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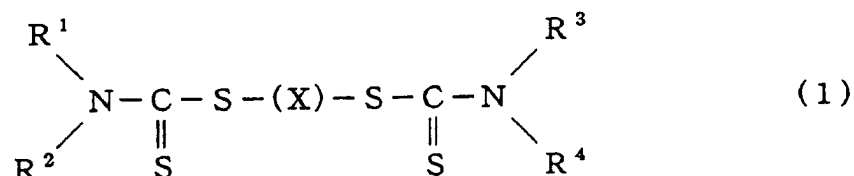
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CARPMAELS AND RANSFORD
43 Bloomsbury Square
London WC1A 2RA (GB)(54) **Grease composition preventing flaking**

(57) A grease composition comprising a lubricant base oil and a metal dithiocarbamate represented by the formula (1):



wherein R¹ to R⁴ may be the same or different and each stands for a hydrocarbon group having 10 to 20 carbon atoms, and X stands for a metal or a metal-containing group. The composition has long life even when used at a high temperature, is not harmful to humans and the environment, and can give an extended anti-flaking life to the rolling bearing.

EP 1 160 308 A2

Description

[0001] The present invention relates to a grease composition. More particularly, the present invention relates to a grease composition for preventing flaking on a race way of a rolling bearing for electrical components and accessory devices for automotive vehicles, e.g., alternators, electromagnetic clutches for car air conditioners, idle pulleys and electric fan motors.

[0002] In automotive vehicles, there is a demand for minimizing an engine room size for increasing cabin space and reducing size and weight of the vehicles. To this end, size and weight of electrical components and accessory devices such as alternators, electromagnetic clutches for car air conditioners, idle pulleys and electric fan motors have further been reduced. On the other hand, there is another demand for higher performance and higher output power of the electrical components and accessories. Therefore, for example, reduction in output power caused by size reduction of an alternator is compensated by increasing the designed speed. Further, to keep up with the demand for quiet operation, the degree of hermetic sealing of the engine room is advanced and hence the engine room tends to be heated, so that components capable of withstanding higher temperatures are required.

[0003] In these electrical components and accessories, rolling bearings are used, and lubrication of the rolling bearings is achieved mainly by using a grease.

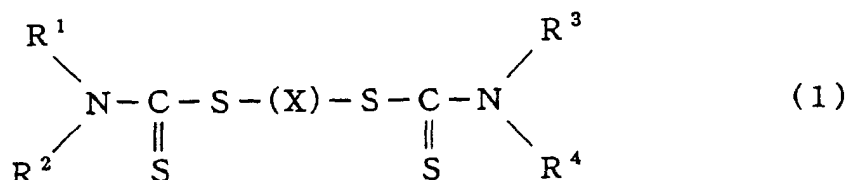
[0004] It has been reported that the high speed rotation and heavy load condition to meet the above demand result in early termination of the life of the rolling bearing by flaking on the raceway.

[0005] For overcoming this problem, JP-A-1-259097, JP-A-3-28299 and JP-A-6-17079 propose grease compositions containing an alkylidiphenyl ether base oil and a urea type thickener. However, none of the grease composition can sufficiently extend flaking life of the rolling bearing. JP-A-3-210394 reports a method for extending flaking life of the rolling bearing by addition of passivation agent. However, when sodium nitrite, one of typical passivation agents, is added to a grease containing amine antioxidant for improving the life of the grease at high temperature, sodium nitrite reacts with amine antioxidant to produce N-nitrosoamine which is harmful to human beings.

[0006] Addition of metal dithiocarbamate has also been taken into consideration in the art. However, a sufficient result has not been obtained yet.

[0007] The object of the present invention is to provide a grease composition which has long life even when used at a high temperature, is not harmful to humans and the environment, and can give an extended anti-flaking life to a rolling bearing.

[0008] According to the present invention, there is provided a grease composition comprising a lubricant base oil and a metal dithiocarbamate represented by the formula (1):



wherein R¹ to R⁴ may be the same or different and each stands for a hydrocarbon group having 10 to 20 carbon atoms, and X stands for a metal or a metal-containing group.

[0009] The grease composition of the present invention contains a lubricant base oil and the specific metal dithiocarbamate represented by the aforementioned formula (1).

[0010] In formula (1), R¹ to R⁴ may be the same or different and each stands for a hydrocarbon group having 10 to 20 carbon atoms. If the number of carbon atoms in these groups is 9 or less, anti-flaking effect at the early stage may be insufficient. The number of the carbon atoms is thus 10 or more, and may preferably be 12 or more. The number of carbon atoms is 20 or less in terms of availability.

[0011] Examples of such hydrocarbon groups may include an alkyl group, an alkenyl group, an alkylcycloalkyl group (i.e., an alkyl-substituted cycloalkyl group), an aryl group, an alkylaryl group (i.e., an alkyl-substituted aryl group), and an arylalkyl group (i.e., an aryl-substituted alkyl group). Among these, an alkyl group and an alkenyl group are particularly preferable for preventing flaking at early stage.

[0012] Examples of the alkyl group may include a decyl group, an undecyl group, a dodecyl group, a tridecyl group, a tetradecyl group, a pentadecyl group, a hexadecyl group, a heptadecyl group, an octadecyl group, a nonadecyl group and an icosyl group, all of which may be straight or branched.

[0013] Examples of the alkenyl group may include a decenyl group, an undecenyl group, a dodecenyl group, a tridecenyl group, a tetradecenyl group, a pentadecenyl group, a hexadecenyl group, a heptadecenyl group, an octadecenyl group such as oleyl group, a nonadecenyl group, and an icosenyl group, all of which may be straight or

branched.

[0014] Examples of the alkylcycloalkyl group may include a cyclopentyl group with one or more alkyl substituents each having 1 to 15 carbon atoms (provided that the total number of carbon atoms of all of the alkyl substituents is 5 to 15), a cyclohexyl group with one or more alkyl substituents each having 1 to 14 carbon atoms (provided that the total number of carbon atoms of all of the alkyl substituents is 4 to 14), a cycloheptyl group with one or more alkyl substituents each having 1 to 13 carbon atoms (provided that the total number of carbon atoms of all of the alkyl substituents is 3 to 13).

[0015] Examples of the aryl group may include a naphthyl group.

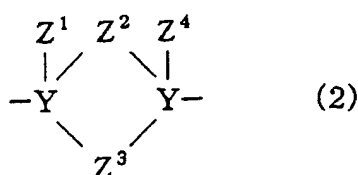
[0016] Examples of the alkylaryl group may include a phenyl group with one or more alkyl substituents each having 1 to 14 carbon atoms (provided that the total number of carbon atoms of all of the alkyl substituents is 4 to 14).

[0017] Examples of the arylalkyl group may include an alkyl group having a phenyl substituent or an alkylaryl substituent.

[0018] In formula (1), X stands for a metal or a metal-containing group.

[0019] Examples of the metal may include Mo, Zn, Pb, Sb, Cu and Ni. Among these metals, Zn, Cu and Ni are particularly preferable in terms of an ecological benefit.

[0020] Examples of the metal-containing group may include the group represented by the following formula (2)



[0021] In formula (2), Y stands for a metal, and each of Z^1 to Z^4 independently stand for a oxygen atom or a sulfur atom. Y may be, for example, Mo, Zn, Pb, Sb, Cu and Ni, and usually Mo.

[0022] Examples of the metal dithiocarbamate represented by the formula (1) may include zinc didecyldithiocarbamate, zinc diundecyldithiocarbamate, zinc didodecyldithiocarbamate, zinc ditridecyldithiocarbamate, zinc ditetradecyldithiocarbamate, zinc dipentadecyldithiocarbamate, zinc dihexadecyldithiocarbamate, zinc diheptadecyldithiocarbamate, zinc dioctadecyldithiocarbamate, zinc dinonadecyldithiocarbamate, zinc diicosyldithiocarbamate, copper didecyldithiocarbamate, copper diundecyldithiocarbamate, copper didodecyldithiocarbamate, copper ditridecyldithiocarbamate, copper ditetradecyldithiocarbamate, copper dipentadecyldithiocarbamate, copper dihexadecyldithiocarbamate, copper diheptadecyldithiocarbamate, copper dioctadecyldithiocarbamate, copper dinonadecyldithiocarbamate, copper diicosyldithiocarbamate, nickel didecyldithiocarbamate, nickel diundecyldithiocarbamate, nickel didodecyldithiocarbamate, nickel ditridecyldithiocarbamate, nickel ditetradecyldithiocarbamate, nickel dipentadecyldithiocarbamate, nickel dihexadecyldithiocarbamate, nickel diheptadecyldithiocarbamate, nickel dioctadecyldithiocarbamate, nickel dinonadecyldithiocarbamate, nickel diicosyldithiocarbamate, molybdenum oxysulfide didecyldithiocarbamate, molybdenum oxysulfide diundecyldithiocarbamate, molybdenum oxysulfide didodecyldithiocarbamate, molybdenum oxysulfide ditridecyldithiocarbamate, molybdenum oxysulfide ditetradecyldithiocarbamate, molybdenum oxysulfide dipentadecyldithiocarbamate, molybdenum oxysulfide dihexadecyldithiocarbamate, molybdenum oxysulfide diheptadecyldithiocarbamate, molybdenum oxysulfide dioctadecyldithiocarbamate, molybdenum oxysulfide dinonadecyldithiocarbamate, molybdenum oxysulfide diicosyldithiocarbamate, lead didecyldithiocarbamate, lead diundecyldithiocarbamate, lead didodecyldithiocarbamate, lead ditridecyldithiocarbamate, lead ditetradecyldithiocarbamate, lead dipentadecyldithiocarbamate, lead dihexadecyldithiocarbamate, lead diheptadecyldithiocarbamate, lead dioctadecyldithiocarbamate, lead dinonadecyldithiocarbamate, lead diicosyldithiocarbamate, antimony didecyldithiocarbamate, antimony diundecyldithiocarbamate, antimony didodecyldithiocarbamate, antimony ditridecyldithiocarbamate, antimony ditetradecyldithiocarbamate, antimony dipentadecyldithiocarbamate, antimony dihexadecyldithiocarbamate, antimony diheptadecyldithiocarbamate, antimony dioctadecyldithiocarbamate, antimony dinonadecyldithiocarbamate and antimony diicosyldithiocarbamate.

[0023] As the metal dithiocarbamate represented by the formula (1) for use in the present invention, those which are commercially available as a diluted form in a mineral oil or kerosene may be employed.

[0024] The lower limit of the content of the metal dithiocarbamate in the present grease composition (net content; i. e., if the metal dithiocarbamate is in diluted form, the effective amount of the metal dithiocarbamate therein with respect to the total amount of the composition) may usually be 0.05 wt%, and preferably 0.25 wt%. The upper limit thereof may usually be 10 wt%, and preferably 5 wt%. If the content is 0.05 wt% or more, sufficient anti-flaking effect may be obtained and shortening of flaking life may be prevented. If the content is more than 10 wt%, the adding amount may fail to measure up to the expected anti-flaking effect, thus not being preferable.

[0025] The lubricant base oil for use in the present invention may include mineral oil and/or synthetic oil.

[0026] The mineral oil may be those obtained by conventional method for producing lubricating oils in the field of petroleum refining. For example, the mineral oil may be prepared by distilling crude oil under atmospheric or reduced pressure to obtain lubricant fractions, and purifying the fractions by one or more treatments including solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, contact dewaxing, hydrofining, washing with sulfuric acid, and clay purification.

[0027] The synthetic oil may be a poly- α -olefin such as polybutene, a 1-octene oligomer, or a 1-decene oligomer, or a hydride of such poly- α -olefin; a diester such as ditiodecyl glutarate, di-2-ethylhexyl adipate, diisodecyl adipate, ditiodecyl adipate, or di-3-ethylhexyl sebacate; a polyol ester such as trimethylolpropane caprylate, trimethylolpropane pelargonate, pentaerythritol-2-ethyl hexanoate, or pentaerythritol pelargonate; alkyl naphthalene; alkylbenzene, polyoxyalkylene glycol; polyphenyl ether; dialkyl diphenyl ether; silicone oil or mixtures thereof.

[0028] The kinematic viscosity of the base oil may usually be 10 to 500 mm²/s, and preferably 20 to 300 mm²/s at 40°C, but not limited thereto.

[0029] In addition to the aforementioned metal dithiocarbamate and lubricant base oil, the grease composition of the present invention may usually contain thickener and other optional additives.

[0030] Examples of the thickener may include soap thickeners such as a metal soap and a complex metal soap; bentone, silica gel, a urea compound, a urea-urethane compound, a urethane compound and mixtures thereof.

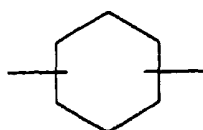
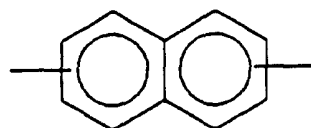
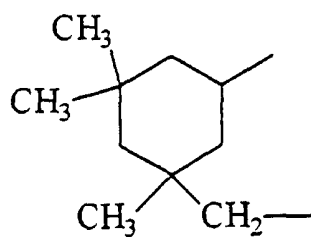
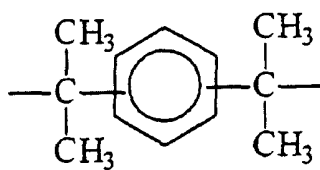
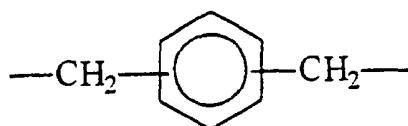
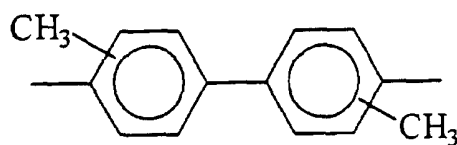
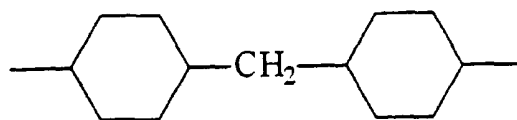
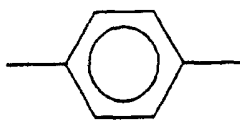
[0031] Examples of the soap thickener may include a sodium soap, a calcium soap, an aluminum soap, and a lithium soap.

[0032] Examples of the urea compound, urea-urethane compound and urethane compound may include a diurea compound, a triurea compound, a tetraurea compound, a polyurea compound (except for the diurea compound, triurea compound and tetraurea compound), a urea-urethane compound, a diurethane compound and mixtures thereof. Among these, particularly preferable are diurea compound, urea-urethane compound, diurethane compound and mixtures thereof. More preferable are the compound represented by the following formula (3):

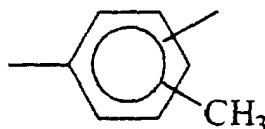
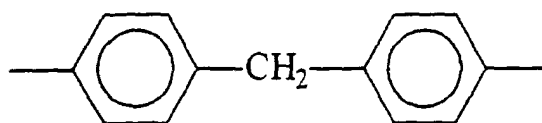


[0033] In formula (3), R⁵ stands for a divalent hydrocarbon group. A and B may be the same or different, and each stands for -NHR⁶, -NR⁷R⁸ OR -OR⁹. Herein R⁶ to R⁹ may be the same or different and each stands for a hydrocarbon residue having 6 to 20 carbon atoms.

[0034] R⁵ in formula (3) is preferably a divalent hydrocarbon group having 6 to 20, particularly 6 to 15 carbon atoms. Examples of the divalent hydrocarbon group may include a straight or branched alkylene group, a straight or branched alkenylene group, a cycloalkylene group, and an aromatic group. Specific examples of R⁵ may include ethylene group, 2,2-dimethyl-4-methylhexylene group and the group represented by the following formulae:



[0035] Among these, the following groups are particularly preferable:



[0036] Examples of the hydrocarbon residue having 6 to 20 carbon atoms as R^6 to R^9 may include a straight or branched alkyl group, a straight or branched alkenyl group, a cycloalkyl group, an alkylcycloalkyl group, an aryl group, an alkylaryl group, or an arylalkyl group. More Specific examples thereof may include straight or branched alkyl groups such as a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group, a tridecyl group, a tetradecyl group, a pentadecyl group, a hexadecyl group, a heptadecyl group, an octadecyl group, a nonadecyl group, or an eicosyl group; a straight or branched alkenyl group such as a hexenyl group, a heptenyl group, an octenyl group, a nonenyl group, a decenyl group, an undecenyl group, a dodecenyl group, a tridecenyl group, a tetradecenyl group, a pentadecenyl group, a hexadecenyl group, a heptadecenyl group, an octadecenyl group, a nonadecenyl group and an eicosenyl group; a cyclohexyl group; alkylcycloalkyl groups such as a methylcyclohexyl group, a dimethylcyclohexyl group, an ethylcyclohexyl group, a diethylcyclohexyl group, a propylcyclohexyl group, an isopropylcyclohexyl group, a 1-methyl-3-propylcyclohexyl group, a butylcyclohexyl group, an amylcyclohexyl group, an amylmethylcyclohexyl group, a hexylcyclohexyl group, a heptylcyclohexyl group, an octylcyclohexyl group, a nonylcyclohexyl group, a decylcyclohexyl group, an undecylcyclohexyl group, a dodecylcyclohexyl group, a tridecylcyclohexyl group, or a tetradecylcyclohexyl group; aryl groups such as a phenyl group or a naphthyl group; alkylaryl groups such as a toluyl group, an ethylphenyl group, a xylyl group, a propylphenyl group, a cumenyl group, a methylnaphthyl group, an ethylnaphthyl group, a dimethylnaphthyl group, or a propylnaphthyl group; or arylalkyl groups such as a benzyl group, a methylbenzyl group, or an ethylbenzyl group. Among these, a cyclohexyl group, an octadecyl group, and a toluyl group are particularly preferred.

[0037] The diurea compound, urea-urethane compound or diurethane compound may be produced by reacting a diisocyanate represented by the formula $OCN-R^5-NCO$, with any of compounds represented by the formulae R^6NH_2 , R^7R^8NH , R^9OH or mixtures thereof, in a base oil at 10 to 200°C. Herein R^5 to R^9 are the same as R^5 to R^9 in the formula (3).

[0038] The content of the thickener in the present composition may usually be 2 wt% or more and preferably 3 wt% or more, and usually 30 wt% or less and preferably 25 wt% or less.

[0039] The grease composition of the present invention may optionally contain a solid lubricant, an extreme pressure agent, an antioxidant, a metal deactivator, an oiliness agent, a rust inhibitor, and a viscosity index improver.

[0040] Examples of the solid lubricant may include a graphite, fluorinated graphite, polytetrafluoroethylene, molybdenum disulfide, antimony sulfide, alkaline (earth) metal borate, magnesium oxide and zinc oxide.

[0041] Examples of the extreme pressure agent may include organic zinc compounds such as zinc dialkyldithiophosphate and zinc diaryldithiophosphate; organic molybdenum compounds such as molybdenum dialkyldithiophosphate and molybdenum diaryldithiophosphate; sulfur compounds such as polysulfide, and sulfurized oil and fat; and phosphates and phosphites.

[0042] Examples of the antioxidants may include phenol compounds such as 2,6-di-*t*-butylphenol and 2,6-di-*t*-butyl-*p*-cresol; amine compounds such as dialkyldiphenylamine, phenyl- α -naphthylamine, *p*-alkylphenyl- α -naphthylamine; sulfur compounds; and phenothiazine compounds.

[0043] Examples of the metal deactivator may include benzotriazole, benzothiazole and sodium nitrate.

[0044] Examples of the oiliness agent may include amines such as laurylamine, myristylamine, palmitylamine, stearylamine and oleylamine; higher alcohols such as lauryl alcohol, myristyl alcohol, palmityl alcohol, stearyl alcohol and oleyl alcohol; higher fatty acids such as lauric acid, myristic acid, palmitic acid, stearic acid and oleic acid; higher fatty acid esters such as methyl laurate, methyl myristate, methyl palmitate, methyl stearate and methyl oleate; amides such as laurylamide, myristylamide, palmitylamide, stearylamine and oleylamide; and oil and fats.

[0045] Examples of the rust inhibitor may include neutral or over-based metal sulfonates of petrol type or synthetic

oil type such as a neutral or over-based calcium sulfonate, a neutral or over-based barium sulfonate, and a neutral or over-based zinc sulfonate; metal soaps; polyvalent alcohol partial esters such as sorbitan fatty acid ester; amines; phosphoric acid; and phosphates.

[0046] Examples of the viscosity index improver may include a polymethacrylate, a polyisobutylene and a polystyrene.

[0047] There is no limitation to production method of the present grease composition. For example, the objective grease composition may usually be produced by adding the metal dithiocarbamate to the base oil, stirring the mixture and optionally passing the mixture through a roll mill.

[0048] The present grease composition may be used for lubricating a rolling bearing, such as electrical components and accessory devices for automotive vehicles, e.g., alternators, electromagnetic clutches for car air conditioners, idle pulleys and electric fan motors. The lubrication may be achieved by filling the rolling bearing with the present grease composition.

[0049] Since the present grease composition contains the specific metal dithiocarbamate, it can exhibit an excellent anti-flaking property in rolling bearings such as electrical components and accessory devices for automotive vehicles, e.g., alternators, electromagnetic clutches for car air conditioners, idle pulleys and electric fan motors, resulting in extension of the life of the rolling bearings.

[0050] The present invention will be explained in further detail with reference to the Examples and Comparative Examples. However, the present invention is not limited thereto.

EXAMPLE 1 AND 2 AND COMPARATIVE EXAMPLES 1 TO 3

[0051] Diphenylmethane-4,4'-diisocyanate was dissolved under heat in base oil shown in Table 1. To this mixture were added the same base oil containing amines shown in Table 1 that had been dissolved therein under heat. The gel substance was obtained, to which the metal dithiocarbamate and other additives were further added. The mixture was stirred and then passed through a roll mill, to obtain grease compositions of Examples 1 and 2 and Comparative Examples 1 to 3.

[0052] These grease compositions of Examples 1 and 2 and Comparative Examples 1 to 3 were then subjected to the engine on-bench test specified as follows. The results are shown in Table 1.

<Engine On-bench Test>

[0053] A single-line deep groove ball bearing fitted with a contact rubber seal having an inner diameter of 12 mm, an outer diameter of 37 mm and a width of 12 mm was filled with 2.0 g of the grease and attached to an engine. The rotation of the engine was quickly accelerated and decelerated from 1000 rpm to 6000 rpm and from 6000 rpm to 1000 rpm (rotation of outer ring of the bearing was from 1900 rpm to 11300 rpm, and from 11300 rpm to 1900 rpm), to continuously rotate the bearing at bearing load of 190 kgf. The running life time was measured until occurrence of flaking in a bearing inner ring race way and fluctuation.

Table 1

		Example		Comparative Example		
		1	2	1	2	3
Base oil (wt%)	Dialkyldiphenyl ether ¹⁾	80.0	-	82.0	80.0	80.0
	Pentaerythritol ester ²⁾	-	77.0	-	-	-
	Poly- α -olefin ³⁾	-	-	-	-	-
Thickener (wt%)		13.0	17.0	13.0	13.0	13.0
Thickener (molar ratio)	Diphenylmethane-4,4'-diisocyanate	5 5	1 1	5 5	5 5	5 5
	Cyclohexylamine	7	1	7	7	7
	Octadecylamine	3	-	3	3	3
	p-toluidine	-	1	-	-	-

1) Kinematic viscosity 100mm²/s(40°C)

2) Kinematic viscosity 50mm²/s(40°C)

3) Kinematic viscosity 40mm²/s(40°C)

Table 1 (continued)

	Example		Comparative Example		
	1	2	1	2	3
Zinc ditridecyldithiocarbamate (wt%)	2.0	-	-	-	-
Molybdenum dioctadecyldithiocarbamate (wt%)	-	1.0	-	-	-
Zinc dipentyldithiocarbamate (wt%)	-	-	-	2.0	-
Molybdenum dioctyldithiocarbamate (wt%)	-	-	-	-	2.0
Antioxidant 4) (wt%)	3.0	3.0	3.0	3.0	3.0
Rust-preventive agent 5) (wt%)	2.0	2.0	2.0	2.0	2.0
Mixture consistency	237	272	240	243	238
Engine on-bench test result (h)	1500 or more	1500 or more	400	750	1000

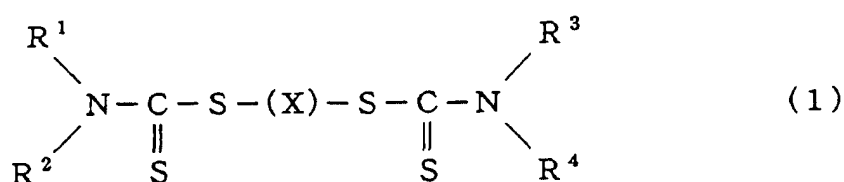
4) Amine type antioxidant

5) Barium sulfonate

[0054] As obvious from the engine on-bench test results in Table 1, the present grease composition can give a longer anti-flaking life than the grease composition of Comparative Example 1 that does not contain the metal dithiocarbamate and than the grease compositions of Comparative Examples 2 and 3 that contains metal dithiocarbamates which have hydrocarbon groups having less than 10 carbon atoms.

Claims

1. A grease composition comprising a lubricant base oil and a metal dithiocarbamate represented by the formula (1):



wherein R^1 to R^4 are the same or different and each stands for a hydrocarbon group having 10 to 20 carbon atoms, and X stands for a metal or a metal-containing group.

2. The grease composition of claim 1 wherein R^1 to R^4 are the same or different and each stands for a hydrocarbon group having 12 to 20 carbon atoms.
3. The grease composition of claim 1 wherein R^1 to R^4 are the same or different and each stands for a group selected from the group consisting of a straight or branched decyl group, undecyl group, dodecyl group, tridecyl group, tetradecyl group, pentadecyl group, hexadecyl group, heptadecyl group, octadecyl group, nonadecyl group and icosyl group; a straight or branched decenyl group, undecenyl group, dodecenyl group, tridecenyl group, tetradecenyl group, pentadecenyl group, hexadecenyl group, heptadecenyl group, octadecenyl group, nonadecenyl group, and icosenyl group; a cyclopentyl group with one or more alkyl substituents each having 1 to 15 carbon atoms; a cyclohexyl group with one or more alkyl substituents each having 1 to 14 carbon atoms; a cycloheptyl group with one or more alkyl substituents each having 1 to 13 carbon atoms; naphthyl group; a phenyl group with one or more alkyl substituents each having 1 to 14 carbon atoms; and an alkyl group having a phenyl substituent and/or an alkylaryl substituent.