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Annex 1 (Patent Application)

Grease compositions for constant velocity joints and method for the preparation

The present invention relates to a lubricating grease composition for constant velocity joints, in particular for constant velocity joints in modern vehicles, to a method of making the grease and to constant velocity joints filled with the grease.

The requirements for lubricants in power transmission systems of modern vehicles have changed as the demand for vehicles with front wheel drive and four wheel drive (4WD) has explosively grown in the last few years. In such vehicles constant velocity joints are used. Constant velocity joints are a special type of universal couplings which can transmit drive from the final reduction gear to a road wheel axle at a constant rotational velocity.

Lubricants are used to reduce friction and wear between moving surfaces. They can be oily, greasy or solid depending on their applications. Lubricating oils are used in engines, hydraulic systems and gears where it is essential that the viscosity of the oil is low enough to remain fluid at all operating temperatures.

Greases are thickened lubricating oils and are kept in place by the high viscosity that the thickeners help to maintain. They are used in bearings, joints and, in general, in applications where it is essential that the lubricants remain attached to the object to be lubricated.

A problem with constant velocity joints, is that whilst they should transfer the power from the engine to the wheels, they have to perform complicated movements for a long time without causing any noise or vibrations.

In order to withstand large variations in temperature and to protect the metal or oth surfaces from wearing, anti-wear additives are required which allow the parts to opera for long periods under severe conditions without wearing.

The grease composition according to the present invention contains a major amount of lubricating base oil. The lubricating base oil is typically a hydrocarbon mineral oil but any other suitable synthetic or natural lubricant base oil can be used. Examples of synthetic base oils are polyalphaolefins, alkyl benzenes and polyolester oils. Natural oils are represented by vegetable and animal oils (also known as triglycerides) but, as they are susceptible to oxidation, they are less preferable.

The thickener used in the present invention is conventional and can be a lithium soap based thickener, a complex soap based thickener, or a diurea based thickener. Lithium soap based thickeners are derived from lithium salts of hydroxycarboxylic acids, like a lithium salt of 12-hydroxystearic acid. Complex soap thickeners are derived from alkali metal or alkaline earth metal salts, suitably lithium or calcium salts of a mixture of hydroxycarboxylic and dicarboxylic acids (like azelaic acid). Diurea based thickeners are derived from the reaction product of aromatic diisocyanates and amines, in particular, diphenylmethane-4, 4'-diisocyanate (DMI) and alkyl, aryl or cycloalkyl amines, like octylamine, aniline (an aromatic amine) or cyclohexylamine.

The anti-wear additives used are metal salts of dialkyl dithiophosphoric and dithiocarbamic acids and mixtures thereof. Particularly useful metal salts are those of molybdenum and zinc. It is essential that the metal salts are oil-soluble. Typically, metal salts of the acids mentioned above having alkyl groups containing 8-18 carbon atoms are oil-soluble. The metal salts form complexes with metal surfaces at high temperatures caused by friction of the movements and thus develop a wear protecting film on the metal surface. Metal dialkyl dithiophosphoric acid and dialkyl dithiocarbamic acid salts that can be used are shortly denoted as e.g., MoDTP, ZnDTP, MoDTC and ZnDTC. Preferably, a combination of two or more of these additives is used.

It is also advantageous to include an ashless anti-wear phosphorus-containing additive, preferably an aromatic phosphite, such as triphenylphosphite (TPP). An ashless compound does not contain any ash-forming residue, such as metal.

Typically, the grease compositions can contain from 5 to 30 wt.% thickener, 0.5 to 10 wt.% metal-containing anti-wear additives and up to 5 wt% ashless anti-wear additives the balance being base oil.

By means of the combination of additives and thickeners according to the invention, temperature-stable, low friction and low noise greases suitable for constant velocity joints can be obtained.

Examples

Preparation of grease thickened by lithium soap

A mineral base oil (2500 g) was mixed with 12-hydroxystearic acid (500 g). An aqueous solution of lithium hydroxide (50 %, 140 g) was added to the mixture and under stirring heated to 180°C for 30 minutes. Mineral base oil (additionally 1930 g) was added to the mixture and cooled below 100°C under stirring to prepare a lithium soap base grease (I).

Preparation of grease thickened by lithium complex soap

A mineral base oil (1000 g) was mixed with 12-hydroxystearic acid (180 g) and azelaic acid (60 g). An aqueous solution of lithium hydroxide (50 %, 110 g) was added to the mixture and under stirring heated to 180°C for 30 minutes. Mineral base oil (additionally 705 g) was added to the mixture and cooled below 100°C under stirring to prepare a lithium complex soap base grease (II).

Preparation of grease thickened by diurea

There were added to a container 880 g of a mineral base oil and 118 g of diphenylmethane-4, 4'-diisocyanate and the mixture was heated to a temperature of 80°C. To another container, there were added 880g of a mineral base oil and 122 g of octylamine followed by heating to a temperature of 80°C. This heated mixture was added under stirring to the first-mentioned container. The mixture was then reacted for 30 minutes under sufficient stirring and heated to 160°C under stirring after which it was allowed to cool to give a diurea base grease (III).

Further diurea greases can be prepared by using aniline or cyclohexylamine or the mixtures in equivalent amounts.

Additives listed in the following table were added to the above-described thickened base greases in amounts defined therein and mixed and milled in a roll mill to adjust the consistency of the mixture to give the grease compositions with grade A. The same base oil is used in each example.

Thereafter the average friction coefficient and wear scar (mm) were measured in the internationally acknowledged SRV test. Friction coefficient values below 0.05 are indicative of very good friction properties and wear scar below 0.5 mm is acceptable and indicative of good wear properties, wherein a lower value indicates a better performance. The greases were filled into constant velocity joints and tested under internationally acknowledged test conditions for noise (rated from 0 to 5, 0 denoting no noise and 5 high noise level) and occurrence of vibration (strong/moderate/slight/none), the test corresponding to driving 10000 km in a 4WD vehicle.

Table

	Examples:						
	1	2	3	4	5	6	7
Li soap base grease (I)	96	95					
Li complex soap base grease (II)			96	95			
Diurea base grease (III)					96	95	96*
MoDTC	2	2	2	2	2	2	2
ZnDTP	2	2	2	2	2	2	1
TPP		1		1		1	1
Friction coefficient	0.040	0.035	0.037	0.035	0.036	0.031	0.032
Wear Scar (mm)	0.45	0.43	0.47	0.45	0.43	0.40	0.41
Noise	2	2	3	2	1	0	1
Occurrence Vibration	slight	none	moderate	slight	none	none	none

* diurea grease was prepared from a mixture of aniline/cyclohexylamine in equivalent amounts

A commercial lithium salt thickened grease containing a molybdenum disulfide additive (MoS2) gave in the same tests the following values for friction coefficient (0.05), wear scar (0.51 mm), noise (5) and moderate to strong vibrations.

The above examples show that, by combining thickeners and additives, low friction, low wear and low noise greases can be obtained. This is particularly advantageous in constant velocity joints and will increase the lifetime of the constant velocity joints in modern vehicles.

Claims

1. Grease composition comprising lubricating base oil, a thickener and at least one additive, characterized in that the additive is selected from metal salts of dialkyl dithiophosphoric acids and metal salts of dialkyl dithiocarbamic acids and their mixtures.

2. Grease composition according to claim 1 wherein the metal salt of dialkyl dithiophosphoric acid and the metal salts of dialkyl dithiocarbamic acid is one or more of MoDTP, ZnDTP, MoDTC or ZnDTC.

3. Grease composition according to claims 1 or 2 also comprising triphenylphosphite (TPP).

4. Grease composition according to claims 1 to 3 wherein the thickener is selected from lithium soap thickeners, lithium complex soap thickeners and diurea thickeners.

5. Method of making a grease composition according to claim 4 comprising

a) reacting a hydroxycarboxylic acid or a mixture of hydroxycarboxylic acids and dicarboxylic acids in lubricating base oil with lithium hydroxide while heating to form a grease or reacting an aromatic isocyanate compound with an alkyl, aryl or cycloalkylamine in a lubricating base oil while heating and reacting to form a grease, and

b) adding the additives to the grease comprising the thickener and milling the grease for a sufficient period of time in order to obtain a homogenous grease composition.

6. A constant velocity joint filled with a grease composition according to any one of claims 1 to 4.

Annex 2 (Communication)

Document 1 discloses grease compositions that preferably contain diurea thickener and anti-wear additives, notably ZnDTP and TPP (see paragraphs 2-4). The subject-matter of claims 1 to 4 is thus not novel over D1 (Articles 52(1), 54(1) and (2) EPC).

Document 2 (see claims 3 and 5; page 1, last paragraph; examples) discloses a grease composition comprising a base oil, a thickener and as additives one or more metal salts of dialkyl dithiophosphoric acid or dialkyl dithiocarbamic acid, selected from MoDTC or ZnDTP. The thickener is a lithium soap or a lithium complex soap, see Table of D2. Also the preparation of the grease is disclosed and its use in constant velocity joint of the Rzeppa type. Therefore, the subject-matter of claims 1, 2 and 4-6 is not novel (Articles 52(1), 54(1) and (2) EPC). It should be noted that D2 also refers to a lithium soap thickened grease comprising TPP, which is an ashless additive (see table).

An independent claim must specify all the technical features necessary to defined invention (Guidelines C-III, 4.5). The present claims fail to conform with the requirements of Article 84, since on page 3, first paragraph it is stated that the additives must be oil-soluble. Thus the claims lack the features essential to the solution of the problem on which the invention is based.

If the applicant wishes to maintain the application, new claims should be filed which take the above objections into account. Care should be taken to ensure that the new claims comply with the requirements of the EPC in respect of clarity, novelty, inventive step, and if necessary unity (Articles 54, 56, 82 and 84 EPC). Care should further be taken that any amendments do not introduce subject-matter which extends beyond the content of the application as originally filed (Article 123(2) EPC).

In the letter of reply, the difference between the new claims and the prior art disclo documents 1 and 2 and its significance should be indicated. The technical problem underlying the invention in view of the closest prior art and the solution to this problem should be readily derivable from the statement of the applicant (Rule 42(1)c EPC and EPO Guidelines, C-IV, 11.7).

In order to facilitate the examination as to whether the new claims contain subject-matter which extend beyond the content of the application as filed, the applicant is requested to indicate precisely where in the application documents any amendments proposed find a basis (Article 123(2) EPC).

Annex 3 (Document 1)

Grease composition for Swiss watches (Journal of Watch Makers)

Watches are high precision instruments. Almost all watches require lubrication and if the lubrication fails, the machinery can suffer damage and metal parts will require replacement. The increased reliability of modern watches is due primarily to the higher quality lubricants used in them. Depending on their construction, the requirements for the lubrication vary.

A very suitable and efficient lubricant for wrist watches is a thickened lubricant oil composition also called a grease. In order to minimize wear an anti-wear additive, such as ZnDTP, is added to the grease. The combination of this additive with the ashless anti-wear additive, TPP, is also recommendable.

Lithium soap thickener is formed in that 12-hydroxystearic acid is reacted with lithium hydroxide at elevated temperature and milled to homogenise the grease.

Lithium complex soap thickener is formed in that a mixture of 12-hydroxystearic acid and dicarboxylic acid, like azelaic or sebacic acid, is reacted with lithium hydroxide at elevated temperature and milled.

Diurea thickener having the following formula:

R1NH-CO-NH-C6H4-p-CH2-C6H4-p-NH-CO-NHR2

(wherein R1 and R2 can be the same or different and are selected from C8-C10-alkyl, aryl or cycloalkyl groups) is formed in that diphenylmethane-4,4'-diisocyanate is reacted at elevated temperature with an alkyl, aryl or cycloalkyl amine or with a mixture thereof and milled.

Diurea based thickeners are preferable because of their long-term stability and their bright colour.

Annex 4 (Document 2)

The present invention relates to a lubricating grease composition for vehicles and in particular automobiles. Greases are thickened lubricating compositions containing base oil, thickener and additives.

The greases are used in constant velocity joints that are special types of universal coupling which transmit drive from the final reduction gear to a road wheel axle at a constant rotational velocity.

The grease according to the invention is used in constant velocity joints of the Rzeppa type. The inventors have found that, for the Rzeppa type joint, a grease composition based on a lithium soap thickener is particularly suitable.

The joints of the Rzeppa type have been known for a long time and have hitherto been filled with molybdenum disulfide (MoS2) greases. MoS2 is an inorganic solid lubricant that has been used in combination with a lithium soap grease thickener to provide anti-wear protection (commercially known as MolyLi).

In modern vehicles, the wear is more pronounced since modern vehicles have to withstand high loads at varying speeds which can very quickly lead to increased wear, if the wear surfaces are not separated by a lubricating film. In known engine and gear oil compositions, very effective anti-wear additives are used. These are typically metal containing organic complexes, examples thereof being metal salts of dialkyl dithiophosphoric acid and dialkyl dithiocarbamic acids. The alkyl groups thereof typically have 4-22 carbon atoms.

According to the invention, grease compositions comprising a lubricating base oil, lithium soap or lithium complex soap based thickener and an anti-wear additive selected from metal dialkyl dithiophosphates (DTP) and metal dialkyl dithiocarbamates (DTC), represented by ZnDTP and MoDTC are used.

Lithium thickener greases are useful at temperatures up to 230°C. The anti-wear additive is used in order to form an effective protective layer to wear surfaces and the combination of the lithium soap thickener with the selected anti-wear additive will protect the joint from excessive wear even at high loads and temperatures.

The present invention thus solves the problem of wear in constant velocity joints, such as Rzeppa type joints.

Examples

Preparation of grease thickened by lithium soap

A mineral base oil (1250 g) was mixed with 12-hydroxystearic acid (250 g). An aqueous solution of lithium hydroxide (50%, 70 g) was added to the mixture and under stirring heated to 180°C for 30 minutes. Mineral base oil (additionally 965 g) was added to the mixture and cooled below 100°C under stirring to prepare a lithium base grease.

Preparation of grease thickened by lithium complex soap

A mineral base oil (500 g) was mixed with 12-hydroxystearic acid (90 g) and azelaic acid (30 g). An aqueous solution of lithium hydroxide (50 %, 55 g) was added to the mixture and under stirring heated to 180°C for 30 minutes. Mineral base oil (additionally 352 g) was added to the mixture and cooled below 100°C under stirring to prepare a lithium complex soap base grease.

The additives listed below in amounts given in the following table were added to the lithium base greases and mixed and milled in a roll mill to adjust the consistency of the mixture to give the final grease compositions of grade A.

ZnDTP zinc dialkyl dithiphosphate (alkyl 8-10 carbons)

MoDTC molybdenum dialkyl dithiocarbamate (alkyl 8-10 carbons)

TPP triphenyl phosphite

MoS2 molybdenum disulfide (as in MolyLi)

Thereafter the average friction coefficient and wear scar (mm) were measured in the internationally acknowledged SRV test. Friction coefficient values below 0.05 are indicative of very good friction properties, wear scar below 0.5 mm is acceptable and indicative of good wear properties, wherein a lower value indicates a better performance.

Table

	Examples:							
	1	2	3	4	5	6	7	8
Li soap base grease	96	96	96	96				
Li complex soap base grease					96	96	96	96
MoS2	4							4
MoDTC		4			4			
ZnDTP			4			4		
TPP				4			4	
Friction coefficient	0.050	0.048	0.047	0.049	0.047	0.046	0.048	0.051
Wear Scar (mm)	0.51	0.50	0.49	0.53	0.50	0.48	0.52	0.51

The examples show that grease compositions comprising the combination of lithium soap or lithium complex soap thickener and a metal containing organic complex anti-wear additive according to the invention reduces friction and prevents wear and is therefore particularly suitable for use in constant velocity joints. It is also contemplated that more than one of the metal complexes can be used together.

Claims

1. Grease composition comprising a lubricating base oil, a thickener and an additive, characterised in that the additive is a metal-containing organic complex.

2. Grease composition according to claim 1 where the thickener is selected from lithium soap thickeners and lithium complex soap thickeners.

3. Grease composition according to claim 1 where the organic complex comprises one or more metal salts of a dialkyl dithiophosphoric acid or a dialkyl dithiocarbamic acid.

4. Grease composition according to claim 3 where the alkyl groups of the organic complex contain 4-22 carbon atoms.

5. Grease composition according to claim 4 where the organic complex is selected from MoDTC and ZnDTP.

6. Method of making a grease composition according to claims 1-3 comprising

a) reacting a hydroxycarboxylic acid or mixture of hydroxycarboxylic acids and dicarboxylic acids in mineral oil with lithium hydroxide at an elevated temperature to make a grease and

b) adding the additives to the grease comprising the thickener and milling the gre
a sufficient period of time in order to obtain a homogenous grease composition.

7. Use of the grease composition of claims 1-5 in a constant velocity joint.

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Claims

1. Grease composition comprising lubricating base oil, a thickener and at least one additive, characterized in that the additive is selected from metal salts of dialkyl dithiophosphoric acids and metal salts of dialkyl dithiocarbamic acids and their mixtures.

2. Grease composition according to claim 1 wherein the metal salt of dialkyl dithiophosphoric acid and the metal salts of dialkyl dithiocarbamic acid is one or more of MoDTP, ZnDTP, MoDTC or ZnDTC.

3. Grease composition according to claims 1 or 2 also comprising triphenylphosphite (TPP).

4. Grease composition according to claims 1 to 3 wherein the thickener is selected from lithium soap thickeners, lithium complex soap thickeners and diurea thickeners.

5. Method of making a grease composition according to claim 4 comprising

a) reacting a hydroxycarboxylic acid or a mixture of hydroxycarboxylic acids and dicarboxylic acids in lubricating base oil with lithium hydroxide while heating to form a grease or reacting an aromatic isocyanate compound with an alkyl, aryl or cycloalkylamine in a lubricating base oil while heating and reacting to form a grease, and

b) adding the additives to the grease comprising the thickener and milling the grease for a sufficient period of time in order to obtain a homogenous grease composition.

6. A constant velocity joint filled with a grease composition according to any one of claims 1 to 4.