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(54) **Use of a noise-reducing grease composition**

(57) The invention provides the use of a grease composition comprising a base oil of mineral and/or synthetic origin, a thickener, a zinc dithiophosphate and an ashless dithiocarbamate as a noise reducing grease composition.

EP 1 188 814 A1

DescriptionField of the invention

5 **[0001]** The present invention relates to the use of a grease composition to reduce noise, particularly in bearing applications.

Background of the invention

10 **[0002]** The primary purpose of lubrication is separation of solid surfaces moving relative to one another to minimise the effects of friction and wear. Grease compositions consist primarily of a fluid lubricant, such as an oil, and a thickener and are widely used to lubricate mechanical components such as joints and bearings. For example, greases are employed in applications where high pressures exist, where oil drip is undesirable or where the motion of the contacting surfaces is discontinuous so that it is difficult to maintain a separating film in a joint or bearing.

15 **[0003]** Bearings are supports provided to locate a revolving or reciprocating shaft and are widely used in industrial, automotive and household applications. When in use bearings may be subjected to extreme rotational forces which can lead to noise or vibrations. Such noise is detrimental to the condition of a bearing and can lead equipment comprising the bearing to suffer from shake or judder and to make acoustic beating noises. Such noise associated problems can prevent the use of bearings in low vibration applications.

20 **[0004]** It is known that the lubrication of mechanical parts with grease compositions may reduce friction and wear. For example, WO 96/02615 relates to a grease composition for constant velocity joints which comprises (a) a base oil; (b) a lithium-containing thickener selected from the group consisting of lithium soap and lithium complex soap; (c) an organic molybdenum compound selected from the group consisting of molybdenum dithiophosphates and molybdenum dithiocarbamates; and (d) a zinc dithiophosphate. At page 7, line 3 of WO 96/02615 it is stated that the organic molybdenum compound as the component (c) undergoes self-decomposition on the surface to be lubricated to thus form a film of a high molecular weight compound having viscoelasticity, which covers the metallic parts on the portions to be lubricated, or to form, through the self-decomposition molybdenum disulfide which serves to reduce the frictional force acting on the parts or any wear thereof.

25 **[0005]** However, there is little information available on grease compositions specifically designed to reduce noise or vibration. Further, in use bearings become extremely hot, causing the viscosity of a grease composition to fall and the noise or vibration to increase.

30 **[0006]** US-A-4648985 describes two- and three-component extreme pressure lubricant additive systems. The two-component system comprises a metal organophosphate and a dithiocarbamate of formulae described therein.

35 **[0007]** Similarly, the three-component system comprises a dithiocarbamate, a metal compound and a phosphate compound of formulae described therein.

[0008] Example 11 of US-A-4648985 relates to a lubricating grease comprising mineral oil, inorganic clay thickener, 4.0% copper octoate, ("12.0% Copper Cem-All", Mooney Chemicals, Inc., Cleveland, Ohio), 4.0% methylene bis (dibutyl dithiocarbamate) (Vanlube 7723), and 9.5% zinc diarene phosphorodithioate (OLOA 260).

40 **[0009]** However, there is no teaching in US-A-4648985 directed towards reducing noise or vibration in joints or bearings employing grease compositions.

[0010] US-A-5922654 relates to lubricant compositions which are said to be suitable for application to parts required to have load bearing properties and extreme pressure properties or parts susceptible to wear, for example to bearings and constant velocity joints.

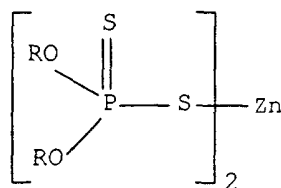
45 **[0011]** Example 2 in Table 3 of US-A-5922654 describes a urea grease comprising piperidine pentamethylenedithiocarbamate (2%), tellurium diethyldithiocarbamate (1.5%) and zinc dialkyldithiophosphate (1%).

[0012] Example 3 in Table 3 of US-A-5922654 concerns a urea grease comprising piperidine pentamethylene dithiocarbamate (1.5%), antimony dialkyldithiocarbamate (1.5%), molybdenum dialkyldithiocarbamate (0.5%) and zinc dialkyl dithiophosphate (0.5%).

50 **[0013]** US-A-5922654 contains no teaching directed towards grease compositions which are designed to reduce noise or vibration.

[0014] GB-A-2255103 describes a grease composition for use in constant velocity joints which is said to reduce wear, control vibrations and improve durability.

55 **[0015]** The grease compositions described in GB-A-2255103 comprise a lubricating oil, urea thickener, (A) 1 - 5% wt. of molybdenum sulfide dialkyldithiocarbamate, (B) 0.2 - 1% wt of molybdenum disulfide, (C) 0.5 - 3% wt. of an extreme pressure additive of zinc dithiophosphate represented by the following general formula:



(wherein R is an alkyl or an aryl group) and (D) 0.5 - 5% wt. of an oiliness agent composed of at least one of vegetable oils and fats as an essential component, provided that a weight ratio of component (B) to component (A) is 0.04-0.5.

[0016] Although it is said in GB-A-2255103 that the compositions described therein control vibrations, no experimental measurements have been given in this respect and the experiments are directed towards friction and wear testing.

Statement of the invention

[0017] It has now surprisingly been found possible to prepare a zinc dithiophosphate-containing grease composition that has advantageous low noise properties.

[0018] The present invention provides the use of a grease composition comprising a base oil of mineral and/or synthetic origin, a thickener, a zinc dithiophosphate, and an ashless dithiocarbamate as a noise-reducing grease composition.

Detailed description of the invention

[0019] The grease composition used in the present invention preferably comprises at least 75% by weight of a base oil based on total composition.

[0020] Base oils for use in the greases employed in the present invention may typically be the same as base oils which would normally be selected for oil lubrication. The base oil may be of mineral and/or synthetic origin. Base oils of mineral origin may be mineral oils, for example those produced by solvent refining or hydroprocessing. Base oils of synthetic origin may typically be mixtures of C₁₀-C₅₀ hydrocarbon polymers, for example liquid polymers of alpha-olefins, ester type synthetic oils or ether type synthetic oils. They may also be a mixture of these oils. Preferably, the base oil is of mineral origin.

[0021] Examples of mineral oils that may conveniently be used include those sold by member companies of the Royal Dutch/Shell Group under the designations "HVI", "MVIN", or "HMVIP". Polyalphaolefins and base oils of the type manufactured by the hydroisomerisation of wax, such as those sold by member companies of the Royal Dutch/Shell Group under the designation "XHVI" (trade mark), may also be used.

[0022] The grease compositions used in the present invention preferably comprise from 2 to 20%, more preferably 5 to 20%, and most preferably 5 to 12% by weight of a thickener based on total composition.

[0023] Thickeners which may be used in the grease compositions employed in the present invention include simple thickeners, for example fatty acid soaps of lithium, calcium, sodium, aluminium and barium; complex thickeners i.e. simple thickeners additionally comprising a complexing agent; clays; and urea type compounds.

[0024] When a urea-type compound is used as a thickener it may be a mono-, di-, tri- and tetra urea compound or a compound containing a urea e.g. a urea-urethane and/or a urea-imide compound.

[0025] Preferred thickeners according to the present invention are soap thickeners more preferably lithium soap thickeners. By lithium soap thickeners it is meant both simple and complex lithium soap thickeners.

[0026] Simple lithium soaps are derived from C₁₀₋₂₄, preferably C₁₅₋₁₈, saturated or unsaturated fatty acids or derivatives thereof. One preferred fatty acid derivative is hydrogenated castor oil, which is the glyceride of 12-hydroxystearic acid. 12-Hydroxystearic acid is a particularly preferred fatty acid.

[0027] Complex lithium soap thickeners are thickeners wherein a complexing agent has been incorporated into a simple lithium soap. Commonly used complexing agents include a low to medium molecular weight acid or dibasic acid or one of its salts, such as benzoic acid or boric acid or a lithium borate.

[0028] Most preferably the thickener employed in the grease compositions used in the present invention is a simple lithium soap thickener.

[0029] The grease composition used in the present invention preferably comprises from 0.1 to 5%; more preferably 0.1 to 2% and most preferably 0.2 to 1% by weight of a zinc dithiophosphate, based on total composition.

[0030] The grease composition may comprise a single zinc dithiophosphate or a combination of two or more zinc dithiophosphates, the or each zinc dithiophosphate being selected from zinc dialkyl-, diaryl- or alkylaryl-dithiophosphates. A preferred zinc dithiophosphate according to the present invention is a zinc dialkyl dithiophosphate. The alkyl moieties of a zinc dialkyl dithiophosphate employed in the present invention may be straight chain or branched chain

and preferably contain from 1 to 20 carbons, more preferably contain from 8 to 20 carbon atoms and most preferably contain from 8 to 12 carbon atoms. Examples of preferred zinc dithiophosphates are 2-ethylhexyl zinc dithiophosphate obtainable from Rhein Chemie Rheinau GmbH. under the designation "Additin RC 3180" and a long chain zinc dithiophosphate obtainable from Rhein Chemie Rheinau GmbH. under the designation "Additin RC 3212", ("Additin" is a trade mark of Rhein Chemie Rheinau GmbH.).

[0031] The grease compositions used in the present invention preferably comprise from 0.1 to 5%, more preferably from 0.1 to 2% and most preferably from 0.2 to 1% by weight of an ashless dithiocarbamate based on total composition.

[0032] The grease composition may comprise a single ashless dithiocarbamate or a combination of two or more ashless dithiocarbamates, the or each ashless dithiocarbamate being selected from ashless dialkyl-, diaryl- or alkylaryl-dithiocarbamates. A preferred ashless dithiocarbamate according to the present invention is an ashless dialkyldithiocarbamate more preferably a methylene-bis-dialkyldithiocarbamate. The alkyl moieties of an ashless dialkyl dithiocarbamate employed in the present invention may be straight or branched chain and preferably contain from 1 to 12 carbon atoms, most preferably 2 to 6 carbon atoms. An example of a preferred ashless dithiocarbamate is methylene-bis-dibutyl-dithiocarbamate obtainable from Rhein Chemie Rheinau GmbH under the designation "Additin RC 6340".

[0033] The grease composition used in the present invention may further comprise conventional grease additives, in amounts normally used in the art, to impart certain desirable characteristics to the grease such as oxidation stability, tackiness, extreme pressure properties, corrosion inhibition and to reduce friction and wear.

[0034] Suitable additives include one or more extreme pressure/antiwear agents, for example, molybdenum dithiophosphate, borates, substituted thiadiazoles, polymeric nitrogen/phosphorus compounds made, for example, by reacting a dialkoxo amine with a substituted organic phosphate, amine phosphates, sulphurised sperm oils of natural or synthetic origin, sulphurised lard, sulphurised esters, sulphurised fatty acid esters, and similar sulphurised materials, organophosphates for example according to the formula $(OR)_3P=O$ where R is an alkyl, aryl or aralkyl group, and triphenyl phosphorothionate; one or more overbased metal-containing detergents, such as calcium or magnesium alkyl salicylates, alkylarylsulphonates or alkylsulphonates; one or more ashless dispersant additives, such as reaction products of polyisobutenyl succinic anhydride and an amine or ester; one or more antioxidants, such as hindered phenols or amines, for example phenyl alpha naphthylamine; one or more antirust additives such as zinc naphthenate; one or more friction-modifying additives; one or more viscosity-index improving agents; one or more pour point depressing additives; and one or more tackiness agents. Solid materials such as graphite, finely divided molybdenum disulphide, talc, metal powders, and various polymers such as polyethylene wax may also be added to impart special properties.

[0035] Where the term aryl is used above, the aryl group is preferably a phenyl group; where the term aralkyl is used, the aralkyl group is preferably a benzyl group.

[0036] Grease compositions used in the present invention may be prepared either by pre-mixing the zinc dithiophosphate, ashless dithiocarbamate and any further additive to be incorporated in base oil and adding the mixture to a base grease comprising base oil and thickener, or by incorporating each additive into the base grease individually. This may be achieved via hot or cold mixing followed by homogenisation to ensure uniform dispersion of additive components.

[0037] Grease compositions used in the present invention display exceptionally low noise and have been found to be very effective in bearing applications. Accordingly, the present invention further provides for the use of a grease composition according to the invention to reduce noise in bearing applications.

[0038] The invention will be further understood from the following illustrative examples. In the examples the various additives are designated as follows:-

(a) ZnDTP (1) is a 2-ethylhexyl zinc dithiophosphate obtained under the designation "Additin RC 3180" from Rhein Chemie Rheinau GmbH.

(b) ZnDTP (2) is a long chain zinc dialkyldithiophosphate obtained under the designation "Additin RC 3212" from Rhein Chemie Rheinau GmbH.

(c) Ashless DTC is a methylene-bis-dibutyldithiocarbamate obtained under the designation "Additin RC 6340" from Rhein Chemie Rheinau GmbH.

(d) MoDTC is a molybdenum oxysulfide dithiocarbamate in the form of a 50/50 w/w solution in mineral oil obtained under the designation "Molyvan 822" from R.T. Vanderbilt Company Inc.

Base Grease

[0039] A simple lithium soap base grease was prepared by adding a slurry of 1.12 % w LiOH.H₂O and water in the proportions of 1 part LiOH.H₂O to 5 parts water to 9.15% w hydrogenated castor oil fatty acid in cold paraffinic base oil having a viscosity of 75mm²/s (obtainable from member companies of the Royal Dutch/Shell Group under the designation "HMVIP 105") and heating the mix in a sealed autoclave to 150 °C. Steam was vented off and heating continued to 220 °C before the reaction mass was cooled at a rate of 1 to 3 °C per minute and the product homogenised

to yield a base grease comprising approximately 8% wt. Li 12-hydroxystearate and 92% wt. paraffinic base oil.

[0040] Example greases according to the invention and Comparative greases were obtained by incorporating additives into the base grease.

5 Noise Testing Procedure

[0041] Grease samples were subjected to noise testing according to the following procedure.

[0042] New bearings of type 608 as described in DIN 623 were cleaned thoroughly in analysis quality n-hexane and then dried in a drying cabinet. Immediately after cooling the bearings were filled with grease. After removal of grease from outside the bearing cage each bearing contained approximately 0.31 to 0.35 g of grease.

[0043] Noise measurements were recorded on a bearing pedestal with a sleeve-bearing-mounted precision shaft. The bearing to be tested was placed on the shaft's arbour; and the outer bearing ring held in place and axially loaded, the degree of axial loading being adjustable. The shaft was then turned by an electric motor acting through flexible drive belts until a preselected speed of rotation is reached. As the bearing rotates it oscillates and these vibrations are registered radially by an acceleration sensor with a polished probe tip, the acceleration sensor being flexibly secured to a sliding carriage whose inherent weight presses the sensor onto the bearing. The acceleration signals were preamplified in a 2626 charge amplifier as supplied by Brüel & Kjaer GmbH.; prefiltered and then processed in an IBM-compatible 486/50 PC fitted with a A/D converter with integral Microstar DAP 2400/e4 signal processor ("Microstar" is a trade name). From the processed acceleration signals an average line for vibrations occurring in a frequency range of 50-20000 Hz was obtained. From this data the amount of noise produced in each test may be compared with that of a calibration grease or a earlier measurement; the difference in noise being expressed as a difference in decibel (dB) level.

[0044] In the following examples a shaft rotation speed of 1800 rpm and a loading of 14 Newtons was applied. Noise measurements were recorded over a period of 7 seconds following a 3 second warming-up period.

25 Examples 1-6 and Comparative Example A

[0045] The grease compositions of Examples 1-6 were prepared by mixing a zinc dithiophosphate and an ashless dithiocarbamate in a paraffinic base oil and then adding the resultant mixture to the simple lithium soap base grease. The components of the prepared greases are shown in Table 1.

[0046] The grease composition of Comparative Example A was prepared in a similar way to those of Examples 1-6, employing molybdenum dithiocarbamate instead of an ashless dithiocarbamate.

[0047] The greases were subjected to noise testing according to the above procedure and the results compared with that of a calibration grease. The performance of the calibration grease and each of grease compositions of Examples 1-6 and Comparative Example A was tested in 3-5 bearings at a temperature of 25 °C with the mean measurement being used. The difference in noise between grease compositions of Examples 1-6 and the calibration grease is shown in Table 1, a negative change in decibel (dB) level indicating a reduction in noise level when compared with the calibration grease. Similarly, the difference in noise between the grease composition of Comparative Example A and the calibration grease is also shown in Table 1. The calibration grease was a commercially available lubricating grease known to have good noise performance obtainable from member companies of the Royal Dutch/Shell Group under the trade name "Alvania RS" ("Alvania" is a trade mark).

[0048] As can be seen from Table 1, it was surprisingly found that the grease compositions of Examples 1-6 display noise readings lower than that of the calibration grease.

[0049] It can further be seen from Table 1, that the grease composition of Example 3 displays superior noise reduction over the analogous molybdenum dithiocarbamate grease of Comparative Example A.

Table 1

	Example						Comparative Example
	1	2	3	4	5	6	
Lithium soap base grease %w	93.75	94	93.75	93.75	94	93.75	A
Extra base oil HMVIP 105 %w	5	5	5	5	5	5	5
ZnDTP (1) %w	0.25	0.5	1	-	-	-	1
ZnDTP (2) %w	-	-	-	0.25	0.5	1	-
Ashless DTC %w	1	0.5	0.25	1	0.5	0.25	-
Mo DTC %w	-	-	-	-	-	-	0.25
Noise Test (dB)	-5.5	-6	-6	-6	-4.5	-6.5	-4.5

Examples 7-10 and Comparative Examples B-G

[0050] Grease compositions 7-10 and Comparative Examples B-G were prepared by incorporating additives directly into the simple lithium base soap grease. The components of the prepared greases are shown in Table 2.

[0051] Grease compositions 7 - 10 and Comparative Examples B-G were subjected to a high temperature performance test wherein a bearing containing a test grease is subjected to noise testing at a temperature of 25 °C to give a calibration reading for that grease, the bearing is then heated to a temperature of 100 °C and operated under the test conditions for 3 hours after which time a further noise measurement is made of the hot bearing and the increase in decibel (dB) level from the calibration measurement recorded. The bearing is then allowed to cool to 25°C and a further noise measurement taken of the cooled bearing and the difference between the calibration measurement again being recorded. Results are shown in Table 2 together with the result obtained for this procedure using commercially available grease "Alvania RS".

[0052] From Table 2 it can be seen that the combination of a zinc dithiophosphate and an ashless dithiocarbamate in a grease composition reduces the increase in noise occurring when the bearings are heated to operational temperature, when compared with a grease comprising either a zinc dithiophosphate or an ashless dithiocarbamate alone (Comparative Examples C+D) or the commercially available low noise grease "Alvania RS". Further, it can be seen that grease compositions according to the invention show performance superior to greases comprising a molybdenum dithiocarbamate in combination with an ashless dithiocarbamate (Comparative Example B) and are at least as effective as compositions comprising a molybdenum dithiocarbamate and a zinc dithiophosphate (Comparative Example E).

Table 2

	Cali. grease	Example						Comparative Example					
		7	8	9	10	B	C	D	E	F	G		
"Alvania RS" %w	100	-	-	-	-	-	-	-	-	-	-		
Lithium soap base grease %w	-	98	98	98.75	98.75	98	98	98	98	98.75	98.75		
Zn DTP (1) %w	-	1	-	-	-	-	-	2	-	-	-		
Zn DTP (2) %w	-	-	1	0.25	1	-	-	-	1	0.25	1		
Ashless DTC %w	-	1	1	1	0.25	1	2	-	-	-	-		
Mo DTC %w	-	-	-	-	-	1	-	-	1	1	0.25		
Noise Test hot bearings (dB)	10	5.5	4.5	5.5	7.5	12.5	9	7	7	7.5	8		
Noise Test cooled bearings (dB)	6	2.5	1.5	2	2	6.5	2	1.5	2	2.5	3.5		

Claims

1. Use of a grease composition comprising a base oil of mineral and/or synthetic origin, a thickener, a zinc dithio-phosphate, and an ashless dithiocarbamate as a noise-reducing grease composition.
2. Use according to claim 1, wherein said grease composition comprises at least 75% by weight of a base oil, from 5 to 20% by weight of a thickener, from 0.1 to 5% by weight of a zinc dithiophosphate and from 0.1 to 5% by weight of an ashless dithiocarbamate, all based on total amount of composition.
3. Use according to claim 1 or 2, wherein the thickener is a lithium soap thickener.
4. Use according to claim 3, wherein the thickener is a simple lithium soap thickener.
5. Use according to any one of claims 1 to 4, wherein the zinc dithiophosphate is a zinc dialkyldithiophosphate having alkyl moieties containing from 8 to 12 carbon atoms.
6. Use according to any one of claims 1 to 5, wherein the ashless dithiocarbamate is an ashless dialkyldithiocarbamate.
7. Use according to any one of claims 1 to 6, wherein the ashless dithiocarbamate is a methylene-bis-dialkyldithiocarbamate.
8. Use according to Claim 6 or 7, wherein the alkyl moieties of the ashless dithiocarbamate contain from 1 to 12 carbon atoms.
9. Use according to any one of claims 1 to 8, to reduce noise in bearings applications.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 01 20 3189

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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A	US 5 133 888 A (WAYNICK JOHN A) 28 July 1992 (1992-07-28) * claim 1 *		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
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MUNICH	4 December 2001	Kazemi, P	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
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**ANNEX TO THE EUROPEAN SEARCH REPORT
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EP 01 20 3189

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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