

DESCRIPTION

Title of Invention

GREASE COMPOSITION

5 Technical Field

[0001]

The invention relates to a grease composition that utilizes a urea-based thickener.

Background Art

10 [0002]

Grease has been mainly used for slide bearings, rolling bearings, and sliding surfaces where it is difficult to maintain adhesion of a lubricant film due to the movement of the contact surface. In particular, urea-based grease that utilizes a urea-based thickener exhibits excellent water resistance, mechanical stability, and heat resistance, and has been widely used for metal-metal sliding parts at a low speed with a high load such as an automotive constant-velocity joint.

[0003]

A grease composition that comprises a base oil, an organomolybdenum compound (e.g., a molybdenum dialkyldithiocarbamate sulfide), a molybdenum disulfide, a zinc dithiophosphate compound, and an aliphatic amide has been proposed as a grease composition used for a constant-velocity joint (see PTL 1 to 3).

However, the above grease composition is insufficient in terms of lubricity and particularly wear resistance, and shows a deterioration in wear resistance during long-term use at a high temperature.

25 Citation List

Patent Literature

[0004]

PTL 1: JP-A-2001-11481

PTL 2: JP-A-2005-226038

PTL 3: JP-A-2008-19288

Summary of Invention

5 Technical Problem

[0005]

An object of the invention is to provide a grease composition that exhibits excellent lubricity, in particular excellent wear resistance, and shows only a small extent of deterioration in wear resistance with long-term use at high temperatures.

10 Solution to Problem

[0006]

The inventors of the invention conducted extensive studies in order to achieve the above object. As a result, the inventors found that, in comparison with a grease composition that is prepared by merely dispersing and mixing an amide compound
15 powder into grease, a grease composition obtained by heating and melting an amide compound in the presence of a lubricant base oil forms a three-dimensional network structure of the amide holding the lubricant base oil therein to afford the grease composition significantly improved wear resistance and to show only a small extent of deterioration in wear resistance with long-term use under high temperatures.

20 The invention was completed based on the above finding, and provides the following.

[0007]

(1) A grease composition comprising at least one base oil selected from a mineral oil-based lubricant base oil and a synthetic lubricant base oil, an amide compound, a
25 solid lubricant, and a urea-based thickener, wherein the amide compound is heated and melted at least once together with the base oil.

(2) The grease composition according to (1), wherein the mineral oil-based lubricant

base oil and the synthetic lubricant base oil have a kinematic viscosity of 1 to 1000 mm²/s at 40°C.

(3) The grease composition according to (1) or (2), wherein the amide compound includes an alkyl group having 6 to 24 carbon atoms.

5 (4) The grease composition according to any one of (1) to (3), wherein the solid lubricant is at least one selected from melamine cyanurate, polytetrafluoroethylene, and boron nitride.

(5) The grease composition according to any one of (1) to (4), wherein the urea-based thickener is at least one selected from an aliphatic diurea compound, an alicyclic diurea compound, and an aromatic diurea compound.

(6) The grease composition according to any one of (1) to (5), the grease composition being used for lubrication of metal-metal sliding parts.

(7) A method for producing a grease composition that comprises at least one base oil selected from a mineral oil-based lubricant base oil and a synthetic lubricant base oil, an amide compound, a solid lubricant, and a urea-based thickener, wherein the method comprises adding the amide compound to the base oil, followed by heating to melt the amide compound at least once.

Advantageous Effects of Invention

[0008]

20 The grease composition according to the invention exhibits excellent water resistance, mechanical stability, and heat resistance, provides excellent wear resistance to metal-metal sliding parts at a low speed with a high load, and shows only a small extent of deterioration in wear resistance with long-term use under high temperatures.

Description of Embodiments

25 [0009]

The grease composition according to the invention comprises a lubricant base oil, an amide compound, a solid lubricant, and a urea-based thickener.

[Lubricant base oil]

A mineral oil-based lubricant base oil or a synthetic lubricant base oil may be used as the lubricant base oil used in connection with the invention. It is preferable to use a lubricant base oil having a kinematic viscosity of 1 to 1000 mm²/s, and more preferably 20 to 300 mm²/s at 40°C. If the kinematic viscosity (at 40°C) of the lubricant base oil falls outside the range of 1 to 1000 mm²/s, it may be difficult to easily prepare a grease composition having the desired consistency.

It is preferable to use a lubricant base oil having a density of 0.75 to 0.95 g/cm³ at 15°C since the dispersibility of the solid lubricant is improved. In order to prepare grease having excellent lubricity, it is preferable to use a lubricant base oil having a viscosity index of 90 or more (more preferably 95 to 250), a pour point of -10°C or less (more preferably -15 to -70°C), and a flash point of 150°C or more.

[0010]

Examples of the mineral oil-based lubricant base oil include lubricant fractions obtained by distilling crude oil under atmospheric pressure optionally followed by distillation under reduced pressure to obtain a distillate, and refining the distillate using various types of refining process. Examples of the refining process include hydrotreating, solvent extraction, solvent dewaxing, hydrodewaxing, washing with sulfuric acid, clay treatment, and the like. The base oil used in connection with the invention can be obtained by combining these processes in an appropriate order. A mixture of a plurality of refined oils having different properties is also useful, wherein the mixture is obtained by using different types of crude oils or distillates and by a different combination and/or order of processes. The base oil obtained by each method may preferably be used as long as the properties of the base oil are adjusted to fall within the above ranges.

[0011]

It is preferable to use a material that exhibits excellent hydrolytic stability as the

synthetic lubricant base oil. Examples of the synthetic lubricant base oil include polyolefins such as a poly- α -olefin, a polybutene, and a copolymer of two or more olefins, polyesters, polyalkylene glycols, alkylbenzenes, alkylnaphthalenes, and the like. It is preferable to use a poly- α -olefin from the viewpoint of availability, cost, viscosity, oxidation stability, and compatibility with a system member. A polymer of 1-dodecene or 1-decene is more preferable as the poly- α -olefin from the viewpoint of cost.

[0012]

These synthetic lubricant base oils may be used either alone or in combination. The synthetic lubricant base oil may be used in combination with the mineral oil-based lubricant base oil.

When using a mixture of a plurality of types of lubricant base oil including a synthetic lubricant base oil, the properties of each base oil are not necessary to fall within the above ranges as long as the base oil mixture satisfies the above properties. Therefore, each synthetic base oil need not necessarily satisfy the above properties, but it is preferable that the properties of each synthetic base oil fall within the above ranges.

The content of the lubricant base oil in the grease composition is preferably 50 to 95 mass%, and more preferably 60 to 85 mass%, based on the total amount of the grease composition. If the content of the lubricant base oil is outside the range of 50 to 95 mass%, it may be difficult to easily prepare a grease composition having the desired consistency.

[0013]

[Amide compound]

The amide compound used in connection with the invention is a monoamide that includes one amide group (-NH-CO-), a bisamide that includes two amide groups, a triamide that includes three amide groups, or the like. The bisamide and the triamide have an advantage in that the frictional resistance in the sliding part can be reduced even when the amide compound is used in a relatively small amount.

The bisamide may be an acid amide of a diamine or an acid amide of a diacid.

It is preferable to use an amide compound having a melting point of 40 to 180°C (more preferably 80 to 180°C, and still more preferably 100 to 170°C) and a molecular weight of 242 to 932 (more preferably 298 to 876).

5 The monoamide is represented by the following general formula (1), the bisamide is represented by the following general formulas (2) and (3), and the triamide is represented by the following general formula (4).

[0014]



[0015]

wherein R^1 , R^2 , and R^3 are independently a hydrocarbon group having 5 to 25 carbon
15 atoms. The hydrocarbon group may be an aliphatic hydrocarbon group, an alicyclic hydrocarbon group, or an aromatic hydrocarbon group. R^2 in the general formula (1) may be a hydrogen atom. A^1 , A^2 , and A^3 are independently an aliphatic hydrocarbon group having 1 to 10 carbon atoms, an alicyclic hydrocarbon group, an aromatic hydrocarbon group, or a divalent hydrocarbon group having 1 to 10 carbon atoms
20 formed by combining these groups, and M is an amide group.

It is preferable that R^2 is a hydrogen atom or a saturated or unsaturated chain hydrocarbon group having 10 to 20 carbon atoms when the amide compound is the monoamide.

It is preferable that A^1 is a divalent saturated chain hydrocarbon group having 1
25 to 4 carbon atoms when the amide compound is the acid amide of a diamine.

Some of the hydrogen atoms of the hydrocarbon group represented by R^1 , R^2 , or A^1 in the general formulas (2) and (3) may be substituted with a hydroxyl group (-OH).

[0016]

An amide compound in which A^1 , A^2 , and A^3 are an aliphatic hydrocarbon group is referred herein to as “aliphatic amide”, an amide compound in which at least one of A^1 , A^2 , and A^3 is an aromatic hydrocarbon group is referred herein to as “aromatic amide”, and an amide compound in which at least one of A^1 , A^2 , and A^3 is an alicyclic hydrocarbon group or an aromatic hydrocarbon group is referred herein to as “non-aliphatic amide”.

It is preferable that R^1 , R^2 , and R^3 is a saturated or unsaturated chain hydrocarbon group having 10 to 20 carbon atoms when the amide compound is the aliphatic amide.

It is preferable that R^1 , R^2 , and R^3 is a saturated or unsaturated chain hydrocarbon group having 10 to 20 carbon atoms or an aromatic hydrocarbon group when the amide compound is the aromatic amide.

The non-aliphatic amide may also be used as the amide compound, but it is preferable to use the aliphatic amide as the amide compound. It is preferable that A^1 is a divalent saturated chain hydrocarbon group having 1 to 4 carbon atoms when the amide compound is the acid amide of a diamine (general formula (3)).

[0017]

Specific examples of the monoamide include saturated fatty acid amides such as lauric acid amide, palmitic acid amide, stearic acid amide, behenic acid amide, and hydroxystearic acid amide, unsaturated fatty acid amides such as oleic acid amide and erucic acid amide, substituted amides of a saturated or unsaturated long-chain fatty acid and a long-chain amine such as stearyl stearic acid amide, oleyl oleic acid amide, oleyl stearic acid amide, and stearyl oleic acid amide, and the like.

[0018]

Specific examples of the acid amide of a diamine represented by the general formula (2) include ethylene bis-stearic acid amide, ethylene bis-isostearic acid amide,

ethylene bis-oleic acid amide, methylene bis-lauric acid amide, hexamethylene bis-oleic acid amide, hexamethylene bis-hydroxystearic acid amide, and the like. Specific examples of the bisamide of a diacid represented by the general formula (3) include N,N'-bis-stearylsebacic acid amide and the like.

5 Among these, the amide compounds represented by the general formula (2) or (3) in which R¹ and R² are independently a saturated chain hydrocarbon group or an unsaturated chain hydrocarbon group having 12 to 20 carbon atoms are preferable.

[0019]

 There are various triamide compounds that are represented by the general
10 formula (4). Specific examples of a compound among the compounds represented by the general formula (4) that can be suitably used in connection with the invention include an N-acylamino acid diamide compound. The N-acyl group included in the N-acylamino acid diamide compound is preferably a linear or branched saturated or unsaturated aliphatic acyl group having 1 to 30 carbon atoms, or an aromatic acyl group
15 in particular, a caproyl group, a capryloyl group, a lauroyl group, a myristoyl group, or a stearoyl group. The amino acid included in the N-acylamino acid diamide compound is preferably aspartic acid or glutamic acid. The amine of the amide group included in the N-acylamino acid diamide compound is preferably a linear or branched saturated or unsaturated aliphatic amine having 1 to 30 carbon atoms, and more preferably
20 butylamine, octylamine, laurylamine, isostearylamine, or stearylamine. In particular, N-lauroyl-L-glutamic acid- α,γ -di-n-butylamide is preferable.

 These amide compounds may be used either alone or in combination. The content of the amide compound in the grease composition is preferably 0.1 to 50 mass%, and more preferably 3 to 35 mass%, based on the total amount of the grease
25 composition.

[0020]

[Solid lubricant]

The solid lubricant is not particularly limited as long as the solid lubricant is normally used as a lubricant. It is preferable to use a layered compound or a fluororesin as the solid lubricant due to excellent lubricity.

A compound having a layered crystal structure such as melamine cyanurate,
5 boron nitride, graphite, mica, and fluorinated graphite is preferable as the layered compound. Note that it is undesirable to use a compound that includes a heavy metal or sulfur from the viewpoint of environmental pollution and the like.

Examples of a preferable fluororesin include a polytetrafluoroethylene (PTFE), a tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA), a
10 tetrafluoroethylene-hexafluoropropylene copolymer (FEP), a tetrafluoroethylene-ethylene copolymer (ETFE), polyvinylidene fluoride (PVDF), polychlorotrifluoroethylene (PCTFE), and the like.

[0021]

These solid lubricants may be used either alone or in combination. A solid
15 lubricant having an appropriate particle size may be selected depending on the application. It is preferable to use a solid lubricant having a particle size (diameter) of 0.2 to 50 μm , and more preferably 1 to 10 μm .

The content of the solid lubricant in the grease composition is preferably 0.1 to 10 mass%, and more preferably 0.2 to 5 mass%, based on the total amount of the grease
20 composition.

[0022]

[Urea-based thickener]

A diurea compound obtained by reacting a diisocyanate with a monoamine, a polyurea compound obtained by reacting a diisocyanate with a monoamine and a
25 diamine, or the like may be used as the urea-based thickener.

Examples of a preferable diisocyanate include phenylene diisocyanate, tolylene diisocyanate, diphenyl diisocyanate, diphenylmethane diisocyanate, octadecane

diisocyanate, decane diisocyanate, hexane diisocyanate, and the like. Examples of a preferable monoamine include octylamine, dodecylamine, hexadecylamine, stearylamine, oleylamine, aniline, p-toluidine, cyclohexylamine, and the like. Examples of a preferable diamine include ethylenediamine, propanediamine, butanediamine, hexanediamine, octanediamine, phenylenediamine, tolylenediamine, xylenediamine, diaminodiphenylmethane, and the like.

These urea-based thickeners may be used either alone or in combination. The content of the urea-based thickener in the grease composition may be appropriately determined as long as the desired consistency can be obtained. For example, the content of the urea-based thickener in the grease composition is preferably 2 to 30 mass%, and more preferably 5 to 20 mass%, based on the total amount of the grease composition.

[0023]

[Additive]

The grease composition according to the invention may optionally include a detergent, a dispersant, an antiwear agent, a viscosity index improver, an antioxidant, an extreme pressure agent, a rust-preventive agent, a corrosion inhibitor, and the like that are normally used for a lubricant or grease in addition to the above components.

[0024]

[Preparation method]

The grease composition according to the invention may be prepared using a normal grease preparation method. It is preferable to heat a mixture comprising the amide compound to a temperature equal to or higher than the melting point of the amide compound at least once, after mixing the amide compound.

Specifically, the grease composition may be prepared by heating the amide compound and the lubricant base oil to a temperature equal to or higher than the melting point of the amide compound, cooling the mixture, and then physically mixing the

cooled mixture with normal grease that comprises the solid lubricant, the thickener, and the lubricant base oil. Alternatively, all of the components including the urea-based thickener may be mixed, heated to a temperature equal to or higher than the melting point of the amide compound, and then cooled.

5 [0025]

When the amide compound is heated to a temperature equal to or higher than the melting point of the amide compound in the presence of at least the lubricant base oil, the lubricant base oil is held in a semi-solid gel state by the amide compound that forms a three-dimensional network structure, but freely moves within the network structure
10 microscopically. This suggests that, when the gel-like composition having lubricity comes in contact with small voids formed in a porous material, the liquid lubricant base oil can move into the small voids from the gel due to a capillary phenomenon, or suggests that, when an excess liquid lubricant base oil is present in the system, the excess liquid lubricant base oil is incorporated in the gel due to a capillary phenomenon
15 through the three-dimensional structure of the gel, for example. The urea-based thickener provides consistency in such a state. The grease composition thus exhibits excellent water resistance, mechanical stability, and heat resistance, provides excellent wear resistance, and shows only a small extent of deterioration in wear resistance with long-term use under high temperatures.

20 **Examples**

[0026]

1. Lubricant base oil

(1) Mineral oil-based lubricant base oil

- Lubricant base oil obtained by distilling atmospheric distillation residue under reduced
25 pressure and subjecting the resulting distillate to solvent refining

Kinematic viscosity at 40°C: 68 mm²/s

Density at 15°C: 0.87 g/cm³

Viscosity index: 100

Pour point: -10°C

Flash point: 250°C

(2) Synthetic lubricant base oil

5 Poly- α -olefin (“Durasyn 170” manufactured by INEOS)

Kinematic viscosity at 40°C: 68 mm²/s

Density at 15°C: 0.83 g/cm³

Viscosity index: 133

Pour point: -45°C

10 Flash point: 250°C

[0027]

2. Amide compound

2-1. Aliphatic amide

(1) Ethylene bis-stearic acid amide (special grade reagent)

15 (2) Ethylene bis-oleic acid amide (special grade reagent)

(3) Stearic acid monoamide (special grade reagent)

2-2. Aromatic amide

(1) m-Xylylene bis-stearic acid amide (special grade reagent)

[0028]

20 3. Solid lubricant

(1) Melamine cyanurate (MCA, average particle size: 4 μ m, “MELAPUR MC25” manufactured by BASF)

(2) Polytetrafluoroethylene (PTFE, average particle size: 4 μ m, “KTL-8N” manufactured by Kitamura Limited)

25 (3) Boron nitride (average particle size: 2 μ m, “HP-P1” manufactured by Mizushima Ferroalloy Co., Ltd.)

The average particle size was measured by laser diffractometry.

[0029]

4. Urea-based thickener

(1) Aliphatic diurea obtained by reacting octadecylamine with methylenediphenyl diisocyanate

5 (2) Alicyclic diurea obtained by reacting cyclohexylamine with methylenediphenyl diisocyanate

(3) Aromatic diurea obtained by reacting p-toluidine with methylenediphenyl diisocyanate

[0030]

10 5. Additive

Diphenylamine was added to each composition as an antioxidant.

[0031]

[Preparation method]

Each component was charged in a vessel in the amount (wt%) shown in Table 1
15 or 2, heated to 150°C, which is a temperature equal to or higher than the melting point of the amide, stirred using a magnetic stirrer, and then cooled to room temperature. The mixture was dispersed under pressure using a roller (triple roll) to prepare a grease composition.

In Comparative Example 7, each component in the amount shown in Table 2
20 was dispersed directly without heating and cooling under pressure using a roller (triple roll) to prepare a grease composition.

[0032]

[Evaluation test]

A friction test was performed at a load of 350 lbf for 15 minutes using a FALEX
25 Pin and Vee Block tester to evaluate the amount of wear of the sample. In order to evaluate the performance when the grease has been used under severe conditions, the FALEX test was also performed using a fresh grease and a degraded grease that is

obtained by leaving the fresh grease at 150°C for 100 hours or 500 hours.

[0033]

[Evaluation results]

When only the mineral oil and the urea-based thickener were mixed, the amount
5 of wear was about 7 mg when using the fresh grease, but was significantly large when
using the degraded grease (Comparative Example 6).

When the mineral oil, the urea-based thickener, and the solid lubricant were
mixed, the amount of wear decreased to some extent when using the fresh grease, but
was large when using the degraded grease (Comparative Examples 1 to 5).

10 When the aliphatic amide was not heated and melted, the amount of wear was
large when using the fresh grease and when using the degraded grease (Comparative
Example 7).

When the mineral oil, the urea-based thickener, the solid lubricant, and the
aliphatic amide were mixed, the amount of wear significantly decreased when using the
15 fresh grease and when using the degraded grease (Examples 1 to 9).

[0034]

[TABLE 1]

Example		1	2	3	4	5	6	7	8	9	10
Lubricant base oil	Mineral oil	7 8	7 2	7 0	7 5	7 2	7 5		7 7	7 5	7 5
	P A O							7 5			
Amide compound	Stearic acid monoamide		1 3								
	Stearic acid bisamide	1 0			1 0	1 0	1 0	1 0	1 5	5	
	Oleic acid bisamide			1 5							
	Aromatic amide										1 0
Solid lubricant	M C A	4	4	4	4			4	4	4	4
	P T F E					4					
	Boron nitride						4				
	Aliphatic diurea	7									
Thickener	Alicyclic diurea		1 0	1 0	1 0	6	1 0	1 0	8	1 5	1 0
	Aromatic diurea					6					
Antioxidant	Diphenylamine	1	1	1	1	1	1	1	1	1	1
Evaluation results	Fresh grease: FALEX amount of wear	1. 0	1. 5	1. 3	1. 2	1. 0	0. 9	1. 0	0. 9	1. 8	1. 5
	100h degraded grease: FALEX amount of wear	1. 5	1. 2	1. 5	1. 5	0. 8	1. 3	1. 4	1. 0	2. 5	2. 0
	500h degraded grease: FALEX amount of wear	1. 8	1. 2	2. 0	1. 5	1. 3	1. 0	1. 3	1. 0	2. 2	2. 1

[0035]

[TABLE 2]

Comparative example		1	2	3	4	5	6	7
Lubricant base oil	Mineral oil	8 5	7 7	7 5	7 7	7 7	7 9	7 5
	Stearic acid bisamide							1 0
Amide compound	M C A	4	4	4	4			4
	P T F E							
Solid lubricant	Boron nitride					4		
	Aliphatic diurea	1 0						
Thickener	Alicyclic diurea		1 8	1 0	1 8	1 8	2 0	1 0
	Aromatic diurea			1 0				
Antioxidant	Diphenylamine	1	1	1	1	1	1	1
	Fresh grease: FALEX amount of wear	4. 5	6. 0	4. 0	4. 5	3. 5	7. 0	2 7
Evaluation results	100h degraded grease: FALEX amount of wear	2 5	2 8	3 0	2 7	3 2	2 8	—
	500h degraded grease: FALEX amount of wear	3 0	3 4	2 8	3 2	3 4	3 8	—

In Comparative Example 7, the grease composition was prepared without heating and cooling after adding stearic acid bisamide.

Industrial Applicability

[0036]

Since the grease composition according to the invention exhibits excellent water resistance, mechanical stability, and heat resistance, provides excellent wear resistance to metal-metal sliding parts at a low speed with a high load, and shows only a small
5 extent of deterioration in wear resistance with long-term use under high temperatures, the grease composition can be used to lubricate a joint, a gear, and a bearing, and the like that have metal-metal sliding parts.

CLAIMS

[Claim 1]

5 A grease composition comprising at least one base oil selected from a mineral oil-based lubricant base oil and a synthetic lubricant base oil, an amide compound, a solid lubricant, and a urea-based thickener, wherein the amide compound is heated and melted at least once together with the base oil.

[Claim 2]

10 The grease composition according to claim 1, wherein the mineral oil-based lubricant base oil and the synthetic lubricant base oil have a kinematic viscosity of 1 to 1000 mm²/s at 40°C.

[Claim 3]

15 The grease composition according to claim 1 or 2, wherein the amide compound includes an alkyl group having 6 to 24 carbon atoms.

[Claim 4]

20 The grease composition according to any one of claims 1 to 3, wherein the solid lubricant is at least one selected from melamine cyanurate, polytetrafluoroethylene, and boron nitride.

[Claim 5]

25 The grease composition according to any one of claims 1 to 4, wherein the urea-based thickener is at least one selected from an aliphatic diurea compound, an alicyclic diurea compound, and an aromatic diurea compound.

[Claim 6]

The grease composition according to any one of claims 1 to 5, the grease composition being used for lubrication of metal-metal sliding parts.

5 [Claim 7]

A method for producing a grease composition that comprises at least one base oil selected from a mineral oil-based lubricant base oil and a synthetic lubricant base oil, an amide compound, a solid lubricant, and a urea-based thickener, wherein the method comprises adding the amide compound to the base oil, followed by heating to melt the

10 amide compound at least once.