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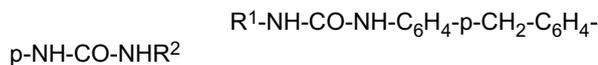
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(54) **Grease composition for ball type constant velocity joints and ball type constant velocity joints containing the grease composition**

(57) A grease composition for use in ball type constant velocity joints, which comprises the following components: a base oil; a diurea thickener of the formula:



wherein R<sup>1</sup> and R<sup>2</sup> are alkyl groups having 8 carbon atoms; molybdenum disulfide; molybdenum dithiocarbamate of the formula:



wherein R<sup>3</sup> and R<sup>4</sup> independently represent an alkyl group having 1 to 24 carbon atoms, m is 0 to 3, n is 4 to 1 and m + n = 4; calcium salts or overbasic calcium salts of petroleum sulfonates; sulfur-phosphorus extreme pressure agent; and e.g. castor oil; is disclosed. The grease composition exhibits excellent wear-resistance and pitting-inhibitory effect.

**Description**

**[0001]** The present invention relates to a grease composition for use in high contact pressure ball type constant velocity joints, in particular, plunging or fixed ball type constant velocity joints. A very high contact pressure is developed between parts of constant velocity joints to be lubricated and the joint parts undergo complicated rolling and sliding motions. This often results in abnormal wear and metal fatigue and, in turn, leads to a spalling phenomenon, i.e., pitting of the joint parts. More specifically, the present invention relates to a grease composition for ball type constant velocity joints which can effectively lubricate such constant velocity joints to effectively reduce wear of joints and to effectively reduce occurrence of pitting in the parts to be lubricated.

**[0002]** Examples of lubricating greases conventionally used in such constant velocity joints include a lithium soap thickened extreme pressure grease containing molybdenum disulfide and a lithium soap thickened extreme pressure grease containing molybdenum disulfide and sulfur-phosphorus extreme pressure agents or a lead naphthenate. However, these greases for constant velocity joints have not always been satisfactory in the severe working conditions which occur in the recent high-performance motorcars.

**[0003]** Recently, the number of four-wheel drive (front engine, front drive type) motorcars have rapidly increased. Motorcars are being made lighter to improve fuel consumption. It is therefore necessary to make constant velocity joints used in these motorcars as lighter and smaller as possible.

**[0004]** The double offset type constant velocity joints and cross groove type constant velocity joints used as plunging type constant velocity joints as well as Birfield joints used as fixed type constant velocity joints have a structure in which torques are transmitted through 6 balls.

**[0005]** These joints cause complicated reciprocating motions such as complicated rolling and sliding motions during rotation at a high contact pressure. Therefore, stresses are repeatedly applied to the balls and the metal surfaces which come in contact with the balls and accordingly, the pitting phenomenon is apt to occur at such portions due to metal fatigue.

**[0006]** The recent improvement in the power of engines is accompanied by an increase in the contact pressure as compared with conventional engines. Motorcars are being made lighter to improve fuel consumption and the size of joints has correspondingly been down-sized. This leads to a relative increase in the contact pressure and thus the conventional greases are not sufficient to reduce the pitting phenomenon. In addition, the greases must also be improved in their heat resistance.

**[0007]** For this purpose, there are proposed a grease composition for use in constant velocity joints, which comprises a urea thickener, molybdenum disulfide and at least one member selected from the group consisting of calcium salts of oxidized waxes, calcium salts of petroleum sulfonates, calcium salts of alkyl aryl sulfonates, calcium salts of salicylate, calcium salts of phenates, overbasic calcium salts of oxidized waxes, overbasic calcium salts of petroleum sulfonates, overbasic calcium salts of alkyl aryl sulfonates, overbasic calcium salts of salicylate, and overbasic calcium salts of phenates (JP-A-9-194871 (=USP 5607906, EP 773280 B1)) and a grease composition for use in constant velocity joints, which comprises, in addition to the above components, a metal-free sulfur-phosphorus extreme pressure agent and molybdenum dithiocarbamate (JP-A-9-324189 (= EP 811675 B1)).

**[0008]** However, these greases for constant velocity joints have not always shown a satisfactory pitting-inhibitory effect when they are used in high contact pressure ball type constant velocity joints.

**[0009]** An object of the present invention is to provide a grease composition for use in high contact pressure ball type constant velocity joints which has an excellent pitting-inhibitory effect as compared with conventional grease compositions for constant velocity joints, and ball type constant velocity joints containing the grease composition.

**[0010]** The inventors of this invention have conducted various studies to develop a grease composition having improved durability and found that the addition of vegetable fats and oils to a conventional constant velocity joint improves the durability of the joints and optionally the increase of relative amount of sulfur-phosphorus extreme pressure agent further improves the durability of the joints. The present invention has been accomplished based on this finding. The present invention provides a grease composition for use in ball type constant velocity joints and ball type constant velocity joints containing the grease composition as shown below.

**[0011]** A grease composition for use in ball type constant velocity joints, according to the present invention comprises the following components:

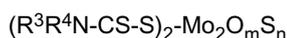
- (a) a base oil selected from the group consisting of mineral oils, ether type synthetic oils, ester type synthetic oils, hydrocarbon type synthetic oils and mixtures thereof,
- (b) a diurea thickener represented by the following formula:



- wherein R<sup>1</sup> and R<sup>2</sup> are alkyl groups having 8 carbon atoms,
- (c) molybdenum disulfide;

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(d) a molybdenum dithiocarbamate represented by the following formula:



- 5 wherein  $R^3$  and  $R^4$  independently represent alkyl groups having 1 to 24 carbon atoms,  $m$  is 0 to 3,  $n$  is 4 to 1 and  $m + n = 4$ ,  
(e) at least one calcium salt selected from the group consisting of calcium salts of petroleum sulfonates, and overbasic calcium salts of petroleum sulfonates,  
10 (f) a sulfur-phosphorus extreme pressure agent in an amount of 1.5 to 10% by weight on the basis of the total weight of the composition, and  
(g) vegetable fats and oils.

In an embodiment of the present invention the above described grease composition is for use in high contact pressure ball type constant velocity joints.

15 In a further embodiment of the present invention the above described grease compositions comprise, on the basis of the total weight of the composition, 1 to 25% by weight of the diurea thickener; 0.1 to 5.0% by weight of the molybdenum disulfide; 0.1 to 5.0% by weight of the molybdenum dithiocarbamate; 0.1 to 5.0% by weight of the calcium salt; 1.5 to 10% by weight of the sulfur phosphorus Extreme pressure agent, and 0.1 to 3.0% by weight of the vegetable fats and oils.

20 **[0012]** In a further embodiment of the present invention the above described grease compositions comprise 2.0 to 5.0% by weight of the sulfur-phosphorus extreme pressure agent.

**[0013]** In a further embodiment of the present invention the above described grease compositions are for use in the ball type fixed constant velocity joints.

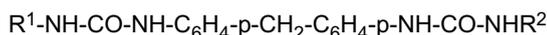
**[0014]** Furthermore, the present invention relates to a ball type constant velocity joint containing the above described grease composition.

25 **[0015]** The grease composition of the present invention for use in ball type constant velocity joints greatly improves the pitting-inhibitory effect and remarkably extends the life of the constant velocity joints containing the grease composition. These effects of the present invention are outstanding when the grease composition is used in constant velocity joints which are used under high contact pressure condition.

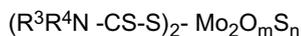
30 **[0016]** Hereinafter, the grease composition for use in ball type constant velocity joints of the present invention will be described in detail.

**[0017]** The grease composition of the present invention comprises the following components (a), (b), (c), (d), (e), (f) and (g):

- 35 (a) a base oil selected from the group consisting of mineral oils, ether type synthetic oils, ester type synthetic oils, hydrocarbon type synthetic oils and mixtures thereof,  
(b) a diurea thickener represented by the following formula:



- 40 wherein  $R^1$  and  $R^2$  are alkyl groups having 8 carbon atoms,  
(c) molybdenum disulfide;  
(d) a molybdenum dithiocarbamate represented by the following formula:



- 45 wherein  $R^3$  and  $R^4$  independently represent alkyl groups having 1 to 24 carbon atoms,  $m$  is 0 to 3,  $n$  is 4 to 1 and  $m + n = 4$ ,  
(e) at least one calcium salt selected from the group consisting of calcium salts of petroleum sulfonates, and overbasic calcium salts of petroleum sulfonates,  
50 (f) a sulfur-phosphorus extreme pressure agent in an amount of 1.5 to 10% by weight on the basis of the total weight of the composition, and  
(g) vegetable fats and oils.

**[0018]** First, Component (a) will be explained.

55 **[0019]** The base oil as Component (a) is not restricted to specific ones and may be, for instance, lubricating oils currently used such as mineral oils, ether type synthetic oils, ester type synthetic oils, hydrocarbon type synthetic oils or mixtures thereof. From the economical point of view, mineral oils are preferred, and a mixture of mineral oils as a major component and synthetic oils is also preferred.

[0020] Kinetic viscosity of the base oils at 100°C is preferably 5 to 30mm<sup>2</sup>/s, more preferably 7 to 25mm<sup>2</sup> /s. If the viscosity is less than 5 mm<sup>2</sup>/s, high-speed durability of constant velocity joints tends to be insufficient, while if it is greater than 30mm<sup>2</sup>/s, high-speed durability of constant velocity joints tends to decrease.

5 [0021] The diurea thickener as Component (b) can be obtained by a reaction between diphenylmethane diisocyanate and octylamine. The reaction is not limited to specific ones but can be done by any known ones.

[0022] The molybdenum disulfide as Component (c) has widely been used as an extreme pressure agent. With regard to the lubricating mechanism thereof, the molybdenum disulfide is easily sheared under the sliding motions through the formation of a thin layer since it has a layer lattice structure and it shows effects of reducing friction and of preventing seizure of joints. There have been known molybdenum disulfide products having various particle sizes, but it is preferable in the present invention to use those having a particle size ranging from 0.25 to 10μm, in particular, 0.55 to 0.85μm expressed in terms of an average particle size as determined by the method called Fisher method (by the use of a Fisher Sub-Sieve sizer).

15 [0023] The calcium salts or overbasic calcium salts as Component (e) are selected from those known as metal cleaning dispersants or rust-inhibitors which are used in lubricants such as engine oils, such as calcium salts of petroleum sulfonates and overbasic calcium salts of petroleum sulfonates which are obtained by sulfonation of aromatic hydrocarbon in lubricating oil fraction.

[0024] Preferred sulfur-phosphorus extreme pressure agents as Component (f) have a sulfur content ranging from 15 to 35% by weight and a phosphorus content ranging from 0.5 to 3% by weight and exhibits excellent effects of inhibiting wear and of preventing seizure of the joints through the well-established balance between the sulfur and phosphorus contents. More specifically, if the sulfur content exceeds the upper limit defined above, the joints tend to easily corrode , while if the phosphorus content exceeds the upper limit defined above, desired wear-inhibiting effect cannot be expected. On the other hand, if sulfur or phosphorus content is less than the corresponding lower limits, desired wear-inhibiting and seizure-preventing effect cannot be expected.

25 [0025] Examples of the vegetable oils and fats as Component (g) include castor oil, rapeseed oil and linseed oil. Among them, castor oil is particularly preferred.

[0026] Preferably, the grease composition for use in ball type constant velocity joints of the present invention comprises, on the basis of the total weight of the composition, 1.0 to 25.0% by weight of the diurea thickener (b), 0.1 to 5.0% by weight of molybdenum disulfide (c), 0.1 to 5.0% by weight of the molybdenum dithiocarbamate (d), 0.1 to 5.0% by weight of the calcium salt (e), 1.5 to 10% by weight of the sulfur-phosphorus extreme pressure agent (f) and 0.1 to 3.0% by weight of the vegetable fats and oils (g).

30 [0027] If the amount of the diurea thickener (b) is less than 1% by weight, the thickening effect thereof tends to become too low to convert the composition into a grease, while if it exceeds 25% by weight, the resulting composition tends to become too hard to ensure the desired effects of the present invention.

[0028] If the amount of the molybdenum disulfide (c) is less than 0.1% by weight, it becomes difficult to obtain the desired effects of the present invention, while if it exceeds 5% by weight, the effects of the present invention may be saturated.

35 [0029] If the amount of the molybdenum dithiocarbamate (d) is less than 0.1% by weight, it becomes difficult to obtain the desired effects of the present invention, while if it exceeds 5% by weight, the effects of the present invention may be saturated.

40 [0030] If the amount of the calcium salt (e) is less than 0.1% by weight, it becomes difficult to obtain the desired effects of the present invention, while if it exceeds 5% by weight, the effects of the present invention may be saturated.

[0031] If the amount of the sulfur-phosphorus extreme pressure agent (f) is less than 1.5% by weight, it becomes difficult to obtain the desired effects of the present invention, while if it exceeds 10% by weight, the effects of the present invention may be saturated.

45 [0032] If the amount of the vegetable fats and oils (g) is less than 0.1% by weight, it becomes difficult to obtain the desired effects of the present invention, while if it exceeds 3% by weight, the effects of the present invention may be saturated.

[0033] The grease composition for use in ball type constant velocity joints of the present invention may further comprise, in addition to the above components (a) to (g), antioxidants, rust inhibitors, and polymer additives which are generally used in conventional lubricating oils and greases. Moreover, extreme pressure agents, friction alleviating agents, agents for wear-resistance, and solid lubricating agents other than the above components (c), (d), (e) and (f) may be added to the grease composition of the present invention. If these additives are used, the amount thereof is preferably 0.1 to 10% by weight of the total weight of the grease composition.

55 [0034] The present invention will hereunder be described in more detail with reference to the following non-limitative Working Example and Comparative

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Examples.

Example 1

5 **[0035]** There were added, to a container, 440 g of a base oil and 58.9 g of diphenylmethane-4,4'-diisocyanate and the mixture was heated to a temperature between 70 and 80°C. To another container, there were added 440 g of a base oil, 61.1 g of octylamine followed by heating at a temperature between 70 and 80°C and addition thereof to the foregoing container. The mixture was then reacted for 30 minutes with sufficient stirring, the temperature of the reaction system was raised up to 160°C with stirring and the reaction system was allowed to cool to give a base aliphatic amine diurea grease. To the base grease, there were added the following additives listed in Table 1 in amounts likewise listed in Table 1 and an optional and additional amount of the base oil and the penetration of the resulting mixture was adjusted to No. 1 grade by a three-stage roll mill.

**[0036]** A mineral oil having the following properties was used as the base oil for the grease.

15 Viscosity:           at 40°C 230 mm<sup>2</sup>/s  
                          at 100°C 20 mm<sup>2</sup>/s

Viscosity Index: 100

20 Comparative Examples 1 to 3

**[0037]** The same procedures as in Example 1 were repeated to prepare a grease of Comparative Example 1 except that castor oil was not added, or a grease of Comparative Example 2 except that the amount of sulfur-phosphorus extreme pressure agent was changed to 1% by weight.

25 **[0038]** A commercially available grease composition for use in constant velocity joints containing graphite, organic molybdenum and sulfur-phosphorus extreme pressure agent in molybdenum disulfide was used as a grease of Comparative Example 3.

**[0039]** The details of the components in Table 1 are as follows and unit of the numerical values in the table is % by weight.

Molybdenum dithiocarbamate A (Trade name; Molyvan A available from R. T. Vanderbilt)  
30 Calcium salt of petroleum sulfonate (Trade name; Sulfol Ca-45 available from Matsumura Petroleum Laboratory Co., Ltd.)  
Sulfur-phosphorus extreme pressure agent (Trade name; Anglamol 99 available from Lubrizol Japan)  
Castor oil (available from Hokoku Corporation)

**[0040]** Physical properties of these grease compositions were evaluated according to the methods detailed below. Penetration thereof are also summarized in Table 1.

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[Penetration] According to JIS K 2220 5.3

[Joint Durability Test]

Joint Type: Fixed type ball joint

Joint Size: BJ87

40

Angle of Joint: 6°

Number of Revolution: 200rpm

Torque:

Joint durability test 1

45

900Nm (conventional conditions under high torque load)

Joint durability test 2

1000Nm (special conditions under torque load limit)

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Table 1

Components	Example 1	Comp. Example 1	Comp. Example 2	Comp. Example 3
Aliphatic diurea base grease	91	92	93	
Molybdenum disulfide	2	2	2	
Molybdenum dithiocarbamate A	1	1	1	
Ca salt of petroleum sulfonate	2	2	2	

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Table continued

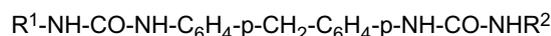
Components	Example 1	Comp. Example 1	Comp. Example 2	Comp. Example 3
Sulfur-phosphorus extreme pressure agent	3	3	1	
Castor oil	1	-	1	
Penetration	325	330	332	330
Joint durability test 1 (total number of revolution)	12,000,000	9,000,000	8,000,000	8,000,000
Joint durability test 2 (total number of revolution)	8,500,000	5,300,000	5,000,000	4,500,000

**[0041]** The results demonstrate that the grease composition for constant velocity joint of Example 1 of the present invention containing castor oil and 3% by weight of the sulfur-phosphorus extreme pressure agent shows better pitting-inhibitory effect, in particular at high contact pressure than those of Comparative Examples 1 and 3 which do not contain castor oil or Comparative Example 2 wherein the amount of the sulfur-phosphorus extreme pressure agent is 1% by weight.

## Claims

1. A grease composition for use in ball type constant velocity joints, which comprises the following components:

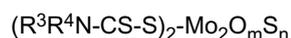
- (a) a base oil selected from the group consisting of mineral oils, ether type synthetic oils, ester type synthetic oils, hydrocarbon type synthetic oils and mixtures thereof,
- (b) a diurea thickener represented by the following formula:



wherein  $R^1$  and  $R^2$  are alkyl groups having 8 carbon atoms,

(c) molybdenum disulfide;

(d) a molybdenum dithiocarbamate represented by the following formula:



wherein  $R^3$  and  $R^4$  independently represent alkyl groups having 1 to 24 carbon atoms,  $m$  is 0 to 3,  $n$  is 4 to 1 and  $m + n = 4$ ,

- (e) at least one calcium salt selected from the group consisting of calcium salts of petroleum sulfonates, and overbasic calcium salts of petroleum sulfonates, (f) a sulfur-phosphorus extreme pressure agent in an amount of 1.5 to 10% by weight on the basis of the total weight of the composition, and
- (g) vegetable fats and oils.

2. The grease composition of claim 1, wherein the grease composition is for use in high contact pressure ball type constant velocity joints.

3. The grease composition of claim 1 or 2, wherein the grease composition comprises, on the basis of the total weight of the composition, 1 to 25% by weight of the diurea thickener; 0.1 to 5.0% by weight of the molybdenum disulfide; 0.1 to 5.0% by weight of the molybdenum dithiocarbamate; 0.1 to 5.0% by weight of the calcium salt; 1.5 to 10% by weight of the sulfur-phosphorus extreme pressure agent, and 0.1 to 3.0% by weight of the vegetable fats and oils.

4. The grease composition of any one of claims 1 to 3, wherein the grease composition comprises 2.0 to 5.0% by weight of the sulfur-phosphorus extreme pressure agent.

5. The grease composition of any one of claims 1 to 4, wherein the grease composition is for use in the ball type fixed constant velocity joints.

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6. A ball type constant velocity joint, containing the grease composition of any one of claims 1 to 4.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y	US 5 207 936 A (ANZAI ET AL) 4 May 1993 (1993-05-04) * column 4, lines 12-32; examples *	1-6	C10M169/00 C10M169/06
D,Y	EP 0 811 675 A (GKN AUTOMOTIVE LIMITED; KYODO YUSHI CO., LTD) 10 December 1997 (1997-12-10) * examples *	1-6	
			TECHNICAL FIELDS SEARCHED (IPC)
			C10M
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 11 January 2006	Examiner Kazemi, P
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ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 05 02 1507

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
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11-01-2006

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5207936	A	04-05-1993	AU 640857 B2	02-09-1993
			AU 1100792 A	17-12-1992
			DE 4204855 A1	08-10-1992
			FR 2674534 A1	02-10-1992
			GB 2255103 A	28-10-1992
			JP 2915611 B2	05-07-1999
			JP 4304300 A	27-10-1992
			KR 147803 B1	01-08-1998
EP 0811675	A	10-12-1997	CN 1168916 A	31-12-1997
			DE 69708974 D1	24-01-2002
			DE 69708974 T2	08-08-2002
			ES 2164991 T3	01-03-2002
			JP 3320611 B2	03-09-2002
			JP 9324189 A	16-12-1997