_2+W_3$ in Comparative Examples 4 and 5 show their respective total thickener amounts instead of $W_1+W_2+W_3$.

Additives:

[0066]

MoDTC (molybdenum dioctyldithiocarbamate)
MoDTP (molybdenum dioctyldithiophosphate)
MoP (molybdenum dibutylphosphate)
Boron type friction modifier (potassium borate type friction modifier)
paraffin oxide (paraffin oxide ester (ester formed between paraffin oxide obtained by oxidizing slack wax and methanol, with a total acid number of 33 mgKOH/g and a saponification number of 130 mgKOH/g))
dihydrogen phosphite (diphenyl hydrogen phosphite)

[0067] The following temperature rise and friction tests were carried out for the grease compositions of Examples 1 to 7 and Comparative Examples 1 to 5.

Temperature Rise Test

[0068] Into a deep groove ball bearing having an inner ring diameter of 55 mm, an outer ring diameter of 90 mm, and a width of 11 mm, 4.0 g of grease were sealed, and the bearing was rotated under a condition with an inner ring rotating speed of 9000 rpm and an axial load of 5000 N. The bearing outer ring temperature at that time was measured,

whereby a temperature rise ΔT was determined. Thus obtained results are shown in Tables 1 and 2.

Friction Test

[0069] Figs. 1A and 1B are perspective and top plan views showing a test piece used in a friction test, respectively. As depicted, a needle holder 2 (14 mm $\times$ 10 mm $\times$ 2.5 mm) formed at the center part of a lower disc 1 (24 mm in diameter $\times$ 7.9 mm) was filled with 1 g of each grease composition. Then, three' needles (each having a size of 3 mm in diameter $\times$ 13.8 mm) were accommodated in the needle holder 2, and an upper disc 4 (20 mm in diameter $\times$ 13 mm) was disposed thereon. These test pieces were set in an SRV friction tester such that the angle θ [deg] (needle set angle) formed between a line l_1, perpendicular to sliding directions of the upper disc 4, passing the center O of the upper face of the lower disc 1 and a line l_2, parallel to the longitudinal direction of the needle 3, passing the center O became 30 deg, and a friction test was carried out under a condition with a frequency of 40 Hz, an amplitude of 3 mm, a load of 1000 N, and a temperature of 80°C. Table 1 and 2 show the respective friction coefficients obtained 10 minutes thereafter when using the individual grease compositions.

Fretting Resistance Test

[0070] Using a Fafnir friction oxidation tester, a fretting resistance test was carried out in conformity to ASTM D4170, so as to measure the amount of wear. Using a thrust bearing 51204 (manufactured by NSK Ltd.) as a bearing, the test was conducted for 2 hours at room temperature. In this test, the grease compositions made 1 day before were used as samples. Tables 1 and 2 show the results.

Measurement of Consistency

[0071] For each of the grease compositions of Examples 1 to 7 and Comparative Examples 1 to 5, consistency was measured after the lapse of 1 day from the making and after the lapse of 3 months from the making. Tables 1 and 2 show the results.

TABLE 1

			Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
Thickener	MDI[mol]		5	10	5	1	10	10	10
	monoamine [mol]	p−toluidine	1	9	7	2	9	9	9
		cyclohexylamine	9	11	3	—	11	11	11
		octadecylamine	—	—	—	—	—	—	—
	$W_1+W_2+W_3$ [mass%]		18	18	18	20	18	18	18
	$\frac{(W_1+0.5\times W_2)}{(W_1+W_2+W_3)}$		0.1	0.45	0.7	1.0	0.45	0.45	0.45
Base oil	PAO [mass%]		80	80	80	78	77	79	77.5
Additive	MoDTC [mass%]		2	2	2	2	—	—	2
	MoDTP [mass%]		—	—	—	—	5	—	—
	MoP [mass%]		—	—	—	—	—	3	—
	boron type friction modifier [mass%]		—	—	—	—	—	—	—
	paraffin oxide [mass%]		—	—	—	—	—	—	2
	dihydrogen phosphite [mass%]		—	—	—	—	—	—	0.5
Temperature rise ΔT (°C)			104	94	100	98	97	102	105
Friction coefficient			0.090	0.070	0.080	0.085	0.080	0.090	0.080
Fretting resistance (amount of wear [mg])			2.9	1.6	2.7	2.8	1.8	1.8	0.2
Consistency (60W)		1 day after making	272	286	295	293	300	291	296
		3 months after making	257	282	298	291	305	288	290

TABLE 2

			Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Thickener	MDI[mol]		1	10	10	1	1
	monoamine [mol]	p—toluidine	—	9	9	—	—
		cyclohexylamine	2	11	11	1	1
		octadecylamine	—	—	—	1	1
	$W_1+W_2+W_3$ [mass%]		18	18	18	(18)	(18)
	$\frac{(W_1+0.5\times W_2)}{(W_1+W_2+W_3)}$		0	0.45	0.45	0	0
Base oil	PAO [mass%]		80	82	80	80	77.5
Additive	MoDTC [mass%]		2	—	—	2	2
	MoDTP [mass%]		—	—	—	—	—
	MoP [mass%]		—	—	—	—	—
	boron type friction modifier [mass%]		—	—	2	—	—
	paraffin oxide [mass%]		—	—	—	—	2
	dihydrogen phosphite [mass%]		—	—	—	—	0.5
Temperature rise ΔT (°C)			138	130	135	>150	>150
Friction coefficient			0.120	0.130	0.095	0.130	0.130
Fretting resistance (amount of wear [mg])			7.0	2.0	2.1	8.5	1.5
Consistency (60W)		1 day after making	275	281	288	270	276
		3 months after making	252	283	289	227	214

[0072] As shown in Table 1, it was verified that the grease compositions of Examples 1 to 7 were excellent in friction characteristics and temperature rise suppression. Also, the grease compositions of Examples 6 and 7 to which a paraffin oxide and a phosphorus compound were added exhibited a very high level of resistance to fretting.

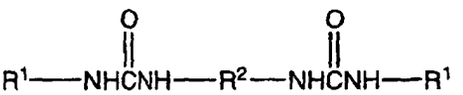
[0073] By contrast, the grease composition of Comparative Example 1 shown in Table 2 was insufficient in terms of friction characteristics, whereas temperature rose greatly when the grease compositions of Comparative Examples 2 and 3 were used.

Industrial Applicability

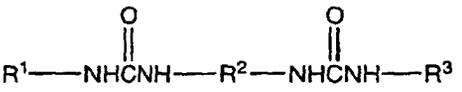
[0074] As explained in the foregoing, by adding the diurea compounds represented by general formulas (1) to (3) and an organic molybdenum compound into a lubricant base oil at their respective specific compounding ratios, the grease composition of the present invention can realize, at a high level, the suppression of the temperature rise in the early stage of use and the reduction of the friction.

Claims

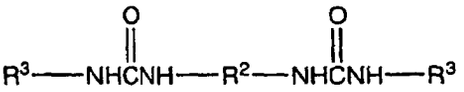
1. A grease composition containing a lubricant base oil, diurea compounds represented by the following general formulas (1) to (3), and an organic molybdenum compound; wherein respective contents of the diurea compounds represented by the following general formulas (1) to (3) satisfy conditions defined by the following expressions (4) and (5); and wherein the organic molybdenum compound is contained by 0.1 to 20 mass% based on the total amount of the grease composition:



(1)



(2)



(3)

where R^1 is a hydrocarbon group containing an aromatic ring, R^2 is a divalent hydrocarbon group, and R^3 is a hydrocarbon group containing an aliphatic ring;

$$5 \leq W_1 + W_2 + W_3 \leq 30 \quad (4)$$

$$0.1 \leq (W_1 + 0.5 \times W_2)/(W_1 + W_2 + W_3) \leq 1.0 \quad (5)$$

where W_1, W_2, and W_3 are respective contents (mass%) of the diurea compounds represented by general formulas (1) to (3) based on the total amount of the grease composition.

Fig.1A

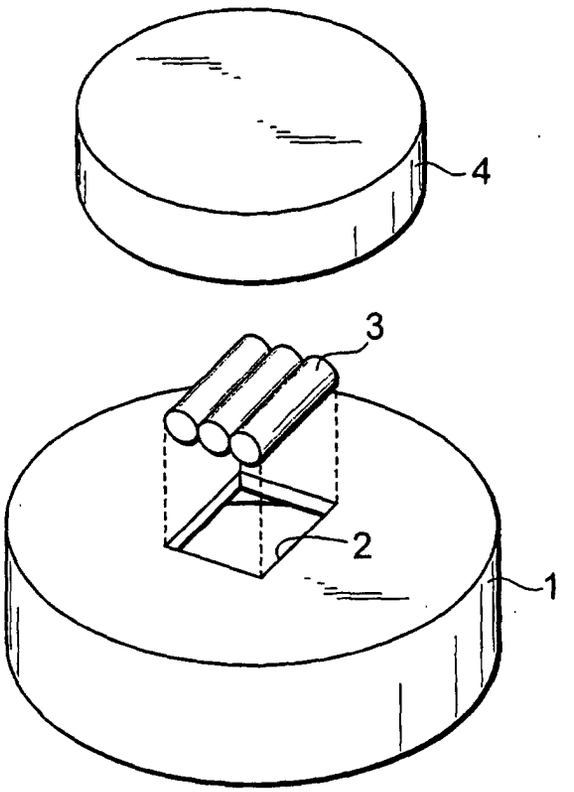
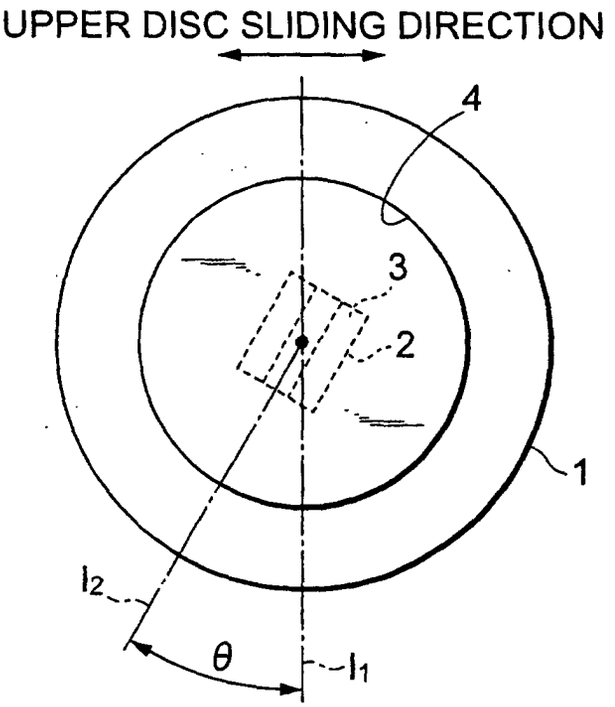


Fig.1B



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP03/05114

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[7] C10M169/06
//(C10M169/06, 115:08, 135:18, 137:04)
C10N30:06, 40:02, 50:10
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
Int.Cl[7] C10M169/06, 115/08, 135/18, 137/04-137/10
C10N30:06, 40:02, 50:10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2003
Kokai Jitsuyo Shinan Koho 1971-2003 Jitsuyo Shinan Toroku Koho 1996-2003

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	EP 773280 A2 (KYODO YUSHI CO., LTD.), 14 May, 1997 (14.05.97), & DE 69624198 T2 & JP 9-194871 A & KR 97027278 A & US 5607906 A	1
X	EP 796910 A1 (KYODO YUSHI CO., LTD. et al.), 24 September, 1997 (24.09.97), & JP 9-255983 A & US 5604187 A	1
X	GB 2323851 A (KYODO YUSHI CO., LTD. et al.), 07 October, 1998 (07.10.98), & AU 9859708 A & DE 19814124 A1 & FR 2761372 A1 & JP 10-273691 A & JP 10-273692 A & KR 98080848 A & US 5952273 A	1

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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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
12 May, 2003 (12.05.03)	27 May, 2003 (27.05.03)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP03/05114

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6355602 B1 (KYODO YUSHI CO., LTD. et al.), 12 March, 2002 (12.03.02), & DE 10031648 A1 & FR 2795737 A1 & JP 2001-11482 A & KR 2001072539 A	1
X	US 6352961 B1 (NSK LTD.), 05 March, 2002 (05.03.02), & JP 11-269478 A	1
X	JP 2002-38177 A (KYODO YUSHI CO., LTD. et al.), 06 February, 2002 (06.02.02), (Family: none)	1
X	JP 4-178499 A (KYODO YUSHI CO., LTD. et al.), 25 June, 1992 (25.06.92), (Family: none)	1
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P,X	JP 2002-180077 A (NTN Corp.), 26 June, 2002 (26.06.02), (Family: none)	1
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