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(54) Grease composition for constant velocity joint

(57) A grease composition for a constant velocity joint containing a base oil, a thickener, boron nitride powders, and a sulfur-phosphorus containing extreme pressure agent. The content of the thickener is 2 to 25 weight %, that of the boron nitride powders is 0.5 to 20 weight %, and that of the sulfur phosphorus containing extreme pressure agent is 0.1 to 10 weight %, each based on a total weight of the grease composition. The grease composition exhibits superior anti-flaking performance and can prolong the life time of a constant velocity joint.

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Description

BACKGROUND OF THE INVENTION

The present invention relates to a grease composition for a constant velocity joint, namely a fixed type joint and a slide type joint.

Generally, in FF type or front engine-front wheel driven type cars, a constant velocity joint is employed in a combination of a fixed type joint, a shaft, and a thrust type joint.

The fixed type joint includes a Birfield joint, a Rzeppa joint, an undercutting free joint, a tripod joint, and the like. The slide type joint includes a double off-set joint, a tripod joint, a closs groove joint, and the like.

As a conventional lubricant charged into such constant velocity joints, an extreme pressure grease is mainly employed in which a base grease consisting of a purified mineral oil and a lithium soap and/or urea thickener is combined with molybdenum disulfide, a lead compound, or the like.

It is required for the grease composition for a constant velocity joint to exhibit performances such as anti- flaking, anti-seizure, abrasion resistance, low friction, or the like. However, the performance of the conventional grease hardly catch up with the tendency to improved performance and quality of cars. Thus, particularly in order to prolong the life time of a constant velocity joint, improvement in the anti-flaking property is desired.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a grease composition for a constant velocity joint which exhibits superior anti-flaking performance and which can prolong the life time of a constant velocity joint.

According to the present invention, there is provided a grease composition for a constant velocity joint comprising a base oil, a thickener, boron nitride powders, and a sulfur- phosphorus containing extreme pressure agent, said thickener being contained in an amount of 2 to 25 weight %, said boron nit ride powders being contained in an amount of 0.5 to 20 weight %, and said sulfur-phosphorus containing extreme pressure agent being contained in an amount of 0.1 to 10 weight %, each based on a total weight of said grease composition.

PREFERRED EMBODIMENTS OF THE INVENTION

The present invention will be explained in more detail hereinbelow.

The base oil contained in the grease composition for a constant velocity joint of the present invention may preferably be a mineral oil and/or a synthetic oil. The mineral oil may be obtained by a conventional method commonly performed in a lube oil production process in oil refining industries. For example, a base oil obtained by distilling a crude oil under atmospheric or reduced pressure to obtain lubricant fractions, and refining the lubricant fractions by at least one treatment selected from solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, contact dewaxing, hydrofining, washing with sulfuric acid, clay treatment, and the like, may be used.

Examples of the synthetic oil may include poly-α-olefins such as polybutene, 1-octen oligomer, and 1-decene oligomer, or hydrides of these poly-α-olefins; diesters such as ditridecyl glutarate, di-2-ethylhexyl adipate, diisbdecyl adipate, ditridecyl adipate, or di-3-ethylhexyl sebacate; polyol esters such as trimethylolpropane caprylate, trimethylolpropane pelargonate, pentaerythritol-2-ethyl hexanoate, or pentaerythritol pelargonate; alkylnaphthalene; alkylbenzene; polyoxyalkylene glycol; polyphenyl ether; dialkyldiphenylether, silicone oil; or perfluoroalkyl ether. These may be used alone or in mixture.

The viscosity range of the base oil may be any of commonly used lube oils, but usually kinematic viscosity at 100 °C of 2 to 40 mm^2/s, preferably 3 to 20 mm^2/s is desirable. Further, the viscosity index of the base oil is preferably not less than 90, more preferably not less than 100.

The grease composition for a constant velocity joint of the present invention contains as a requisite component a thickener. The thickener may be selected from a variety of thickeners, for example, soap thickeners such as a metal soap, and a complex metal soap; and non-soap thickeners such as bentone, silica gel, urea compounds, urea-urethane compounds, and urethane compounds. Among these, urea compounds, urea-urethane compounds, urethane compounds, and mixtures thereof are particularly preferred in view of their heat resistance.

Examples of the soap thickener may include, for example, sodium soap, calcium soap, aluminum soap, or lithium soap.

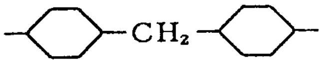
Examples of the urea compounds, urea-urethane compounds, and urethane compounds may include, for example, diurea compounds, trirurea compounds, tetraurea compounds, other polyurea compounds, urea-urethane compounds, diurethane compounds, and mixtures thereof. Among these, diurea compounds, urea-urethane compounds, diurethane compounds, and mixtures thereof are particularly preferred. Specifically, a compound or a mixture of compounds represented by the formula (1) is preferred:

$$\text{A-CONH-R}^1\text{-NHCO-B} \qquad (1)$$

wherein R^1 stands for a divalent hydrocarbon group, A and B may be the same or different groups and each stands for $-NHR^2$, $-NR^3R^4$, or $-OR^5$, wherein R^2, R^3, R^4, and R^5 are the same or different groups and each stands for a hydrocarbon residue having 6 to 20 carbon atoms.

In the above formula (1), R^1 stands for a divalent hydrocarbon group having preferably 6 to 20, more preferably 6 to 15 carbon atoms. Examples of the divalent hydrocarbon group may include a straight chain or branched alkylene group, a straight chain or branched alkenylene group, a cycloalkylene group, or an aromatic group. Specific examples of R^1 may include ethylene group, 2,2-dimethyl-4-methylhexylene group, and groups represented by the formulae (a) to (j) below:


· · (a) ,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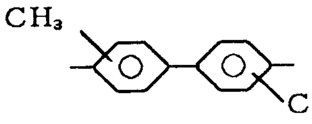
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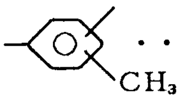
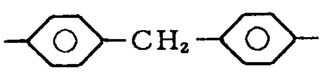
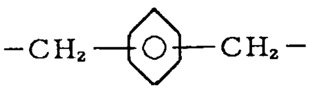
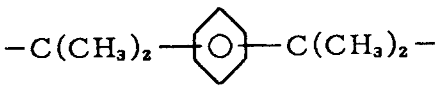
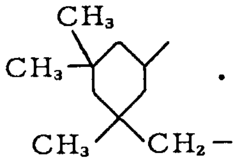
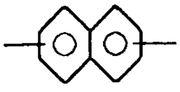

· · (d) ,

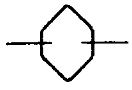

· · (e) ,


· · (f),


· · (g) ,


· · (h),


· · (i) ,


· · (j) .

Among these, (d) and (e) are particularly preferred.

In the above formula (1), R^2, R^3, R^4, and R^5 may stand for a straight chain or branched alkyl group, a straight chain or branched alkenyl group, a cycloalkyl group, an alkylcycloalkyl group, an aryl group, an alkylaryl group, or an arylalkyl group. Specifically, for example, they may stand for a straight chain or branched alkyl group such as hexyl group, heptyl group, octyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group, tetradecyl group, pentadecyl group, hexadecyl group, heptadecyl group, octadecyl group, nonadecyl group, or eicocyl group; a straight chain or branched alkenyl group such as hexenyl group, heptenyl group, octenyl group, nonenyl group, decenyl group, undecenyl group, dodecenyl group, tridecenyl group, tetradecenyl group, pentadecenyl group, hexadecenyl group, heptadecenyl group, octadecenyl group, nonadecenyl group, or eicocenyl group; cyclohexyl group; an alkylcycloalkyl group such as methylcyclohexyl group, dimethylcyclohexyl group, ethylcyclohexyl group, diethylcyclohexyl group, propylcyclohexyl group, isopropylcyclohexyl group, 1-methyl-3-propylcyclohexyl group, butylcyclohexyl group, amylcyclohexyl group, amylmethylcyclohexyl group, hexylcyclohexyl group, heptylcyclohexyl group, octylcylcohexyl group, nonylcyclohexyl group, decylcyclohexyl group, undecylcyclohexyl group, dodecylcyclohexyl group, tridecylcyclohexyl group or tetradecylcyclohexyl group; an aryl group such as phenyl group or naphthyl group; an alkylaryl group such as toluyl group, ethylphenyl group, xylyl group, propylphenyl group, cumenyl group, methylnaphthyl group, ethylnaphthyl group, dimethylnaphthyl group or propylnaphthyl group; or an arylalkyl group such as benzyl group, methylbenzyl group or ethylbenzyl group. Among these, cyclohexyl group, octadecyl group, and toluyl group are particularly preferred.

The diurea compound, the urea-urethane compound, or the diurethane compound may be prepared by reacting diisocyanate represented by the formula $OCN\text{-}R^1\text{-}NCO$ with a compound represented by the formula R^2NH_2, R^3R^4NH, or R^5OH or mixtures thereof in the base oil at 10 to 200 °C. In this case, R^1, R^2, R^3, R^4 , and R^6 are the same as those in the formula (1).

The content of the thickener is 2 to 25 weight %, preferably 3 to 20 weight % of the total weight of the grease composition. If the content of the thickener is less than 2 weight %, the effect of the thickener is not enough so that the composition cannot be in a sufficiently greasy state. If the content of the thickener is more than 25 weight %, the composition becomes too hard for grease so that the composition cannot exhibit sufficient lubricating performance.

The grease composition of the present invention contains as a requisite component boron nitride powders. The particle size of the boron nitride powders is not particularly limited, but the average particle size thereof is usually 0.05 to 20 µm, preferably 0.4 to 15 µm, more preferably 5 to 10 µm.

The content of the boron nitride powders is 0.5 to 20 weight %, preferably 1 to 20 weight % of the total weight of the grease composition. If the content of the boron nitride powders is less than 0.5 weight %, enough anti-flaking performance cannot be exhibited, and the anti-seizure performance of a constant velocity joint becomes insufficient. If the content of the boron nitride powders is more than 20 weight %, abrasion (wear due to abrasive effect of powder particles) is promoted, and the life time of a constant velocity joint becomes insufficient.

The grease composition of the present invention contains as a requisite component a sulfur-phosphorus containing extreme pressure agent. The sulfur-phosphorus containing extreme pressure agent may not only be a single extreme pressure agent containing both sulfur and phosphorus, but also be a combination of a sulfur containing extreme pressure agent containing only sulfur and a phosphorus containing extreme pressure agent containing only phosphorus, provided that the sulfur-phosphorus containing extreme pressure agent does not contain metal dithiophosphates such as molybdenum dithiophosphate or zinc dithiophosphate.

The ratio of the sulfur atoms to the phosphorus atoms in the sulfur-phosphorus containing extreme pressure agent is preferably in the range between 100 : 25 and 100 : 1.

Examples of the sulfur containing extreme pressure agent may include sulfurized oils and fats, metal fenates cross-linked with sulfur, dihydrocarbyl polysulfide, dithiocarbamates, monosulfide, sulfoxide, sulfinate, or mixtures thereof. Among these, sulfurized oils and fats, dihydrocarbyl polysulfide, and mixtures thereof are particularly preferred.

The sulfurized oils and fats are compounds obtained by adding sulfur to animal or vegetable oils and fats having unsaturated bond such as olive oil, caster oil, tea seed oil, rice bran oil, cotton seed oil, rape seed oil, corn oil, beef tallow, neatsfoot oil, sperm oil, or whale paraffin, followed by heating the mixture. The content of sulfur in the sulfurized oils and fats is usually 5 to 15 weight %, preferably 8 to 12 weight %.

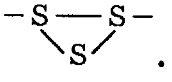
Examples of the metal fenate cross-linked with sulfur may include alkaline earth metal salts of sulfides of alkylphenol to which an alkyl group(s) having 8 to 30, preferably 9 to 20 carbon atoms is added. Specific examples of the alkyl group may include octyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group, tetradecyl group, pentadecyl group, hexadecyl group, heptadecyl group, octadecyl group, nonadecyl group, icosyl group, henicosyl group, docosyl group, tricosyl group, tetracosyl group, pentacosyl group, hexacosyl group, heptacosyl group, octacosyl group, nonacosyl group, or triacontyl group, and these groups may either be straight chain or branched. Among these, an alkyl group derived from nonene, or olefins or alcohols having 5 to 8 carbon atoms is particularly preferred. The alkaline earth metal may preferably be magnesium, calcium, or barium.

The dihydrocarbyl polysulfide is a compound represented by the formula (2):

$$R^6 - (S)_z - R^7 \quad \cdots \quad (2)$$

wherein R^6 and R^7 may be the same or different groups and each may preferably stand for an alkyl group having 3 to 18, preferably 6 to 15 carbon atoms derived from propylene or isobutene, or an aryl group, an alkylaryl group, or an arylalkyl group, each having 6 to 8 carbon atoms. Examples of these groups may include, for example, alkyl groups such as isopropyl group, branched hexyl group derived from propylene dimer, branched nonyl group derived from propylene trimer, branched dodecyl group derived from propylene tetramer, branched pentadecyl group derived from propylene pentamer, branched octadecyl group derived from propylene hexamer, tert-butyl group, branched octyl group derived from isobutene dimer, branched dodecyl group derived from isobutene trimer, or branched hexadecyl group derived from isobutene tetramer (these alkyl groups include all of branch isomers) ; alkylaryl groups such as phenyl group, tolyl group, ethylphenyl group, or xylyl group (an alkyl group portion of these alkylaryl groups may be straight chain or branched, and substituting position of an alkyl group portion on an aryl group is arbitrary); or arylalkyl groups such as benzyl group, or phenylethyl group (substituting position of a phenyl group is arbitrary).

z in the formula (2) above stands for an integer of 1 to 5, preferably 2 to 4. When z is 3 or larger, the sulfur atoms may form a circle, for example,

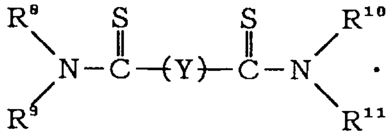


Specific examples of the dihydrocarbyl polysulfide may include dibutyl polysulfide, dihexyl polysulfide, dioctyl polysulfide, dinonyl polysulfide, didecyl polysulfide, didodecyl polysulfide, ditetradecyl polysulfide, dihexadecyl polysulfide, dioctadecyl polysulfide, dieicosyl polysulfide, diphenyl polysulfide, dibenzyl polysulfide, diphenethyl polysulfide, polypropenyl polysulfide, polybutenyl polysulfide, or mixtures thereof. Among these, polypropenyl polysulfide, polybutenyl polysulfide, and mixtures thereof are particularly preferred.

The polypropenyl polysulfide, polybutenyl polysulfide, or mixtures thereof may be obtained by sulfurizing an olefin hydrocarbon such as propylene, isobutene, dimer, trimer, or tetramer of these monomers, or mixtures of these monomers and/or polymers thereof with sulfur, sulfur halide (e.g. sulfur monochloride or sulfur dichloride), sulfurized hydrogen, or mixtures thereof.

The content of sulfur in the dihydrocarbyl polysulfide is usually 30 to 50 weight %, preferably 40 to 45 weight %.

The dithiocarbamate may be an alkyldithiocarbamyl compound represented by the formula (3):



· · · (3)

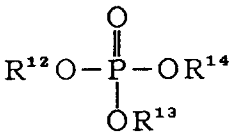
wherein R^8, R^9, R^{10}, and R^{11} are the same or different groups and each stands for a straight chain or branched alkyl group having 1 to 18, preferably 1 to 10 carbon atoms, for example, an alkyl group such as methyl group, ethyl group, propyl group, n-butyl group, isobutyl group, pentyl group, isopentyl group, hexyl group, heptyl group, octyl group, 2-ethylhexyl group, nonyl group, decyl group, tridecyl group, or octadecyl group.

In the formula (3), (Y) stands for S, S-S, S-CH_2-S, S-$(CH_2)_2$-S, S-$(CH_2)_3$-S, or S-Zn-S.

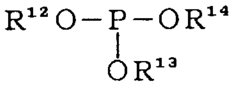
Specific examples of the alkyldithiocarbamyl compound may include methylene bis (dibutyldithiocarbamate), bis (dimethylthiocarbamyl) monosulfide, bis(dimethylthiocarbamyl) disulfide, bis(dibutylthiocarbamyl) disulfide, bis (dipentylthiocarbamyl) disulfide, bis (dioctylthiocarbamyl) disulfide, or zinc dipentyldithiocarbamate.

The phosphorus containing extreme pressure agent may be a phosphate, a phosphite, a phosphinate, a phosphonate, or an amine salt thereof, or mixtures thereof. Among these, phosphates, phosphites, and mixtures thereof are particularly preferred.

The phosphate herein is a compound represented by the formula (4), and the phosphite herein is a compound represented by the formula (5):



$$R^{12}O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OR^{13}}{|}}{P}}-OR^{14} \quad \cdots (4),$$



$$R^{12}O-\underset{\underset{\displaystyle OR^{13}}{|}}{P}-OR^{14} \quad \cdots (5)$$

wherein R^{12} stands for an alkyl group, a cycloalkyl group, an alkylcycloalkyl group, an alkenyl group, an aryl group, an alkylaryl group, or an arylalkyl group, each having 1 to 24 carbon atoms, R^{13} and R^{14} each stands for a hydrogen atom, an alkyl group, a cycloalkyl group, an alkylcycloalkyl group, an alkenyl group, an aryl group, an alkylaryl group, or an arylalkyl group, each having 1 to 24 carbon atoms.

Specific examples of R^{13}, R^{13}, and R^{14} other than hydrogen atom may include methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, octyl group, nonyl group, decyl group, dodecyl group, tetradecyl group, hexadecyl group, octadecyl group, eicosyl group, docosyl group, tetracosyl group, cyclopentyl group, cyclohexyl group, methylcyclohexyl group, ethylcyclohexyl group, dimethylcyclohexyl group, cycloheptyl group, phenyl group, tolyl group, xylyl group, ethylphenyl group, propylphenyl group, butylphenyl group, pentylphenyl group, hexylphenyl group, nonylphenyl group, decylphenyl group, dodecylphenyl group, tetradecylphenyl group, hexadecylphenyl group, octadecylphenyl group, benzyl group, or phenethyl group.

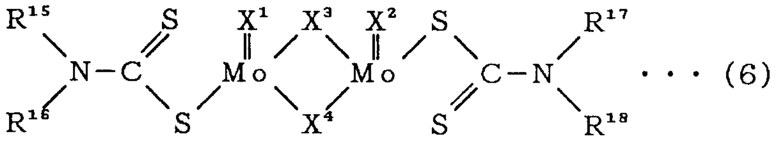
Specific examples of the phosphorus containing extreme pressure agent may include tributyl phosphate, benzyl diphenyl phosphate, ethyl diphenyl phosphate, octyl diphenyl phosphate, triphenyl phosphate, tricresylphosphate, tritolyl phosphate, 2-ethylhexyl diphenyl phosphate, tributyl phosphite, or dilauryl phosphite.

Particularly preferred combination of the sulfur containing extreme pressure agent and the phosphorus containing extreme pressure agent may be a combination of the dihydrocarbyl polysulfide and the phosphate, or a combination of the sulfurized oils and fats and the phosphate.

The single extreme pressure agent containing both sulfur and phosphorus may be a thiophosphate, a thiophosphite, or mixtures thereof. The thiophosphate and the thiophosphite may be compounds represented by the formulae (4) and (5) of the phosphate and phosphite wherein at least one oxygen atom is substituted by a sulfur atom.

The content of the sulfur-phosphorus containing extreme pressure agent in the grease composition of the present invention is 0.1 to 10 weight %, preferably 1 to 5 weight % of the total weight of the grease composition. If the content of the sulfur-phosphorus containing extreme pressure agent is less than 0.1 weight %, the anti- seizure performance of a constant velocity joint is not sufficient. Even if the content of the sulfur-phosphorus containing extreme pressure agent is more than 10 weight %, the increase in the content will not meet the improvement in the performance of grease composition, thus being not economical.

The grease composition for a constant velocity joint of the present invention may optionally contain molybdenum dithiocarbamate as an extreme pressure agent in addition to the sulfur-phosphorus containing extreme pressure agent. Specifically, the molybdenum dithiocarbamate represented by the formula (6) may be employed:



· · · (6)

wherein R^{15}, R^{16}, R^{17}, and R^{18} are the same or different groups and each stands for a hydrocarbon group such as alkyl group, alkenyl group, aryl group, alkylaryl group, or arylalkyl group, among which an alkyl group is particularly preferred.

Specific examples of R^{15}, R^{16}, R^{17}, and R^{18} may include straight chain or branched alkyl groups having 2 to 18, preferably 8 to 13 carbon atoms such as ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, octyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group, tetradecyl group, pentadecyl group, hexadecyl group, heptadecyl group, or octadecyl group; alkylaryl groups such as butylphenyl group or nonylphenyl group. Further X^1, X^2, X^3 , and X^4 each stands for a sulfur atom or an oxygen atom.

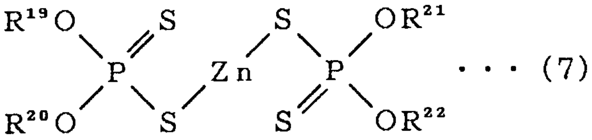
Specific examples of the molybdenum dithiocarbamate may include molybdenum sulfide diethyl dithiocarbamate, molybdenum sulfide dipropyl dithiocarbamate, molybdenum sulfide dibutyl dithiocarbamate, molybdenum sulfide dipentyl dithiocarbamate, molybdenum sulfide dihexyl dithiocarbamate, molybdenum sulfide dioctyl dithiocarbamate, molybdenum sulfide didecyl dithiocarbamate, molybdenum sulfide didbdecyl dithiocarbamate, molybdenum sulfide ditridecyl dithiocarbamate, molybdenum sulfide di(butylphenyl) dithiocarbamate, molybdenum sulfide di(nonylphenyl) dithiocarbamate, molybdenum oxysulfide diethyl dithiocarbamate, molybdenum oxysulfide dipropyl dithiocarbamate, molybdenum oxysulfide dibutyl dithiocarbamate, molybdenum oxysulfide dipentyl dithiocarbamate, molybdenum oxysulfide dihexyl dithiocarbamate, molybdenum oxysulfide dioctyl dithiocarbamate, molybdenum oxysulfide didecyl dithiocarbamate, molybdenum oxysulfide didodecyl dithiocarbamate, molybdenum oxysulfide ditridecyl dithiocarbamate, molybdenum oxysulfide di(butylphenyl) dithiocarbamate, or molybdenum oxysulfide di(nonylphenyl)dithiocarbamate. These compounds may be used alone or in mixture.

The content of the molybdenum dithiocarbamate, if contained, in the grease composition of the present invention is usually 0.1 to 10 weight %, preferably 1 to 5 weight % of the total weight of the grease composition.

When both the molybdenum dithiocarbamate and the sulfur-phosphorus containing extreme pressure agent are employed in combination, the ratio of the molybdenum dithiocarbamate to the sulfur-phosphorus containing extreme pressure agent is usually 1 : 5 to 5 : 1, preferably 1 : 3 to 3 : 1 by weight.

The grease composition of the present invention may additionally be admixed with an organozinc compound for further improving the anti-flaking performance. Examples of the organozinc compound may include, for example, zinc dithiophosphate, zinc dithiocarbamate, zinc salts of fatty acids, or zinc naphthenate.

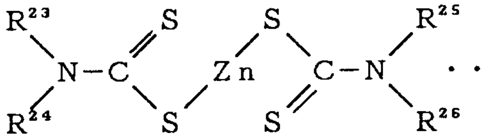
The zinc dithiophosphate may be a compound represented by the formula (7):



· · · (7)

wherein R^{19} , R^{20}, R^{21}, and R^{22} are the same or different groups and each stands for a straight chain or branched primary or secondary alkyl group, aryl group, or arylalkyl group, each having 2 to 18 carbon atoms, such as ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, octyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group, tetradecyl group, pentadecyl group, hexadecyl group, heptadecyl group, or octadecyl group.

The zinc dithiocarbamate may be a compound represented by the formula (8):

 · · · (8)

wherein R^{23}, R^{24}, R^{26}, and R^{26} are the same or different groups and each stands for an alkyl group, an alkenyl group, an aryl group, an alkylaryl group, or an arylalkyl group, each having 2 to 18 carbon atoms, specifically, an alkyl group such as ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, octyl group, nonyl group, decyl group, undecyl group, dodecyl group, tridecyl group, tetradecyl group, pentadecyl group, hexadecyl group, heptadecyl group, or octadecyl group (these alkyl groups may be straight chain or branched, and may be primary or secondary); or an alkylaryl group such as butylphenyl group or nonylphenyl group (an alkyl portion of these alkylaryl groups may be straight chain or branched, and a substituting position of an alkyl portion on the aryl group is arbitrary).

The zinc salt of a fatty acid may be a compound represented by the formula (9) $(R^{27}COO)_2Zn$ (9), wherein R^{27} stands for an alkyl group or an alkenyl group, each having 3 to 22 carbon atoms.

The zinc naphthenate may be a compound represented by the formula (10)

$$(R^{28}\text{—}(CH_2)_m\text{—}COO)_2Zn \quad \cdots (10),$$

wherein R^{28} stands for a cycloalkyl group such as cyclopentyl group, cyclohexyl group, alkylcyclopentyl group, or alkylcyclohexyl group, and m stands for an integer.

The content of the organozinc compound, if contained, in the grease composition of the present invention is usually 0.1 to 10 weight %, preferably 1 to 5 weight % of the total weight of the grease composition.

Further, the grease composition for a constant velocity joint of the present invention may be admixed with additional additives such as a solid lubricant, an extreme pressure agent other than the sulfur-phosphorus containing extreme pressure agent and the molybdenum dithiocarbamate, an anti-oxidant, an oilness agent, a rust-inhibitor, or a viscosity index improver, if required, for further improving the performance of the grease composition, as long as the additional additives do not damage the properties of the grease composition.

Examples of the solid lubricant may include, for example, carbon black, fluorinated carbon black, polytetrafluoroethylene, molybdenum disulfide, antimony sulfide, or an alkali or an alkaline earth metal borate.

Examples of the extreme pressure agent other than the sulfur-phosphorus containing extreme pressure agent and the molybdenum dithiocarbamate may include chlorine compounds such as chlorinated paraffin or a chlorinated ester; or molybdenum compounds such as molybdenum dithiophosphate.

Examples of the anti-oxidant may include phenol compounds such as 2,6-di-t-butylphenol, or 2,6-di-t-butyl-p-cresol; amine compounds such as dialkyldiphenyl amine, phenyl-α-naphthyl amine, or p-alkylphenyl-α-naphthyl amine; sulfur compounds; or phenothiazine compounds.

Examples of the oilness agent may include amines such as lauryl amine, myristyl amine, palmityl amine, stearyl amine, or oleyl amine; higher alcohols such as lauryl alcohol, myristyl alcohol, palmityl alcohol, stearyl alcohol, or oleyl alcohol; higher fatty acids such as lauric acid, myristic acid, palmitic acid, stearic acid, or oleylic acid; fatty acid esters such as methyl laurate, methyl myristate, methyl palmitate, methyl stearate, or methyl oleate; amidos such as lauryl amido, myristyl amido, palmityl amido, stearyl amido, or oleyl amido; or fats and oils.

Examples of the rust-inhibitor may include metal soaps; synthetic sulfonates such as petroleum sulfonate, alkylbenzene sulfonate, or dinonylnaphthalene sulfonate; partial esters of polyalcohol such as sorbitan fatty acid ester; amines; phosphoric acid; or phosphates.

Examples of the viscosity index improver may include polymethacrylate, polyisobutylene, or polystyrene.

The grease composition for a constant velocity joint of the present invention may be prepared, for example, by adding the thickener, the boron nit ride powders, the sulfur-phosphorus containing extreme pressure agent, and optionally the molybdenum dithiocarbamate, the organozinc compound, or other additives mentioned above, to the base oil, agitating the resulting mixture, and passing the mixture through a roll mill. Alternatively, raw material components of the thickener may preliminarily be added to the base oil, dissolved and mixed together by stirring, so that the thickener may be prepared simultaneously with the preparation of the grease composition of the present invention.

The grease composition for a constant velocity joint of the present invention is superior in the antiflaking performance, and can prolong the life time of a constant velocity joint.

EXAMPLES

The present invention will be explained in more detail with reference to Examples and Comparative Examples. However, the present invention is not limited thereto.

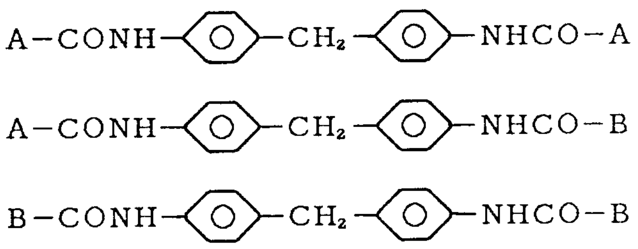
Example 1

88.0 g of diphenylmethane-4,4'-diisocyanate were added to 350 g of mineral oil, and the mixture was heated to 60 °C to obtain a homogeneous solution. Then another solution obtained by dissolving 26.2 g of dodecylalcohol in 200 g of the same mineral oil by heating was added to the former solution, and the mixture was agitated vigorously. To the mixture, another solution obtained by dissolving 55.8 g of cyclohexylamine in 205 g of the same mineral oil was added, and the resulting mixture was again agitated vigorously to obtain a gel. The gel was kept at 100 °C for 30 minutes under agitation, admixed with additives containing a thickener, boron nitride powders, and an extreme pressure agent. The obtained mixture was agitated and passed through a three-roll roll mill, thereby preparing a grease composition. The obtained grease composition was evaluated by the following method. The result is shown in Table 1. The composition of the grease composition is shown below.

Composition

Thickener	17.0 weight %
Mineral oil (126 mm^2 /s @40°C)	77.5 weight %
Boron nitride powders (average particle size: 0.7 µm)	1.5 weight %
Sulfurized oils and fats (sulfur content: 9 to 10 weight %)	2.0 weight %
Tributylphosphite	1.0 weight %
Amine anti-oxidant (mixture consistency: 283)	1.0 weight %

The thickener employed in this Example is a mixture of the following compounds:



wherein A stands for an N-cyclohexylamino group, B stands for a dodecyloxy group, and the ratio of A to B in the mixture is 80 : 20.

On-Bench Durability Test

Using a commercially available Birfield joint of #87 size, the life time of the joint was evaluated under the condition of the predetermined high speed rotation and high torque.

Comparative Example 1

A grease composition having similar composition to that of Example 1 was prepared in the same way as in Example 1 except that the sulfurized oils and fats and tributylphosphite were not added but replaced by the mineral oil of the equivalent weight. The obtained grease composition was evaluated in the same way as in Example 1. The result is shown in Table 1. The composition of the grease composition is shown below.

Composition

Thickener (same as that of Example 1)	17.0 weight %
Mineral oil (126 mm^2/s @40°C)	80.5 weight %
Boron nitride powders (average particle size: 0.7 µm)	1.5 weight %
Amine anti-oxidant (mixture consistency: 298)	1.0 weight %

Comparative Example 2

A grease composition having similar composition to that of Example 1 was prepared in the same way as in Example 1 except that boron nitride powders were not added by replaced by the mineral oil of the equivalent weight. The obtained grease composition was evaluated in the same way as in Example 1. The result is shown in Table 1. The composition of the grease composition is shown below.

Composition

Thickener (same as that in Example 1)	17.0 weight %
Mineral oil (126 mm^2/s @40°C)	79.0 weight %
Sulfurized oils and fats (sulfur content: 9 to 10 weight %)	2.0 weight %
Tributylphosphite	1.0 weight %
Amine anti-oxidant (mixture consistency: 307)	1.0 weight %

Comparative Example 3

A grease composition having similar composition to that of Example 1 was prepared in the same way as in Example 1 except that tributylphosphite was not added but replaced by the mineral oil of the equivalent weight. The obtained grease composition was evaluated in the same way as in Example 1. The result is shown in Table 1. The composition of the grease composition is shown below.

Composition

Thickener (same as that of Example 1)	17.0 weight %
Mineral oil (126 mm^2/s @40°C)	78.5 weight %
Boron nitride powders (average particle size: 0.7 µm)	1.5 weight %
Sulfurized oils and fats (sulfur content: 9 to 10 weight %)	2.0 weight %
Amine anti-oxidant (mixture consistency: 289)	1.0 weight %

Comparative Example 4

A grease composition having similar composition to that of Example 1 was prepared in the same way as in Example 1 except that the sulfurized oils and fats were not added but replaced by the mineral oil of the equivalent weight. The obtained grease composition was evaluated in the same way as in Example 1. The result is shown in Table 1. The composition of the grease composition is shown below.

Composition

Thickener (same as that of Example 1)	17.0 weight %
Mineral oil (126 mm^2 /s @40°C)	79.5 weight %
Boron nitride powders (average particle size: 0.7 µm)	1.5 weight %
Tributyl phosphite	1.0 weight %
Amine anti-oxidant (mixture consistency: 304)	1.0 weight %

Example 2

75 g of lithium-12-hydroxystearate were added to 550 g of mineral oil, and the former was dissolved in the latter by heating to 200 °C under agitation. To the resulting mixture, 320 g of the mineral oil was added, and rapidly cooled to obtain a gel. The gel was kept at 100 °C for 30 minutes under agitation, and admixed with the additives. The obtained mixture was passed through a three-roll roll mill, thereby preparing a grease composition. The obtained grease composition was evaluated by the same way as in Example 1. The result is shown in Table 1. The composition of the grease composition is shown below.

Composition

Lithium-12-hydroxystearate	7.5 weight %
Mineral oil (126 mm^2 /s @40°C)	87.0 weight %
Boron nitride powders (average particle size: 0.7 µm)	1.5 weight %
Sulfurized oils and fats (sulfur content: 9 to 10 weight %)	2.0 weight %
Tricresyl phosphate	1.0 weight %
Amine anti-oxidant (mixture consistency: 288)	1.0 weight %

Example 3

A grease composition having similar composition to that of Example 2 was prepared in the same way as in Example 2 except that tricresyl phosphate was replaced by tributylphosphite of the equivalent weight. The obtained grease composition was evaluated in the same way as in Example 1. The result is shown in Table 1. The composition of the grease composition is shown below.

Composition

Lithium-12-hydroxystearate	7.5 weight %
Mineral oil (126 mm^2 /s @40°C)	87.0 weight %
Boron nitride powders (average particle size: 0.7 μm)	1.5 weight %
Sulfurized oils and fats (sulfur content: 9 to 10 weight %)	2.0 weight %
Tributylphosphite	1.0 weight %
Amine anti-oxidant (mixture consistency: 286)	1.0 weight %

Example 4

A grease composition having similar composition to that of Example 2 was prepared in the same way as in Example 2 except that the sulfurized oils and fats were replaced by polysulfide of the equivalent weight. The obtained grease composition was evaluated in the same way as in Example 1. The result is shown in Table 1. The composition of the grease composition is shown below.

Composition

Lithium-12-hydroxystearate	7.5 weight %
Mineral oil (126 mm^2/s @40°C)	87.0 weight %
Boron nitride powders (average particle size: 3 μm)	1.5 weight %
Dihydrocarbyl polysulfide (sulfur content: 42 weight %)	2.0 weight %
Tricresyl phosphate	1.0 weight %
Amine anti-oxidant (mixture consistency: 285)	1.0 weight %

Example 5

A grease composition having similar composition to that of Example 2 was prepared in the same way as in Example 2 except that tricresyl phosphate was replaced by tributylphosphite of the equivalent weight and the sulfurized oils and fats were replaced by polysulfide of the equivalent weight. The obtained grease composition was evaluated in the same way as in Example 1. The result is shown in Table 1. The composition of the grease composition is shown below.

Composition

Lithium-12-hydroxystearate	7.5 weight %
Mineral oil (126 mm^2/s @40°C)	87.0 weight %
Boron nitride powders (average particle size: 0.7 µm)	1.5 weight %
Dihydrocarbyl polysulfide (sulfur content: 42 weight %)	2.0 weight %
Tributyl phosphite	1.0 weight %
Amine anti-oxidant (mixture consistency: 287)	1.0 weight %

Comparative Example 5

A grease composition having similar composition to that of Example 2 was prepared in the same way as in Example 2 except that the sulfurized oils and fats and tricresyl phosphate were not added but replaced by the mineral oil of the equivalent weight. The obtained grease composition was evaluated in the same way as in Example 1. The result is shown in Table 1. The composition of the grease composition is shown below.

Composition

Lithium-12-hydroxystearate	7.5 weight %
Mineral oil (126 mm^2/s @40°C)	90.0 weight %
Boron nitride powders (average particle size: 3 µm)	1.5 weight %
Amine anti-oxidant (mixture consistency: 298)	1.0 weight %

Comparative Example 6

A grease composition having similar composition to that of Example 5 was prepared in the same way as in Example 2 except that the boron nit ride powders were not added but replaced by the mineral oil of the equivalent weight. The obtained grease composition was evaluated in the same way as in Example 1. The result is shown in Table 1. The composition of the grease composition is shown below.

Composition

Lithium-12-hydroxystearate	7.5 weight %
Mineral oil (126 mm^2/s @40°C)	88.5 weight %
Dihydrocarbyl polysulfide (sulfur content: 42 weight %)	2.0 weight %
Tributyl phosphite	1.0 weight %
Amine anti-oxidant (mixture consistency: 295)	1.0 weight %

Example 6

A grease composition having similar composition to that of Example 5 was prepared in the same way as in Example 2 except that molybdenum dithiocarbamate was added. The obtained grease composition was evaluated in the same way as in Example 1. The result is shown in Table 1. The composition of the grease composition is shown below.

Composition

Lithium-12-hydroxystearate	7.5 weight %
Mineral oil (126 mm^2/s @40°C)	84.0 weight %
Boron nitride powders (average particle size: 5 µm)	1.5 weight %
Molybdenum dibutyl dithiocarbamate	3.0 weight %
Dihydrocarbyl polysulfide (sulfur content: 42 weight %)	2.0 weight %
Tributyl phosphite	1.0 weight %
Amine anti-oxidant (mixture consistency: 292)	1.0 weight %

Example 7

A grease composition having similar composition to that of Example 4 was prepared in the same way as in Example 2 except that molybdenum dithiocarbamate was added. The obtained grease composition was evaluated in the same way as in Example 1. The result is shown in Table 1. The composition of the grease composition is shown below.

Composition

Lithium-12-hydroxystearate	7.5 weight %
Mineral oil (126 mm^2/s @40°C)	84.0 weight %
Boron nitride powders (average particle size: 3 µm)	1.5 weight %
Molybdenum dibutyl dithiocarbamate	3.0 weight %
Dihydrocarbyl polysulfide (sulfur content: 42 weight %)	2.0 weight %
Tricresyl phosphate	1.0 weight %
Amine anti-oxidant (mixture consistency: 290)	1.0 weight %

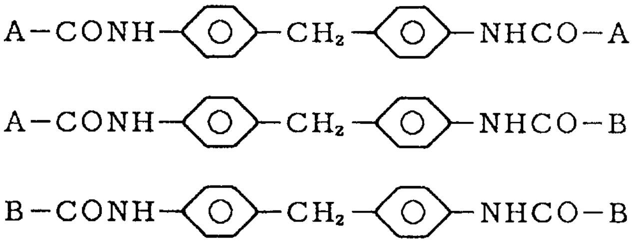
Example 8

36.5 g of diphenylmethane-4,4'-diisocyanate were added to 350 g of mineral oil, and the mixture was heated to 60 °C to obtain 8 homogeneous solution. Then another solution obtained by dissolving 39.1 g of octadecyl alcohol in 250 g of the same mineral oil by heating was added to the former solution, and the resulting mixture was agitated vigorously. To the mixture, another solution obtained by dissolving 14.4 g of cyclohexylamine in 195 g of the same mineral oil was added, and the obtained mixture was again agitated vigorously to obtain a gel. The gel was kept at 100 °C°C for 30 minutes under agitation, and admixed with the additives. The obtained mixture was agitated and passed through a three-roll roll mill, thereby preparing a grease composition. The obtained grease composition was evaluated in the same way as in Example 1. The result is shown in Table 1. The composition of the grease composition is shown below.

Composition

Thickener	9.0 weight %
Mineral oil (126 mm^2/s @40°C)	79.5 weight %
Boron nitride powders (average particle size: 7 µm)	1.5 weight %
Molybdenum dibutyl dithiocarbamate	3.0 weight %
Molybdenum disulfide	2.0 weight %
Dihydrocarbyl polysulfide (sulfur content: 42 weight %)	2.0 weight %
Tributylphosphate	2.0 weight %
Amine anti-oxidant (mixture consistency: 314)	1.0 weight %

The thickener employed in this Example is a mixture of the following compounds:



wherein A stands for an N-cyclohexylamino group, B stands for an octadecyloxy group, and the ratio of A to B in the mixture is 80 : 20.

Table 1

	Average Life Time (hr.)
Example 1	145
2	142
3	139
4	150
5	144
6	155
7	153
8	161
Comp. Ex. 1	0
2	80
3	60
4	48
5	0
6	94

As seen from the results in Table 1, the grease composition of the present invention can prolong the life time of a constant velocity joint as compared to the grease compositions shown in Comparative Examples. The life time of the joints employed in Comparative Examples 1, 2, and 5 were over by occurrence of seizing, while that of the joins employed in Comparative Examples 3, 4, and 6 were over by occurrence of flaking.

Claims

1. A grease composition for a constant velocity joint comprising a base oil, a thickener, boron nitride powders, and a sulfur-phosphorus containing extreme pressure agent, said thickener being contained in an amount of 2 to 25 weight %, said boron nitride powders being contained in an amount of 0.5 to 20 weight %, and said sulfur-phosphorus containing extreme pressure agent being contained in an amount of 0.1 to 10 weight %, each based on a total weight of said grease composition.

2. The grease composition as claimed in claim 1 wherein kinematic viscosity of the base oil at 100 °C is 2 to 40 mm^2/s, and viscosity index of the base oil is not less than 90.

3. The grease composition as claimed in claim 1 wherein the thickener is selected from the group consisting of a diurea compound represented by the formula (1), a urea-urethane compound represented by the formula (1), a diurethane compound represented by the formula (1), and mixtures thereof:

$$A\text{-}CONH\text{-}R^1\text{-}NHCO\text{-}B \qquad (1)$$

wherein R^1 stands for a divalent hydrocarbon group, A and B are the same or different groups and each stands for $-NHR^2$, $-NR^3R^4$, or $-OR^5$, wherein R^2, R^3, R^4, and R^6 are the same or different groups and each stands for a hydrocarbon residue having 6 to 20 carbon atoms.

4. The grease composition as claimed in claim 1 wherein an average particle size of the boron nitride powders is 0.05 to 20 μm.

5. The grease composition as claimed in claim 1 wherein a ratio of sulfur atoms to phosphorus atoms contained in the sulfur-phosphorus containing extreme pressure agent is in a range between 100 : 25 and 100 : 1.

6. The grease composition as claimed in claim 1 wherein the sulfur-phosphorus containing extreme pressure agent is selected from the group consisting of a single extreme pressure agent containing both sulfur and phosphorus, a mixture of a sulfur containing extreme pressure agent containing only sulfur and a phosphorus containing extreme pressure agent containing only phosphorus, and mixtures thereof.

7. The grease composition as claimed in claim 1 further comprising an additive selected from the group consisting of a molybdenum dithiocarbamate as an extreme pressure agent, an organozinc compound, and mixtures thereof.

8. The grease composition as claimed in claim 7 wherein a content of the molybdenum dithiocarbamate or the organozinc compound is 0.1 to 10 weight % of the total weight of the grease composition.

9. The grease composition as claimed in claim 7 wherein a ratio of the molybdenum dithiocarbamate and the sulfur-phosphorus containing extreme pressure agent contained in the grease composition is in a range between 1 : 5 and 5 : 1 by weight.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 11 5965

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 508 115 (NIPPON OIL KK) 14 October 1992 * page 2, line 44; examples 2-4 * * page 3, line 1-17 * * page 17, line 47 - page 18, line 2 *	1-9	C10M169/06 //(C10M169/06, 115:08,117:00, 125:26,135:06, 135:18,137:02, 137:04, 137:10), C10N10:12, C10N30:00, C10N40:00, C10N50:10
Y	---	1-9	
Y	GB-A-2 255 346 (NTN TOYO BEARING CO LTD) 4 November 1992 * page 1, line 19-23; table 1 * * page 3, line 12 - page 4, line 4 * ---	1-9	
Y	WO-A-94 11470 (GKN TECHNOLOGY LTD ;FISH GARETH (GB)) 26 May 1994 * figure 7; examples 1,4,7 * ---	1-9	
A	GB-A-2 185 492 (NTN TOYO BEARING CO LTD) 22 July 1987 ---		
A	US-A-3 196 109 (ESSO RESEARCH AND ENGINEERING CO) 20 July 1965 -----		

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C10M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	17 January 1997	Kazemi, P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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E : earlier patent document, but published on, or after the filing date
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