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(54) GREASE COMPOSITION FOR USE IN CONSTANT VELOCITY JOINTS

SCHMIERFETTZUSAMMENSETZUNG ZUR VERWENDUNG IN DOPPELGELENKEN

COMPOSITION DE GRAISSE DESTINÉE À ÊTRE UTILISÉE DANS DES JOINTS HOMOCINÉTIQUES

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(73) Proprietor: **GKN Driveline International GmbH**
53797 Lohmar (DE)

(72) Inventors:
- **E, JISHENG**
  53773 Hennef (DE)
- **REHER, Frank**
  53721 Siegburg (DE)
- **ROSENKRANZ, Stefanie**
  53343 Wachtberg-Oberbachem (DE)
- **FALK, Bernd**
  63165 Mühlheim am Main (DE)
- **GASPER, Lothar**
  50933 Köln (DE)
- **WITZDAM, Mario**
  53773 Hennef (DE)

(74) Representative: **Geskes, Christoph et al**
Geskes Patent- und Rechtsanwälte
Gustav-Heinemann-Ufer 74b
50968 Köln (DE)

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Description

[0001] The present invention relates to a lubricating grease which is intended primarily for use in constant velocity universal joints, especially ball joints or tripod joints, which are used in the drivelines of motor vehicles. Further, the present invention relates to a constant velocity joint comprising the grease composition in accordance with the present invention.

[0002] The motions of components within constant velocity joints (CVJ) are complex with a combination of rolling, sliding and spinning. When the joints are under torque, the components are loaded together which can not only cause wear on the contact surfaces of the components, but also rolling contact fatigue and significant frictional forces between the surfaces. The wear can result in failure of the joints and the frictional forces can give rise to noise, vibration and harshness (NVH) in the driveline. NVH is normally "measured" by determining the axial forces generated in plunging type CVJ. Ideally the greases used in constant velocity joints need not only to reduce wear, but also have to have a low coefficient of friction to reduce the frictional forces and to reduce or prevent NVH.

[0003] Constant velocity joints also have sealing boots of elastomeric material which are usually of bellows shape, one end being connected to the outer part of the CVJ and the other end to the interconnecting or output shaft of the CVJ. The boot retains the grease in the joint and keeps out dirt and water.

[0004] Not only must the grease reduce wear and friction and prevent the premature initiation of rolling contact fatigue in a CVJ, it must also be compatible with the elastomeric material of which the boot is made. Otherwise there is a degradation of the boot material which causes premature failure of the boot, allowing the escape of the grease and ultimately failure of the CVJ. The two main types of material used for CVJ boots are polychloroprene rubber (CR) and thermoplastic elastomer (TPE), especially ether-ester block co-polymer thermoplastic elastomer (TPC-ET).

[0005] Typical CVJ greases have base oils which are blends of naphthenic (saturated rings) and paraffinic (straight and branched saturated chains) mineral oils. Synthetic oils may also be added. It is known that said base oils have a large influence on the deterioration (swelling or shrinking) of both boots made of CR and TPC-ET. Both mineral and synthetic base oils extract the plasticisers and other oil soluble protective agents from the boot materials. Paraffinic mineral oils and poly-α-olefin (PAO) synthetic base oils diffuse very little into especially boots made of rubber material causing shrinkage, but on the other hand naphthenic mineral oils and synthetic esters diffuse into boot materials and act as plasticisers and can cause swelling. The exchange of plasticiser or plasticiser compositions for the naphthenic mineral oil can significantly reduce the boot performance, especially at low temperatures, and may cause the boot to fail by cold cracking, ultimately resulting in failure of the CVJ. If significant swelling or softening occurs, the maximum high speed capability of the boot is reduced due to the poor stability at speed and/or excessive radial expansion.

[0006] JP 11 035963 A discloses a lubricating grease composition comprising 100 pts.wt. base grease comprising 40 to 95 wt.% of at least one base oil selected from mineral oils or synthetic oils, and 5 to 60 wt.% calcium sulfonate complex thickener; and, blended therewith, further 1 to 20 pts.wt. organic molybdenum compound and 1.5 to 30 pts.wt. of a nonpolar polymer.

[0007] JP 11 131086 A discloses a lubricating grease composition for a bearing in an iron manufacturing machine, obtained by blending 100 pts.wt. of base grease comprising (A) 40-95 wt.% of at least one kind of base oil selected from mineral oil and synthetic oil, (B) 5-60 wt.% of a calcium sulfonate complex-based thickening agent with (C) 1-15 pts.wt. of molybdenum dialkyldithiocarbamate, 1-10 pts.wt. of an organized bentonite and a thiadiazole-based metallic deactivator, and (D) 0.5-7 pts.wt. of an amorphous polypropylene and 1-10 pts.wt. of polyethylene wax.

[0008] In order to solve the aforesaid problems, US 6,656,890 B1 suggests a special base oil combination comprising 10 to 35% by weight of one or more poly-α-olefins, 3 to 15% by weight of one or more synthetic organic esters, 20 to 30% by weight of one or more naphthenic oils, the remainder of the combination being one or more paraffinic oils, and, further, a lithium soap thickener, and a sulphur-free friction modifier, that may be a organo-molybdenum complex, and molybdenum dithiophosphate, and a zinc dialkyldithiophosphate and further additives such as corrosion inhibitors, antioxidants, extreme pressure additives, and tackiness agents. However, the friction coefficient and the wear of grease compositions according to US 6,656,890 B1 as measured in SRV (abbreviation for the German words Schwingungen, Reibung, Verschleiß) tests needs to be improved.

[0009] Thus, it is the object of the present invention to provide for a grease composition, primarily for use in constant velocity joints, which has a good compatibility with boots made of rubber or thermoplastic elastomer, and which also gives enhanced endurance, low wear and low friction in use in CVJ.

[0010] Said object of the present invention is solved by a grease composition for use in constant velocity joints comprising

a) 65 wt.-% to 86.9 wt.-% of a base oil composition;
b) 16 % by weight to 20 % by weight of at least one calcium sulphonate soap and/or calcium sulphonate complex soap as a thickener; and
c) 0.3 wt.-% to 2.0 wt.-% of at least one trinuclear molybdenum compound and 0.5 wt.-% to 2.0 wt.-% of at least

one molybdenum dithiocarbamate.

[0011] As far as the tem % by weight is used with respect to the components being comprised from the claimed grease composition, the term % by weight is referred to the total amount of the grease composition throughout this specification, except where expressively stated otherwise.

[0012] Preferably, the base oil composition used in the grease composition in accordance with the present invention comprises poly-α-olefines, napthenic oils, paraffinic oils, and/or synthetic organic esters.

[0013] As a base oil composition according to the present invention, a base oil composition as disclosed in US 6,656,890 B1 may preferably be used, the disclosure of which is incorporated insofar herein by reference,. However, any further kind of base oil composition, especially a blend of mineral oils, a blend of synthetic oils or a blend of a mixture of mineral and synthetic oils may be used. The base oil composition should preferably have a kinematic viscosity of between about 32 and about 250mm^2/s at 40°C and between about 5 and about 25mm^2/s at 100°C. The mineral oils preferably are selected from the group comprising at least one naphthenic oil and/or at least one paraffinic oil. The synthetic oils usable in the present invention are selected from a group comprising at least one poly-α-olefin (PAO) and/or at least one synthetic organic ester. The organic synthetic ester is preferably a di-carboxylic acid derivative having subgroups based on aliphatic alcohols. Preferably, the aliphatic alcohols have primary, straight or branched carbon chains with 2 to 20 carbon atoms. Preferably, the organic synthetic ester is selected from a group comprising sebacic acid-bis(2-ethylhexylester) ("dioctyl sebacate" (DOS)), adipic acid-bis-(2-ethylhexylester) ("dioctyl adipate" (DOA)), and/or azelaic acid-bis (2-ethylhexylester) ("dioctyl azelate (DOZ)).

[0014] If poly-α-olefin is present in the base oil composition, preferably poly-α-olefins are selected having a viscosity in a range from about 2 to about 40 centistokes at 100°C. The naphthenic oils selected for the base oil composition have preferably a viscosity in a range between about 3 to about 370 mm^2/s, more preferably about 20 to about 150 mm^2/s at 40°C, whereas if paraffinic oils were present in the base oil composition, preferably the paraffinic oils have a viscosity in a range between about 9 to about 170 mm^2/s at 40°C.

[0015] The at least one calcium sulphonate soap and/or calcium sulphonate complex soap used as a thickener in the grease composition in accordance with the present invention is, in principle, a reaction product of aliphatic or fatty acids and/or hydroxy aliphatic and/or fatty acids. The fatty acids or hydroxy fatty acids are selected preferably from a group comprising 12 to 30, preferably 12 to 24, most preferably 12 to 18 carbon atoms. The aliphatic and/or fatty acids may be selected from a group comprising dodecanoic acid, palmitic acid, stearic acid, oleic acid, ricinoleic acid and/or 12-hydroxystearic acid. Hydroxy aliphatic and/or fatty acids are preferred due to their higher thickening properties. The calcium sulfonate that may be used in the preparation of the calcium sulfonate grease and/or the calcium sulfonate complex grease is selected from the group comprising at least one calcium sulfonate and/or at least one overbased calcium sulfonate. Overbased calcium sulfonates are preferred In accordance with the present invention, especially overbased calcium sulfonates having a metal ratio of about 6 to 35.

[0016] A calcium sulfonate soap that may be used as a thickener may be prepared from the reaction of the aforesaid calcium sulfonate components and aliphatic and/or fatty acids and/or hydroxy and/or fatty acids in the presence of other agents, especially converting agents, comprising, among others, water, alcohols, for instance biphenol, isobutanol, n-pentanol, or mixtures thereof or mixtures of alcohols with water, alkylene glycols, monoloweralkyl others of alkylene glycols such as monomethylether of ethylene glycol, lower aliphatic carboxylic acids, for example acetic acid and propionic acid, ketones, aldehydes, amines, phosphorus acids, alkyl and aromatic amines, imidazoilines, alkanolamines, boron acids, including boric acid, tetraboric acid, metaboric acid, and esters of such boron acids, and, also, carbon dioxide as such, or better in combination with water. Calcium sulphonate complex soaps that may be used as a thickener in accordance with the present invention may be used prepared from at least one anphatic and/or fatty acid or hydroxyallphatic and/or fatty acid, at least one of the calcium sulphonate compounds mentioned above together with a complexing agent, for example a borate of one or more dicarboxylic acids or a mixture of short and/or medium chained carboxylic acids. The use of a calcium sulphonate complex soap as a thickener In accordance with the present invention allows the grease composition according to the present invention to operate up to a temperature of about 180°C, whereas simple calcium sulphonate soaps that may be used as a thickener in accordance with the present invention, the grease composition will only operate up to a temperature of about 120°C. However, mixtures of all of the aforesaid soaps may also be used.

[0017] Further molybdenum containing additives that can be present in the grease composition in accordance with the present invention are preferably selected from a group comprising molybdenum dithiophosphate, MoS_2, and/or an S-free and P-free organic molybdenum compound. The at least one tri-nuclear molybdenum compound is of the following general formula

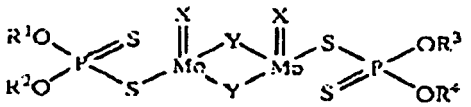
$$Mo_3S_kL_nQ_z \qquad (I)$$

wherein L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render

the compound soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 though 7, Q is selected from the group of neutral electron donating compounds such as amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values.

[0018] The number of carbon atoms present in the tri-nuclear molybdenum compound among all the ligands, organo groups is at least 21 carbon atoms, preferably at least 25, more preferably at least 30, and most preferably at least 35. Tri-nuclear molybdenum compounds usable in the present invention are disclosed in US 6,172,013 B1, the disclosure of which is incorporated in the present invention insofar by reference. The presence of at least 0.25% by weight of the tri-nuclear molybdenum compound is preferred and significantly lowers the friction coefficient as well as the wear when used in CVJs.

[0019] The molybdenum dithiophosphate (MoDTP) is preferably present in the grease composition according to the present invention in an amount in a range between about 0.3 % by weight, more preferred about 0.5 % by weight, most preferred about 1.0 % by weight, to about 3.5 % by weight, most preferred about 3 % by weight, in each case referred to the total amount of the grease composition. However, also any further molybdenum containing compound may be present in the grease composition according to the present invention, of which organic molybdenum compounds are preferred. The grease composition according to the present invention may contain one or more MoDTC and/or MoDTP, and especially mixtures thereof. The MoDTP according to the present invention is of the following general formula:



(II)

wherein X or Y represents S or O and each of R^1 to R^4 inclusive may be the same or different and each represents a primary (straight chain) or secondary (branched chain) alkyl group having between 6 and 30 carbon atoms.

[0020] The MoDTC according to the present invention is of the following general formula:

$$[(R^5)(R^6)N\text{-}CS\text{-}S]_2\text{-}Mo_2O_mS_n \qquad (III)$$

wherein R^5 and R^6 each independently represents an alkyl group having 1 to 24, preferably 3 to 18 carbon atoms; m ranges from 0 to 3 and n ranges from 4 to 1, provided that m+n=4.

[0021] The molybdenum containing additive is selected from a group comprising at least one molybdenum dithiocarbamate and at least one tri-nuclear molybdenum compound. In accordance with the present invention, the grease composition comprises 0.3 % by weight to 2.0 % of at least one tri-nuclear molybdenum compound, and preferably 0.3 % by weight to 1.25 % by weight.

[0022] In accordance with the present invention, the grease composition comprises 0.5 to 3 % by weight of at least one solid or liquid molybdenum dithiocarbamate, preferably 0.8 % by weight to 2 % by weight. In a further preferred embodiment of the present invention, the molybdenum dithiocarbamate is a solid molybdenum dithiocarbamate.

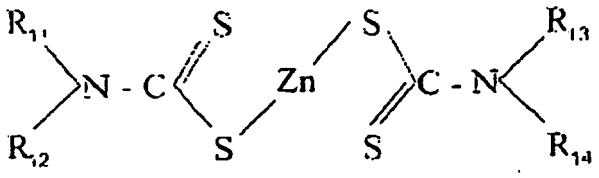
[0023] According to a further embodiment of the present invention, the grease composition further comprises at least one anti-oxidation agent, at least one corrosion inhibitor, at least one anti-wear agent, at least one wax, at least one friction modifier and/or at least one extreme pressure agent.

[0024] As a friction modifier, at least one zinc compound additive, more preferably a zinc compound additive in an amount of about 0.1 % by weight to about 3.5 % by weight, preferably to about 2.5 % by weight, more preferably to about 0.5 % by weight to about 2.0 % by weight, referred to the total amount of the grease composition, is used. The most preferred zinc compound additive is selected from the group comprising at least one of zinc dithiophosphates (ZnDTP) and/or zinc dithiocarbamates (ZnDTC), and ZnDTPs are most preferred. The zinc dithiophosphate is preferably selected from the group of zinc dialkyldithiophosphate of the following general formula:

$$(R^7O)(R^6O)SP\text{-}S\text{-}Zn\text{-}S\text{-}PS(OR^9)(OR^{10}) \qquad (IV)$$

wherein each of R^7 to R^{10} inclusive may be the same or different and each represents a primary or secondary alkyl group of which primary alkyl groups are most preferred having 1 to 24, preferably 3 to 20, most preferably 3 to 5 carbon atoms. In particular, excellent effects can be expected if the substituants R^7, R^8, R^9 and R^{10} represent a combination of primary and secondary alkyl groups, each having 3 to 8 carbon atoms.

[0025] The zinc dithiocarbamate may be preferably selected from zinc dialkyldithiocarbamate of the following general formula:



(V)

wherein R^{11}, R^{12}, R^{13}, and R^{14} may be same or different and each represents an alkyl group having 1 to 24 carbon atoms or an aryl group having 6 to 30 carbon atoms.

[0026] By adding at least one zinc compound additive to the grease composition according to the invention, the friction coefficient as well as the wear in CVJ are diminished further significantly.

[0027] The EP agent is preferably a metal-free polysulfide or a mixture thereof, e.g. sulphurised fatty acid methyl ester agents, with preferably a viscosity of about 25mm^2/s at 40°C, being present preferably in an amount between about 0.1 to about 3 % by weight, preferably 0.3 to about 2 % by weight, referred to the total amount of the grease composition. The total inactive sulphur amount of the EP agent at room temperature preferably ranges from about 8 to about 50 % by weight, preferably to about 45 % by weight. The active sulphur amount as measured in accordance with ASTM D1662 may be about up to 1 % by weight, preferably up to about 8 % by weight at 100°C, and preferably up to about 20 % by weight at 140°C, the weight percent being referred to the amount of the EP agent itself. Such EP agents exhibit excellent effects with respect to the prevention of scuffing of contacting CVJ internal components. If the sulphur content exceeds the upper limit defined above, it may promote the initiation of rolling contact fatigue and wear of the contacting metal components and may lead to degradation of the CVJ boot material.

[0028] As an anti-oxidation agent, the grease composition of the present invention may comprise an amine, preferably an aromatic amine, more preferably phenyl-α-naphthylamine or diphenylamine or derivatives thereof. The anti-oxidation agent is used to prevent deterioration of the grease composition associated with oxidation. The grease composition according to the present invention may range between about 0.1 to about 2 % by weight, referred to the total amount to the grease composition, of an anti-oxidant agent in order to inhibit the oxidation degradation of the base oil composition, as well as to lengthen the life of the grease composition, thus prolonging the life of the CVJ.

[0029] Typically, the last operation before the assembly of CVJ is a wash to remove machining debris, and it is therefore necessary for the grease to absorb any traces of remaining water and to prevent the water from causing corrosion and adversely effecting the performance of the CVJ, thus a corrosion inhibitor is required. As a corrosion inhibitor, the grease composition according to the present invention may comprise at least one metal or dimetal salt selected from the group consisting of metal salts of oxidised waxes, metal salts of petroleum sulphonates, especially prepared by sulphonating aromatic hydrocarbon components present in fractions of lubricating oils, and/or metal salts of alkyl aromatic sulphonates, such as dinonylnaphthalene sulphonic acids, alkylbenzene sulphonic acids, or overbased alkylbenzene sulphonic acids. Examples of the metal salts include sodium salts, potassium salts, calcium salts, magnesium salts, zinc salts, quaternary ammonium salts, the calcium salts being most preferred. Calcium salts of oxidised waxes also ensure an excellent effect. Especially preferred is disodium sebacate as corrosion inhibitor.

[0030] Anti-wear agents according to the present invention prevent a metal-to-metal contact by adding film-forming compounds to protect the surface either by physical absorption or chemical reaction. ZnDTP-compounds may also be used as anti-wear agents. As anticorrosion agents according to the present invention preferably calcium sulphonate salts are used, preferably an amount between about 0.5 to about 3% by weight, referred to the total amount of the grease composition.

[0031] As a wax compound, the grease composition of the present invention may comprise any kind of waxes, preferably oiliness waxes, known in the state of the art to be used in grease composition or mixtures thereof, of which montan waxes, especially ester montan waxes being a reaction product of at least one acid montan wax with an ester, and polyolefin waxes including micronized montan and/or polyolefin waxes, or mixtures thereof are most preferred. Montan waxes in the sense of the present invention preferably comprises esters of C_{22}-C_{34}-fatty acids and probably wax alcohols having 24 to 28 carbon atoms. Esters may be present in the montan wax in accordance with the present invention in an amount in a range of about 35% by weight to about 70% by weight. Further, free fatty acids as well as free wax alcohols as well as montan resins may be present. Useful montan waxes are offered for example by the company Clariant GmbH, 86005 Augsburg, Germany, especially montan waxes offered and sold under the trade name "Licowax". Usable polefin waxes in the sense of the present invention are especially polypropylene and/or polyethylene waxes or mixtures thereof, also including modified polyolefin waxes, obtained especially by copolymerization of ethylene with useful co-monomers like vinyl esters or acrylic acid. The wax has preferably a viscosity of at least about 50 mPa*s at 100°C, more preferred of at least about 100 mPa*s at 100°C, and most preferred of at least about 200 mPa*s at 100°C, measured in accordance with DIN 53 018.The wax used in the grease composition may be supplied as a powder or flakes, and is added to the grease composition with a long perod of stirring, preferably at elevated temperatures, especially at temperatures about 80°C to about 100°C.

[0032] Traditional friction modifiers that may also be used in the present invention such as fatty acid amides and fatty amine phosphates have been used in greases and other lubricants for many years (see, e.g., the modifiers disclosed in Klamann, Dieter - "Lubricants", Verlag Chemie GmbH 1983, 1st edition, chapter 9.6). Their role is to give the lubricant stable but not necessarily low friction over a wide range of operating conditions.

[0033] In a further embodiment of the present invention, the grease composition claimed comprises 0.3 wt.-% to 2 wt.-%, preferably to 1.25 wt.-%, of at least one trinuclear molybdenum compound and 0.8 wt.-% to 3 wt.-%, preferably to 2 wt.-%, of at least one molybdenum dithiocarbamate.

[0034] Most preferred the grease composition according to the present invention comprises 16 wt.-% to 20 wt.-% of at least one calcium sulphonate soap and/or calcium sulphonate complex soap, 0.3 wt.-% to 0.7 wt.-% of at least a trinuclear molybdenum compound, 0.75 wt.-% to 1.8 wt.-% of at least one molybdenum diothiocarbamate, and 66.45 wt.-% to 86.9 wt.-% of a base oil composition. The grease composition claimed may further comprise other agents as mentioned above.

[0035] Further, the present invention refers to the use of a grease composition in accordance with the present invention in constant velocity joints, and, further, to a constant velocity joint comprising a grease composition as claimed. The constant velocity joint especially encompasses a boot, the boot being filled with the grease composition in accordance with the present invention, at least in part, the boot having a first attachment region which is assigned to a joint, and a second attachment region which is assigned to a shaft. The boot may be fixed with usual clamp devices on the joint and/or shaft.

[0036] The invention will be explained in more detail in the following examples.

Examples

[0037] In order to determine the effect of the lowering of the friction coefficient as well as the wear by the grease composition according to the invention, SRV tests are carried out using an Optimol Instruments SRV tester. Flat disc lower specimen made of the 100Cr6 standard bearing steel from Optimol Instruments Prüftechnik GmbH, Westendstrasse 125, Munich, properly cleaned using a solvent are prepared and contacted with the grease composition to be examined. The SRV test is an industry standard test and is especially relevant for the testing of greases for CVJ. The test consists of an upper ball specimen with a diameter of 10 mm made from 100Cr6 bearing steel reciprocating under load on the flat disc lower specimen indicated above. In tests for mimicking tripod joints a frequency of 40 Hz with an applied load of 500 N were applied for 60 minutes (including running-in) at 80°C. The stroke was 3.0 mm. The friction coefficients obtained were recorded on computer. For each grease, the reported value is an average of two data at the end of tests in two runs. Wear is measured using a profilometer and a digital planimeter. By using the profilometer, a profile of the cross section in the middle of the worn surfaces can be obtained. The area (S) of this cross section can be measured by using the digital planimeter. The wear quantity is assessed by V=SI, where V is the volume of the wear and I is the stroke. The wear rate (W_r) is obtained from W_r=V/L [μm^3/m], where L is the total sliding distance in the tests. For the running-in, it is started with an applied load of 50 N for 1 minute under the above-specified conditions. Afterwards, the applied load is increased for 30 seconds by 50 N up to 500 N.

[0038] Further, tests regarding the properties of a rubber boot and a TPE-boot, respectively, equipped with a grease composition in accordance with the present invention according to example C4 compared with two commercial grease compositions A and B were carried out with respect to the change of a hardness (shore D) and the percentage change of tensile, elongation, and volume before and after a heat ageing of the boot material immersed in a grease at 125°C for 336 hours. Said values are measured in accordance with ISO 868 (shore D), ISO 37 (tensile change and elongation change), and ISO 2781 (volume change).

[0039] The commercial greases used in comparative examples A and B are Axel CaSX 51646, obtained from Axel Christiernsson B.V., Heijningen, Netherlands, (comparative example A) and Super Grease 2 obtained from Tianjin Lubricant and Grease Co. Ltd. (Jinzhi), Sinopec Corp., Tianjin, P.R. China (comparative example B).

[0040] The following substances are used in the examined grease compositions in accordance to the present invention.

Base oil composition (oil blend)

[0041] The base oil composition used has a kinematic viscosity of about 165 mm^2/s at 40°C and about 16 mm^2/s at 100°C. The base oil blend may be a mixture of one or more paraffinic oils in a range between about 10 to about 60 % by weight, preferably about 20 to 40% by weight, one or more naphthenic oils in a range between about 30 to about 80 % by weight, preferably about 55 to about 80% by weight, and, if necessary, one or more poly-α-olefins (PAO) in a range between about 5 to about 40 % by weight, referred to the total amount of the oil mixture. The oil blend may further contain DOS in a range between about 2 to about 10 % by weight, referred to a total amount of the oil mixture. The concrete oil blend used in the examples is made of 73% by weight of naphthenic oil SR130, produced by AB Nynäs Petroleum, Stockholm, Sweden, 25% by weight of paraffinc oil NS650, obtained by Kuwait Petroleum Europoort B.V, Europoort,

Netherlands, and 2% by weight of DOS.

[0042] The naphthenic oils are selected with a range of viscosity between about 20 to about 180 mm^2/s at 40°C, paraffinic oils between about 25 to about 400 mm^2/s at 40°C, and PAO between about 6 and about 40 mm^2/s at 100°C.

Calcium sulphonate soap

[0043] The calcium sulphonate soap used in the examples of the present invention is an overbased calcium sulphonate soap obtained from a reaction of overbased calcium sulphonate with a metal ratio of about 6 to 35 with 12-hydroxystearic acid in the presence of a solvent neutral oil, calcium carbonate, isopropyl alcohol and phosphoric acid. A possible method for producing the calcium sulphonate soap used is described in US 5,126,062.

Tri-molecular molybdenum compound (TNMoS)

[0044] The tri-molecular molybdenum compound used in the grease compositions according to the present invention is a sulphur-containing tri-nuclear molybdenum compound obtainable under the trade name C9455B by Infineum International Ltd., UK. Its structure is defined in US 6,172,013 B1.

Further molybdenum compounds

[0045] A molybdenum dithophosphate (MoDTP) sold under the commercial name Sakuralube 300 (S-300) by Asahi Denka Co. Ltd., Japan, with the chemical formula 2-Ethylhexyl molybdenum dithiophosphate, diluted with mineral oil, is used. Further, a solid molybdenum dithiocarbamate (MoDTC solid) sold under the trade name Sakuralube 600 (S-600), produced by Asahi Denka Co. Limited, Japan, or under the trade name Molyvan A, produced by R.T. Vanderbilt Company, Inc, USA, is used.

[0046] Further, a molybdenum dithiocarbamate sold under the trade name Sakuralube 200 (MoDTC S-200) in the liquid state, produced by Asahi Denka Co. Limited, Japan, is used as well as a S-free and P-free organic molybdenum additive sold under the trade name S-701 by Asahi Denka Co. Limited, Japan, being a molybdenum amine complex with the general formula $R_2N\text{-}Mo_xO_yH$, as well as usual MoS_2.

Further additives

[0047] As a friction modifier a zinc compound additive, namely zinc dithiophosphate ZnDTP, sold by Infineum International Ltd., Oxfordshire, UK, under the trade name C9425, is used, being a zinc dialkyldithiophosphate with primary and/or secondary alkyl groups, especially having 3 to 8 C-atoms, preferably having 4 to 5 C-atoms, diluted with mineral oil.

[0048] First, the advantages of the grease composition according to the present invention were examined by measuring the friction coefficient and the welding load of the six different greases, as listed in Table 1:

Table 1

Grease Composition [wt%]	Example A1	Example A2	Example A3	Example A4	Example A5	Example A6	Example A7	Example A8
TNMoS	-	-	-	-	0.5	-	-	-
ZnDTP	-	-	-	-	-	-	-	0.5
MoDTP	-	-	0.5	-	-	-	-	-
MoDTC solid	-	-	-	0.5	-	-	-	-
MoDTC S-200	-	0.5	-	-	-	-	-	-
S-710	-	-	-	-	-	0.5	-	-
MoS_2	-	-	-	-	-	-	0.5	-
Calcium sulphonate soap	18	18	18	18	18	18	18	18
oil blend	82	81.5	81.5	81.5	81.5	81.5	81.5	81.5

[0049] The results from the SRV-measurements of the friction coefficient as well as the welding load measurements of Examples A1 to A8 may be derived from Fig. 1. and Fig. 2. Examples A1 to A8 are only comparative examples. The lowest friction coefficient, and, however, the highest wear is measured when adding a simple MoS_2, whereas a very low wear as measured with respect to Example A3 with an increased friction coefficient compared with Example A1 being a grease composition only composed of the base oil and a calcium sulphonate soap. Further, also Examples A2 and A5 show good results with respect to the wear.

[0050] In a further series of tests, the amount of the TNMoS as well as of the MoDTC solid is amended. Ten grease compositions were prepared in accordance with Table 2. Examples B1 to B7 are only comparative examples.

Table 2

Grease Composition [wt%]	Example B1	Example B2 = A5	Example B3	Example B4 = A4	Example B5	Example B6	Example B7	Example B8	Example B9	Example B10
TNMoS	0.3	0.5	1.0	-	-	-	-	0.5	0.5	0.5
MoDTC solid	-	-	-	0.5	1	1.5	2	1	1.5	2
Calcium sulphonate soap	18	18	18	18	18	18	18	18	18	18
oil blend	81.7	81.5	81.0	81.5	81	80.5	80	80.5	80	79.5

[0051] In Examples B1 to B3 the amount of the TNMoS is amended, wherein in Examples B4 to B7 the amount of MoDTC solid is amended. Examples B8 to B10 refer to mixtures of 0.5 wt.-% TNMoS to different amounts of MoDTC solid. The results from the SRV measurements with respect to the friction coefficient as well as the welding load may be derived from Fig. 3 and Fig. 4.

[0052] Example B3 shows the lowest friction coefficient, however, the results for the wear are only in the midrange of the results obtained. Further, low friction coefficients were measured with respect to Examples B9 to B10, of which Example B9 shows one of the lowest wear measured. Said test results show that especially combinations of different molybdenum containing compounds are preferable, and that the ranges of the molybdenum compounds used are very sensitive with respect to the friction coefficient and wear measured.

[0053] In a third test series, the effect of addition of an amount of 0.5 wt.-% of different molybdenum containing compounds and ZnDTP to the amount of 1.5 wt.-% MoDTC solid is studied. The grease compositions C1 to C6 examined are defined in Table 3.

Table 3

Grease Composition [wt%]	Example C1 = A1	Example C2 = A2	Example C3	Example C4 = B9	Example C5	Example C6
TNMoS	-	-	-	0.5	-	-
ZnDTP	-	-	-	-	0.5	-
MoDTP	-	-	0.5	-	-	-
MoDTC solid	-	1.5	1.5	1.5	1.5	1.5
MoDTC S-200	-	0.5	-	-	-	-
MoS_2	-	-	-	-	-	0.5
Calcium sulphonate soap	18	18	18	18	18	18
oil blend	82	80	80	80	80	80

[0054] The results from the SRV measurements of the friction coefficient as well as the measurement of the welding load may be derived from Fig. 5 and 6. Examples C1 to C3 and C5 as well as C6 are only comparative examples. One may easily derive that composition C4 being a composition of 1.5 wt.-% of MoDTC solid in the solid state and the tri-nuclear molybdenum compound in an amount of 0.5 wt.-% is most preferred, because both the friction coefficient as well as the wear are considerably lower when compared to the results of the other compositions.

[0055] Further, combinations of three molybdenum compound additives or two molybdenum compound additives together with ZnDTP are examined in accordance with Table 4. The amount of MoDTC solid is not varied. Examples D1 to D3 are only comparative examples.

Table 4

Grease Composition [wt%]	Example D1=A1	Example D2	Example D3	Example D4	Example D5
TNMoS	-	-	-	0.5	0.5
ZnDTP	-	0.5	0.5	0.5	-
MoDTC solid	-	1.5	1.5	1.5	1.5
MoDTC S-200	-	0.5	-	-	-
MoDTP	-	-	0.5	-	0.5
Calcium sulphonate soap	18	18	18	18	18
Oil blend	82	79.5	79.5	79.5	79.5

[0056] As may be derived from Fig. 7 and 8 referring to examples D1 to D5, the lowest friction coefficient was measured with respect to example D5, whereas the wear was very low in examples D2 and D4. However, due to the lowest friction

coefficient, grease composition D5 being very similar to grease composition C4 appears to be advantageous.

[0057] Finally, measurements of the properties of boots equipped with the different greases were carried out. A grease composition in accordance with example C4 was compared with comparative examples A and B being commercially available grease compositions. The results are listed in Table 5.

Table 5

	Example C4	Comparative Example A	Comparative Example B
compatibility with rubber			
Hardness change (shore D A)	-9	+1	0
Tensile change (%)	-4,5	-5,4	-2,3
Elongation change (%)	-17,7	-17,9	-17,6
Volume change (%)	+8,9	-3,0	-2,8
compatibility with TPE			
Hardness change (shore D A)	-6	-7	-5
Tensile change (%)	-40,4	-63,9	-11,7
Elongation change (%)	-16,5	-72,4	+1,3
Volume change (%)	+12,9	+10,0	+9,2

[0058] As may be derived from Table 5, especially in combination with boots made of TPE-material preferable properties with respect to the tensile change and elongation change were measured. Endurance tests carried out with respect to example C4 show that the endurance of constant velocity joints may be enhanced up to a twofold lifetime compared to joints equipped with boots with commercially available greases such as comparative examples A and B.

[0059] In summary, the grease composition in accordance with the present invention has an advantageous and significant influence on the friction coefficient and the wear, leading to a good extreme pressure performance. Especially preferred are combinations of two or three different molybdenum containing compounds being added to the grease composition in an amount up to 3.5 weight % in total, of which the addition of a tri-nuclear molybdenum compound as well as a molybdenum dithiocarbamate, preferably in the solid state, in combination are most preferred.

Claims

1. A grease composition for use in constant velocity joints comprising

   a) 65 wt.-% to 86.9 wt.-% of a base oil composition;
   b) 16 % by weight to 20 % by weight of at least one calcium sulphonate soap and/or calcium sulphonate complex soap as a thickener; and
   c) 0.3 wt.-% to 2.0 wt.-% of at least one trinuclear molybdenum compound and 0.5 wt.-% to 3 wt.-% of at least one molybdenum dithiocarbamate.

2. A grease composition according to claim 1, **characterized in that** the molybdenum dithiocarbamate is a solid molybdenum dithiocarbamate.

3. A grease composition according to claims 1 to 2, **characterized in that** it further comprises at least one molybdenum dithiophosphate.

4. A grease composition according to anyone of the preceding claims, **characterized in that** the base oil composition comprises poly-α-olefins, naphthenic oils, paraffinic oils, and/or synthetic organic esters.

5. A grease composition according to anyone of the preceding claims, **characterized in that** it further comprises at least one anti-oxidation agent, at least one corrosion inhibitor, at least one anti-wear-agent, at least one wax, at least one friction modifier and/or at least one extreme pressure agent.

6. Use of a grease composition according to anyone of the preceding claims 1 to 5 in constant velocity joints.

7. Constant velocity joint comprising a grease composition according to anyone of claims 1 to 5.

Patentansprüche

1. Eine Fettmischung zur Verwendung in Gleichlaufgelenken umfassend

   a) 65 Gew.-% bis 86,9 Gew.-% einer Baslsölmischung;
   b) 16 Gew.-% bis 20 Gew.-% wenigstens einer Calciumsulfonatseife und/oder Calciumsulfonatkomplexseife als Verdickungsmittel;
   c) 0,3 Gew.-% bis 2,0 Gew.-% wenigstens einer dreikernigen Molybdänverbindung und 0,5 Gew.-% bis 3 Gew.-% wenigstens eines Molybdändithlocarbamates.

2. Fettmischung gemäß Anspruch 1, **dadurch gekennzeichnet, dass** das Molybdändithiocarbamat ein festes Molybdändlthiocarbamat ist.

3. Fettmischung gemäß Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** diese weiterhin wenigstens ein Molybdändithiophosphat umfasst.

4. Fettmischung gemäß einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die Basisölmischung Poly-α-Olefine, naphthenische Öle, paraffinsiche Öle und/oder synthetische organische Ester umfasst.

5. Fettmischung gemäß einem der vorhergehenden Ansprüche, dadurch gekennzelchnet, dass diese weiterhin wenigstens ein Antioxidationsmittel, wenigstens ein Korrosionsschutzmittel, wenigstens ein Antiverschleißmittel, wenigstens ein Wachs, wenigstens einen Friktionsmodifizierer und/oder wenigstens ein EP (extrem pressure)-Mittel umfasst.

6. Verwendung einer Fettmischung gemäß einem der vorhergehenden Ansprüche 1 bis 5 in Gleichlaufgelenken.

7. Gleichlaufgelenk umfassend eine Fettmischung gemäß einem der Ansprüche 1 bis 5.

Revendications

1. Une composition de graisse destinée à des joints homocinétiques comportant :

   a) 65% à 89% en poids d'une composition à base d'huile
   b) 16% à 20% en poids d'au moins un savon au sulfonate de calcium et/ou un savon complexe au sulfonate de calcium comme épaississant et
   c) 0.3 % à 2.0 % en poids d'au mois un composé de molybdène trinucléaire et 0.5 à 3 en poids d'au moins un dithiocarbamate de molybdène

2. Une composition de graisse selon la revendication 1 **caractérisée en ce que** le dithiocarbamate de molybdène est un dithiocarbamate solide.

3. Une composition de graisse selon la revendication 1 ou 2 **caractérisée en ce que** elle comprend en outre au moins un dithiophosphate.

4. Une composition de graisse selon l'une quelconque des revendications précédentes **caractérisée en ce que** la composition à base d'huile comprend des poly-a-oléfines; des huiles naphténiques; des huiles parafiniques et/ou des esters organiques synthétiques.

5. Une composition de graisse selon l'une quelconque des revendications précédentes **caractérisée en ce que** elle comprend en outre au moins un agent anti-oxydant, au moins un inhibiteur de corrosion, au moins un agent anti-usure, au moins une cire, au moins un modificateur de friction et/ou au moins un agent de pression extrême.

6. Utilisation d'une composition de graisse selon les revendications 1 à 5 dans des joints homocinétiques.

7. Joint homocinétique comportant une composition de graisse selon l'une quelconque des revendications 1 à 5.

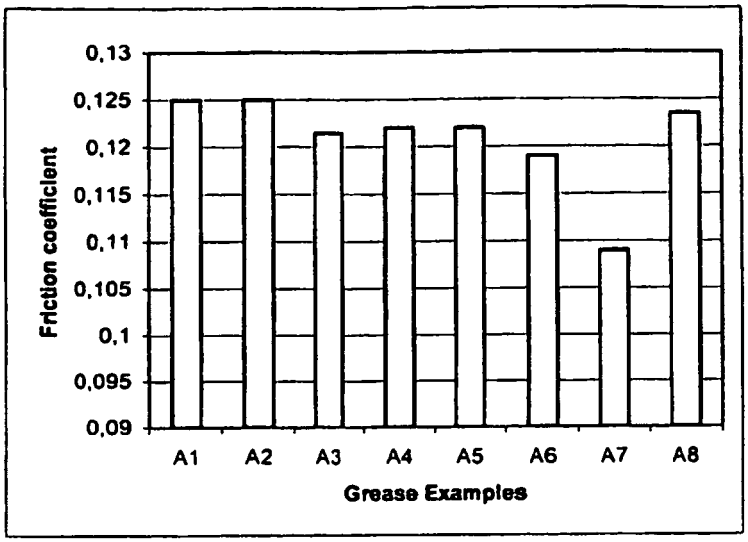

0,13
0,125
0,12
0,115
0,11
0,105
0,1
0,095
0,09
Friction coefficient
A1
A2
A3
A4
A5
A6
A7
A8
Grease Examples

Fig. 1

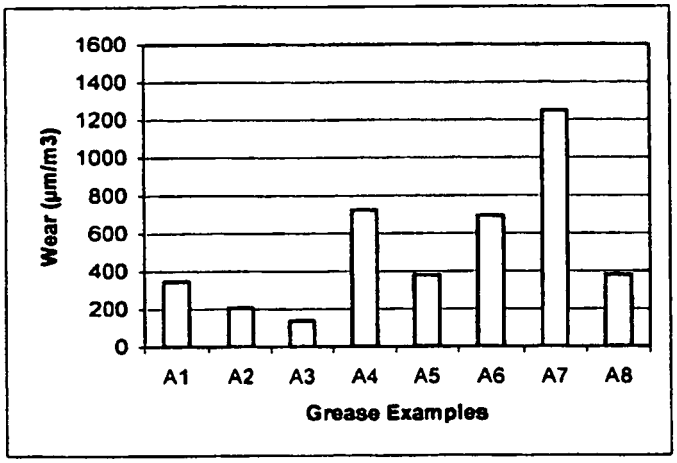

1600
1400
1200
1000
800
600
400
200
0
Wear (µm/m3)
A1
A2
A3
A4
A5
A6
A7
A8
Grease Examples

Fig. 2

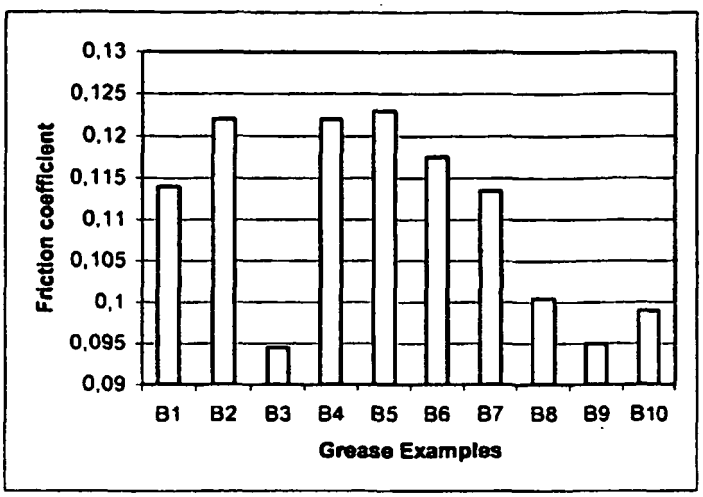

0,13
0,125
0,12
0,115
0,11
0,105
0,1
0,095
0,09
Friction coefficient
B1 B2 B3 B4 B5 B6 B7 B8 B9 B10
Grease Examples

Fig. 3

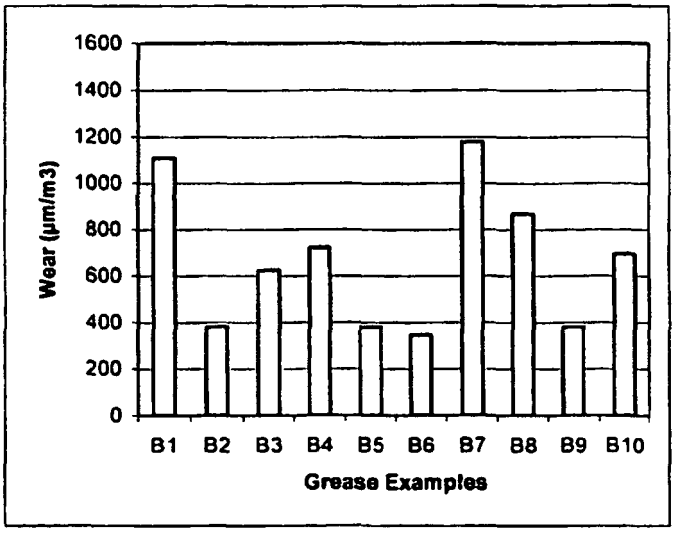

1600
1400
1200
1000
800
600
400
200
0
Wear (µm/m3)
B1 B2 B3 B4 B5 B6 B7 B8 B9 B10
Grease Examples

Fig. 4

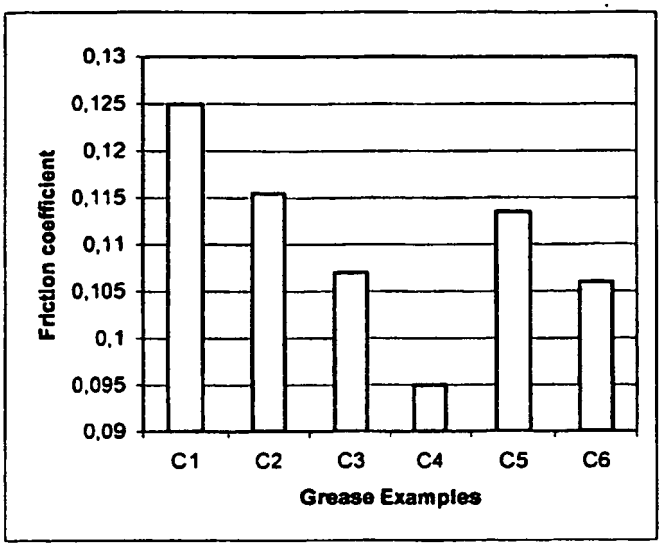

0,13
0,125
0,12
0,115
0,11
0,105
0,1
0,095
0,09
Friction coefficient
C1
C2
C3
C4
C5
C6
Grease Examples

Fig. 5

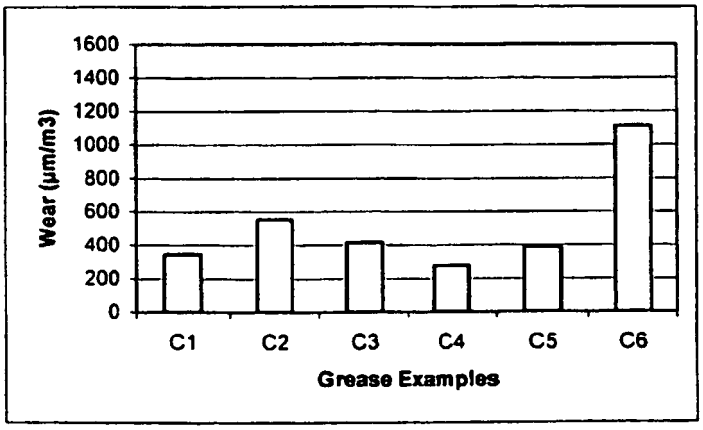

1600
1400
1200
1000
800
600
400
200
0
Wear (µm/m3)
C1
C2
C3
C4
C5
C6
Grease Examples

Fig. 6

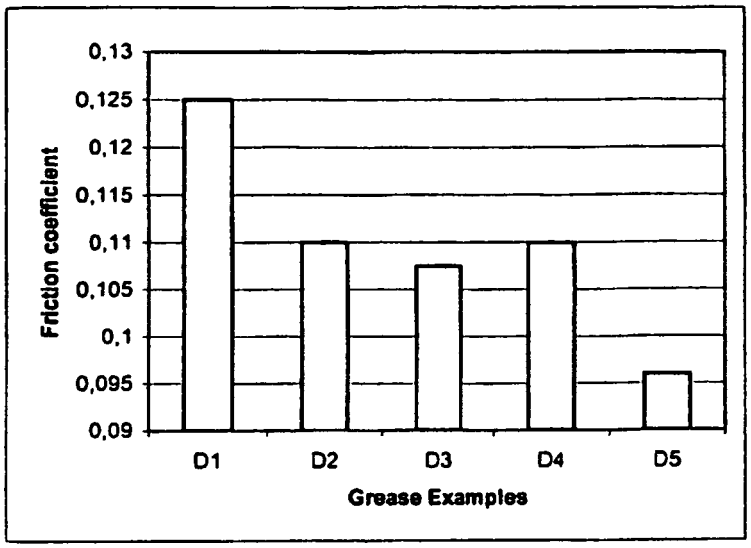

0,13
0,125
0,12
0,115
0,11
0,105
0,1
0,095
0,09
Friction coefficient
D1
D2
D3
D4
D5
Grease Examples

Fig. 7

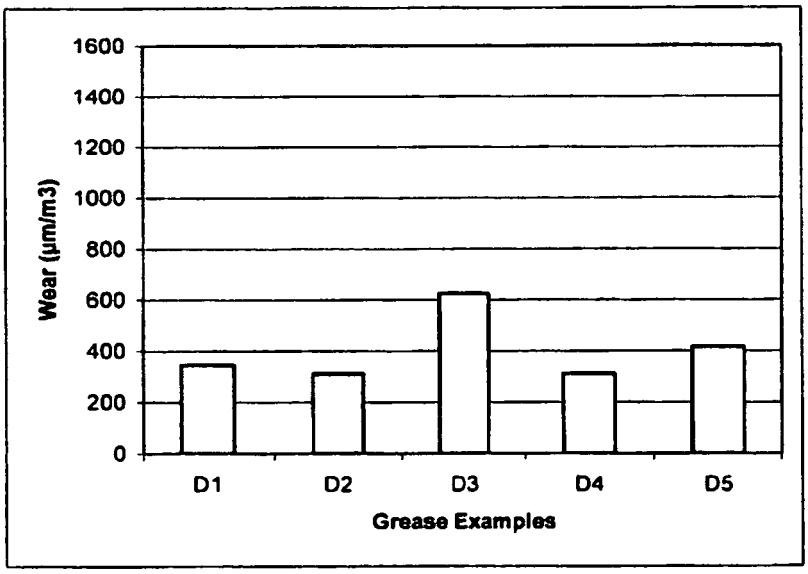

1600
1400
1200
1000
800
600
400
200
0
Wear (µm/m3)
D1
D2
D3
D4
D5
Grease Examples

Fig. 8

REFERENCES CITED IN THE DESCRIPTION

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