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(54) **GREASE COMPOSITION**

SCHMIERFETTZUSAMMENSETZUNG

COMPOSITION DE GRAISSE

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(73) Proprietor: **Shell Internationale Research Maatschappij B.V.**
2596 HR Den Haag (NL)

(72) Inventors:
- **TANAKA, Keiji**
  Tokyo
  Minato-ku 135-8074 (JP)
- **FUJIMAKI, Yoshitomo**
  Aikou
  Kanagawa 243-0303 (JP)

(74) Representative: **Shell Legal Services IP**
PO Box 384
2501 CJ The Hague (NL)

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Description

Field of the invention

[0001] This invention relates to a grease composition, and more specifically to a urea grease.

Background of the Invention

[0002] In the prior art, various kinds of urea-based greases have been proposed, depending on the applications. For example, Japanese Laid-open Patent 2000-198994 has disclosed a water-resistant urea-based grease, to be used in environments where it is in contact with water, characterised in that the urea-based grease is made to contain 0.2 to 15 wt% of a metal salicylate of specific structure. Japanese Laid-open Patent 2005-008745 has also disclosed a urea grease composition for use in constant velocity joints characterised in that the urea grease is made to contain a sulphurised molybdenum dialkyldithiocarbamate of specific structure, a triphenyl phosphorothionate of specific structure and a stearic acid metal salt.

[0003] Admixture of water is absolutely undesirable for grease lubrication. For this reason, steps are taken even in the design of machinery, by improving the structure of seals, to prevent as much as possible ingress of water from the outside. However, depending on the machine parts and given the operating environment, there are often points at which ingress of water cannot be avoided. For example, various bucket pins in construction machinery used outdoors, or sliding friction parts of their gears or cranes, bearings in various kinds of rolling machines in steelworks, wheel bearings or constant velocity joints in cars, bearings in water pumps or outboard motors, and bearings in washing machines are in environments where they are in contact with water, and it is often the case that water intrudes and causes damage through abnormal wear or flaking of machine parts. In the aforementioned Patent Reference 1, this situation is addressed by offering a urea-based grease having the property of maintaining a stable lubricating film in that the grease structure is not liable to break down even in operating environments where water has ingress to the grease and in that any water particles are present in a microscopic state even when there has been ingress of water into the grease through churning. However, although the greases disclosed in Patent References 1 and 2, not to mention others, do have satisfactory water-resistant life, even they have an issue with the water-resistant lubrication wear performance being unsatisfactory.

Summary of the Invention

[0004] This invention, therefore, addresses this situation by offering a urea-based grease exhibiting a long-term water-resistant life while having superior water-resistant lubrication wear performance.

[0005] By dint of repeated and intensive investigations in order to achieve the aforementioned goal, the present invention has been perfected by discovering that the above mentioned problems can be resolved by blending additives of three different kinds of constituents into a grease which uses a urea as a thickener.

[0006] More specifically, the invention is defined by the appended claims.

[0007] By virtue of this invention it is possible to offer a urea-based grease exhibiting a long-term water-resistant life while having superior water-resistant lubrication wear performance.

Brief Description of the Drawing

[0008] Figure 1 is a drawing showing an outline of a water-resistant lubrication life test rig.

Detailed description of the Invention

[0009] The grease composition pertaining to the present embodiment is a blend of specific additives to a urea grease. A detailed explanation is given below of the specific constituents, amounts of each constituent, method of preparation, physical properties and applications of the grease composition in this embodiment.

[0010] The invention is defined in and by the appended claims.

Grease composition (constituents)

- Base oil

[0011] There is no special restriction on the base oil used in the grease composition of the present embodiment. For example, it is possible to use the mineral oils, synthetic oils and animal or plant oils used in normal grease compositions. As specific examples mention may be made of those of Groups 1 to 5 of the base oil categories of the API (American

Petroleum Institute). What is meant by an API base oil category here is a classification in a range of base oil materials as defined by the American Petroleum Institute in order to create guidelines for lubricating oil base oils.

[0012] In this invention, there is no special restriction on the kind of mineral oil but, as preferred examples, mention may be made of paraffinic or naphthenic mineral oils obtained by means of one kind or a combination of two or more kinds of refining treatments such as solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, catalytic dewaxing, hydrorefining, sulphuric acid cleaning or clay treatment on lubricating oil fractions obtained by atmospheric distillation or vacuum distillation of crude oil.

[0013] In this invention, there is no special restriction on the kind of synthetic oil but, as preferred examples, mention may be made of poly-α-olefin (PAO) or hydrocarbon-based synthetic oils (oligomers). What is meant by a PAO is an α-olefin single polymer or copolymer. The α-olefins are compounds having a C-C double bond at the terminals and examples are butene, butadiene, hexene, cyclohexene, methylcyclohexene, octene, nonene, decene, dodecene, tetradecene, hexadecene, octadecene and eicosene. As examples of hydrocarbon-based synthetic oils (oligomers), mention may be made of ethylene, propylene and single polymers or copolymers of isobutene. These compounds may be used singly or in mixtures of two or more kinds. Also, provided they have a C-C double bond at a terminal, these compounds may have whichever structure the isomer structure can take, and may have either a branched structure or a straight-chain structure. It is also possible to combine use of two or more kinds of these structural isomers or double-bond position isomers. Of these olefins, those more preferred for use are straight-chain olefins of carbon number 6 to 30, because the flash point is too low with a carbon number of 5 or less and the viscosity is too high, and so not practical, with a carbon number of 31 or higher.

[0014] In this invention it is also possible to use as the base oil GTL (gas-to-liquid) oils synthesised by the Fischer-Tropsch process which is a technology for producing liquid fuels from natural gas. Compared with mineral oil base oils refined from crude oil, GTLs have a very low sulphur content and aromatic content, and a very high paraffin constituent ratio, so that they have superior oxidative stability and very small evaporation losses, which means they are ideal for possible use as a base oil in this invention.

• Thickener

[0015] Provided it is a urea thickener of the known art, there is no special restriction on the urea thickener used in the present embodiment, but ideally it will be a diurea thickener obtained by reacting 1 mol of a diisocyanate and 2 mol of a primary monoamine, a diurea thickener obtained by reacting 2 mol of a monoisocyanate and 2 mol of a primary diamine or a tetraurea thickener obtained by reacting 2 mol of a diisocyanate and 2 mol of a primary monoamine plus 1 mol of a primary diamine, or a triurea-monourethane thickener obtained by reacting 2 mol of a diisocyanate and 1 mol of a primary monoamine plus 1 mol of a primary diamine and further 1 mol of a higher alcohol. A diurea or a tetraurea thickener is best. These may be used as one kind or in combinations of two or more kinds.

[0016] As examples of the isocyanates which constitute the raw material, mention may be made of 4,4'-diphenylmethane diisocyanate (MDI), tolylene diisocyanate (TDI), 3,3'-dimethyl-4,4'-biphenylene diisocyanate (TODI), hexamethylene diisocyanate (HDI), naphthalene diisocyanate (NDI) and octadecyl diisocyanate (ODI). As examples of primary amines, mention may be made of octylamine (caprylamine), iso-octylamine, laurylamine, myristylamine, palmitylamine, stearylamine, iso-stearlyamine, behenylamine, oleylamine, linoleylamine, beef tallow amine, coconut amine, hydrogenated beef tallow amine, soybean amine, cyclohexylamine, aniline, p-chloroanaline, phenethylamine, o-toluidine, m-toluidine, p-toluidine and 2-naphthylamine. As examples of diamines, mention may be made of ethylenediamine, trimethylenediamine (propylenediamine), tetramethylenediamine (butylenediamine), pentamethylenediamine, hexamethylenediamine, 1,7-diaminoheptane, 1,8-diaminooctane, 1,9-diaminononane, 1,10-diaminodecane, o-phenylenediamine, m-phenylenediamine and p-phenylenediamine, and as salts thereof mention may be made of N-cocoalkyl-1,2-ethylenediamine, N-beef tallow alkyl-1,2-ethylenediamine, N-hardened beef tallow alkyl-1,2-ethylenediamine, N-cocoalkyl-1,3-propylenediamine, N-beef tallow alkyl-1,3-propylene diamine, N-hardened beef tallow alkyl-1,3-propylenediamine, N-cocoalkyl-1,4-butylenediamine, N-beef tallow alkyl-1,4-butylenediamine and N-hardened beef tallow alkyl-1,4-butylenediamine. As examples of higher alcohols, mention may be made of lauryl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol, behenyl alcohol, lanolin alcohol, hexyldecanol, octyldodecanol and isostearyl alcohol.

• Other thickeners

[0017] It is also possible to use thickeners other than urea compounds (other thickeners) together with the aforementioned thickener (urea) in the grease composition of the present embodiment. As examples of these other thickeners, mention may be made of tricalcium phosphate, alkali metal soaps, complex alkali metal soaps, alkaline earth metal soaps, complex alkaline earth metal soaps, alkali metal sulphonates, alkaline earth metal sulphonates, other metal soaps, metal terephthalate salts, monoureas, triurea-monourethanes, or polyureas other than diureas or tetraureas, or clays, silicas (silicon oxides) such as silica aerogels, and fluororesins such as polytetrafluoroethylene. These may be

used as one kind or in combinations of two or more kinds. It is also possible to use any other substances apart from these which can impart a thickening effect to the liquid matter.

• Additives

[0018] The grease composition of the present embodiment has specified additives (first, second and third constituents) added to the grease containing the aforementioned thickener (urea). By adding these additives to the urea-based grease composition both long-term water-resistant life and superior water-resistant lubrication wear performance are manifested.

• First constituent

[0019] The first additive constituent used in the present embodiment is an alkaline earth metal salicylate and/or an alkaline earth metal phenate.

[0020] As examples first of alkaline earth metal salicylates, mention may be made of the alkali metal salicylates known as metallic detergents. Alkaline earth metal salts of alkylsalicylic acids are ideal. Here, salts of magnesium and/or calcium as the alkaline earth metal are ideal, and calcium salts in particular are ideal. For the aforementioned alkyl groups, those of carbon number 4 to 30 are ideal, but 6 to 18 straight-chain or branched alkyl groups are even better. In addition, these may be straight-chain or branched and they may be primary alkyl groups, secondary alkyl groups or tertiary alkyl groups.

[0021] As examples next of the alkaline earth metal phenates, mention may be made of the alkali metal salicylates known as metallic detergents, and mention may be made of alkaline earth metal salts of alkylphenols, alkylphenol sulphides and alkylphenol Mannich reaction products, and especially the magnesium salts and/or calcium salts. Calcium salts in particular are ideal.

[0022] The alkaline earth metal salicylate and/or alkaline earth phenate based metallic detergents here are preferably metallic detergents having a total base number (BN) as stipulated in JIS K2501 (perchloric acid titration) of 5 to 600 mg KOH/g, but more preferably metallic detergents of 50 to 500 mg KOH/g, and still more preferably metallic detergents of 100 to 400 mg KOH/g. If the BN is within this range, should there be ingress of water into the urea grease of this invention, it will disperse more homogeneously in the base oil and will be more likely to maintain this state. The action will be to make further improvements in respect of the occurrence of rust and reduction of lubricity associated with the weakening and softening of the grease structure due to the influence of the water and also with free water due to insufficient moisture dispersion. The additive constituents of the metallic detergents may also contains salts of organic acids of one type or salts or organic acids of more than one type, and these may also be mixtures of neutral metallic detergents, overbased metallic detergents or both.

• Second constituent

[0023] The second additive constituent used in the present embodiment is a metal soap, specifically a stearic acid metal salt. As examples of the non-aqueous stearic acid metal salt here, mention may be made of salts of alkali metals (for example, lithium), alkaline earth metals (for example, magnesium, calcium or barium), aluminium and zinc. Special preference is given to the use of calcium and/or magnesium salts. Said constituent may be used as one kind or as a combination of a plurality of kinds.

• Third constituent

[0024] The third additive constituent used in the present embodiment is a calcium sulphonate and/or a zinc naphthenate.

[0025] The calcium sulphonate first is an ordinary calcium sulphonate, and as examples mention may be made of calcium salts of petroleum sulphonic acids, calcium salts of alkylaromatic sulphonic acids, overbased calcium salts of petroleum sulphonic acids and overbased calcium salts of alkyl aromatic sulphonic acids. Said constituents may be used singly or in mixtures.

[0026] The zinc naphthenate next is an ordinary zinc naphthenate, and as examples mention may be made of complex mixtures of naphthenic acid derived from selected crude oil fractions, ordinarily by reacting those fractions with a sodium hydroxide solution and then acidifying and refining them. The molecular weight of the naphthenic acid before the reaction with the zinc compound is preferably in the range 150 to 500, but more preferably 180 to 330.

• Freely chosen constituents

[0027] To the grease composition of the present embodiment it is possible further to add additives such as freely chosen anti-oxidants, rust preventatives, oiliness agents, extreme pressure additives, anti-wear agents, solid lubricants, metal deactivators, polymers, non-metallic detergents, colourants and water repellents, the total amount of the freely

chosen constituents, taking the total amount of the grease composition as 100 parts by mass, being approximately 0.1 to 20 parts by mass. Examples of anti-oxidants are 2,6-di-t-butyl-4-methylphenol, 2,6-di-t-butyl-para-cresol, p,p'-dioctyldiphenylamine, N-phenyl-α-naphthylamine or phenothiazine. Examples of rust preventatives are paraffin oxide, carboxylic acid metal salts, sulphonic acid metal salts, carboxylate esters, sulphonate esters, salicylate esters, succinate esters, sorbitan esters and various amine salts. Examples of oiliness agents and extreme pressure additives plus anti-wear agents include sulphurised zinc dialkyldithiophosphates, sulphurised zinc diaryldithiophosphates, sulphurised zinc dialkyldithiocarbamates, sulphurised zinc diaryldithiocarbamates, sulphurised molybdenum dialkyldithiophosphates, molybdenum diaryldithiophosphates, sulphurised molybdenum dialkyldithiocarbamates, sulphurised molybdenum diaryldithiocarbamates, organomolybdenum complexes, sulphurised olefins, triphenyl phosphate, triphenyl phosphorothionate, tricresyl phosphate, other phosphate esters and sulphurised oils and fats. Examples of solid lubricants include molybdenum disulphide, graphite, boron nitride, melamine cyanurate, PTFE (polytetrafluoroethylene), tungsten disulphide and graphite fluoride. As examples of metal deactivators mention may be made of N,N'-disalicylidene-1,2-diaminopropane, benzotriazoles, benzoimidazoles, benzothiazoles and thiadiazoles. As examples of polymers, mention may be made of polybutenes, polyisobutenes, polyisobutylenes, polyisopropenes and polymethacrylates. As examples of non-metallic detergents mention may be made of succinimides.

[0028] In particular, the grease composition of the present embodiment ideally contains alkyl organic acids and/or alkyl organic acid esters. As to what is meant here by alkyl organic acids or alkyl organic acid esters, mention may be made of formic acid, acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, isovaleric acid, caproic acid, enanthic acid (heptanoic acid), capric acid, 2-ethylhexanoic acid, pelargonic acid, undecylic acid, lauric acid, linderic acid, tridecylic acid, myristic acid, tsuzuic acid, physetoleic acid, myristoleic acid, pentadecylic acid, palmitic acid, palmitoylic acid, margaric acid, stearic acid, isostearic acid, petrosilinic acid, elaidic acid, oleic acid, vaccenic acid, linolic acid, linolenic acid, elaeostearic acid, eicosadienoic acid, eicosatrienoic acid, stearidonic acid, nonadecylic acid, tuberculostearic acid, arachidic acid, arachidonic acid, paulinic acid, eicosapentaenoic acid, heneicosylic acid, behenic acid, erucic acid, docosapentaenoic acid, docosahexaenoic acid, tricosylic acid, lignoceric acid, nervonic acid, cerotic acid, montanic acid, melissic acid and/or ester compounds comprised of these. By incorporating said constituent it becomes possible to maintain a long water-resistant lubrication life and to increase the water-resistant lubrication anti-wear performance.

Grease composition (amounts of each constituent in the blend)

[0029] Given next is an explanation of the amounts of base oil, thickeners, and additives in the blend of the grease composition of the present embodiment. As regards the amounts of freely chosen constituents in the blend, if they are necessary, they should be incorporated in the above mentioned amounts.

1. Base oil

[0030] The amount of base oil in the blend, taking the total amount of the grease composition as 100 parts by mass, will be preferably 50 to 95 parts by mass, but more preferably 60 to 90 parts by mass and yet more preferably 70 to 85 parts by mass.

2. Thickeners

[0031] The total amount of thickeners in the blend, taking the total amount of the grease composition as 100 parts by mass, will be preferably 3 to 50 parts by mass, but more preferably 5 to 40 parts by mass and yet more preferably 7 to 30 parts by mass. Also, the amount of the aforementioned urea compound in the blend, taking the total amount of the grease composition as 100 parts by mass, is 0.5 to 50 parts by mass. If the amount of the aforementioned urea in the blend is less than 0.5 parts by mass, it will become difficult to maintain sufficient hardness as a grease, and it will be prone to seep from the lubrication points no matter how much ingress of water there is, so that the targeted lubrication performance cannot be displayed. If there is more than 50 parts by mass, the grease will become too hard and the supply of base oil will be insufficient, so that there will be a likelihood of a reduction in lubrication performance. Costs will also rise.

3. Additives

• First constituent

[0032] The incorporated amount of alkaline earth metal salicylate and/or alkaline earth metal phenate metallic detergent, which is the first additive constituent, taking the total grease composition as 100 parts by mass, is 0.1 to 10 parts

by mass, but more preferably 0.3 to 7 parts by mass, and yet more preferably 0.5 to 5 parts by mass. If the amount of metallic detergent is less than 0.1 part by mass, although this will not impact on the hardness of the grease (it will not cause it to soften), it will not be possible sufficiently to disperse particles of water that have been mixed in the grease, and it may be difficult to maintain a stable lubricating film. If it is greater than 10 parts by mass, although this will improve dispersion of the water, the tendency of the grease to soften because of shearing will increase, and it will be prone to seep from lubrication points, so that it may not be possible to exhibit the targeted lubrication performance.

• Second constituent

[0033] The incorporated amount of metal soap being a non-aqueous stearic acid metal salt, which is the second additive constituent, taking the total grease composition as 100 parts by mass, is 0.1 to 10 parts by mass, but more preferably 0.3 to 7 parts by mass, and yet more preferably 0.5 to 5 parts by mass. If the amount of metal soap is less than 0.1 part by mass, it will not be possible sufficiently to disperse particles of water that have been mixed in the grease, and it may be difficult to maintain a stable lubricating film. If it is greater than 10 parts by mass, although this will improve dispersion of the water, costs will simply rise and no further effect can be expected.

Third constituent

[0034] The incorporated amount of calcium sulphonate and/or naphthenate, which is the third additive constituent, taking the total grease composition as 100 parts by mass, is 0.1 to 10 parts by mass, but more preferably 0.3 to 7 parts by mass, and yet more preferably 0.5 to 5 parts by mass. If the amount of these additives is less than 0.1 part by mass, it may become difficult to exhibit the above mentioned effects, and if it is greater than 10 parts by mass, inhibition of the occurrence of rust can be expected but the grease will become prone to seep out from lubrication points because of shearing, so that it may become difficult to obtain the targeted lubrication performance.

Physical characteristics of grease composition

• Worked penetration

[0035] In worked penetration tests, the grease composition of the present embodiment will preferably have a penetration of No. 00 to No. 4 (175 to 430), but more preferably a penetration of No. 2 to No. 3 (220 to 295). The penetration expresses the visual hardness. The values used here for penetration are for worked penetration as measured in accordance with JIS K 2220 7.

• Dropping point

[0036] The grease composition of the present embodiment has no correlation with the dropping point in terms of performance, but as a criterion for the structure of the urea grease thickener to achieve proper cohesion, it is preferably not less than or in excess of 180°C. The dropping point refers to the temperature at which a viscous grease loses the structure of the thickener as the temperature goes on rising. Measurement of the dropping point here is done in accordance with JIS K 2220 8.

• Shear stability when containing water

[0037] In a worked penetration test after a roll stability test, the grease composition of the present embodiment will preferably have a post-test penetration of not more than 395, and the difference between before the test and after the test will be not more than 90, but more preferably the post-test penetration will be not more than 355 and the difference between before the test and after the test will be not more than 70. If the post-test penetration exceeds 395, grease will become prone to leak out from the lubrication points of bearings and the like, and it may become impossible to supply lubricating grease to rubbing or sliding parts. If the difference between before the test and after the test exceeds 90, it will not be possible, in the first place, to describe the thickener structure as stable in respect of shear, and with long use softening may become severe and seepage will be accelerated. Shear stability with contained water here is determined in accordance with the roll stability test stipulated in ASTM D1831. Specifically, 10% by internal proportion of distilled water is blended with a pre-supplied grease (10% water to 90% grease) and made to disperse uniformly. 50 g of this grease is weighed out and supplied to the roll stability test, where shear is applied for 24 hours at 40°C. The grease is then removed and the worked penetration at 25°C is measured. To obtain the test's before-and-after penetration, the value of the penetration before the test is subtracted from the penetration after the test.

• Water-resistant lubrication life test

[0038] The lubrication life in a water-resistant lubrication life test of the grease composition of the present embodiment is preferably not less than 180 hours, but more preferably not less than 240 hours and yet more preferably not less than 300 hours. The procedure for the water-resistant lubrication life test is as follows. Figure 1 shows the outline of the water-resistant lubrication life test apparatus. As shown in said drawing, the test apparatus is designed to evaluate the lubrication life of a bearing while water is injected into the grease. This procedure is an improved version of the water-rinse water-resistance test apparatus stipulated in JIS K 2220 5.12. Specifically, circulating water is not sprayed (300 ml/min) into the bearing outer wheel guard (seal plate) of the test ball bearing as in the JIS, but distilled water is injected into the grease directly inside the housing, which means that it is possible to inject a more precise amount of water, which improves the reliability of the test and allows the lubrication life to be measured as accurately as possible. As to the specific method, 5.0 g of sample grease is packed into the test bearing and the bearing is installed in the housing, after which 100 ml of distilled water heated to 40°C is injected into the housing each minute, whilst running at 3,000 rpm. The injected water is discharged to the outside via the inside of the test bearing. As regards the grease life, this is taken to be the time for the bearing to reach a high torque because of unsatisfactory lubrication by the supplied grease, for the brake mechanism to actuate when the electric current of the motor which drives the bearing has exceeded 200% of the current in stable operation, and for the drive motor to come to a stop. The weight of the bearing before and after the test is also taken and calculated as the amount of wear of the bearing.

• Test conditions

[0039]

Test bearing: No. 22208EAE4 (self-centring rolling bearing)
Grease packing amount: 5.0 g
Speed: 3,000 rpm
Radial load: 15 kgf
Water temperature: 40°C
Water flow: 100 ml/min

Applications of grease composition

[0040] The grease composition of the present embodiment can of course be used in machinery, bearings and gears generally, but it can also exhibit superior performance in environments that are more severe for grease lubrication, for example in applications where there is the possibility of water ingress. For example, in cars, it is ideal for use in the lubrication of water pumps, cooling fan motors, starters, alternators and various actuator parts in the engine area, propeller shafts, constant velocity joints (CVJ), wheel bearings and clutches in the power train, and various other parts such as electric power steering (EPS), electric powered windows, damping devices, ball joints, door hinges, handles and brake expanders. In addition, it is preferred for use in various kinds of bearings and interfitting parts where there is the possibility of ingress of water in construction machinery such as power shovels, bulldozers and cranes, in the steelmaking industry, in paper mills, in forestry machinery, in agricultural machinery, in chemical plant, in electricity generation installations and in railway stock. As to other applications, mention may be made of seamless pipe joints and to bearings in outboard motors; for these applications it is also ideal.

Detailed Description of the Drawings

[0041] In Figure 1, the following references indicate the following parts:

A	=	Housing
B	=	Motor
C	=	Ammeter
D	=	Drained water
E	=	Hot water
F	=	Constant hot-water tank

(continued)

G	=	Roller pump
H	=	Inside the housing
I	=	Test bearing Self-centring roller bearing No. 22208EAE4 Speed: 3,000 rpm

Examples

[0042] The invention is next explained by means of examples of embodiment and comparative examples, but the invention is in no way limited by these examples.

Raw materials

[0043] The raw materials used in Examples of Embodiment 1 to 7 and Comparative Examples 1 to 3 were as follows.

Base oil:

[0044] * Base oil A: Mixture, in the proportions of 80 parts by mass to 20 parts by mass, of a paraffinic mineral oil obtained by dewaxing and solvent refining and belonging to Group 1 of the API (American Petroleum Institute) classification (kinematic viscosity at 100°C 11.25 mm^2/s, viscosity index 97) and a naphthenic mineral oil belonging to Group (kinematic viscosity at 100°C 10.71 mm^2/s, viscosity index 30).

Thickeners:

[0045]

* Urea A: Diurea thickener synthesised from 4,4'-diphenylmethane diisocyanate and octylamine plus laurylamine.
* Urea B: Diurea thickener synthesised from 4,4'-diphenylmethane diisocyanate and octylamine plus oleylamine.
* Urea C: Diurea thickener synthesised from 4,4'-diphenylmethane diisocyanate and stearylamine plus hexamethylenediamine.

Additives:

[0046]

* Additive A: Calcium salicylate (M7125, made by Infineum Ltd.) (BN 350 mg KOH/g)
* Additive B: Calcium salicylate (M7121, made by Infineum Ltd.) (BN 225 mg KOH/g)
* Additive E: Calcium phenate (Lz6490, made by Lubrizol Corp.) (BN 145 mg KOH/g)
* Additive G: Calcium 12-hydroxystearate (SC-12H, made by Sakai Chemical Industry Co. Ltd.)
* Additive H: Calcium stearate (calcium stearate made by NOF Corp.)
* Additive M: Calcium sulphonate (Na-sul729, made by King Industries, Inc.) (BN 0.26 mg KOH/g)
* Additive N: Calcium sulphonate (Lz5342, made by Lubrizol Corp.) (BN 307 mg KOH/g)
* Additive O: Zinc naphthenate (DAILUBE Z510, made by DIC Corp.)
* Additive P: Alkyl organic acid/alkyl organic acid ester and zinc·calcium complex salt (K-CORR G-1086A, made by King Industries, Inc.)
* Additive Q: Sodium sulphonate (Lz5318A, made by Lubrizol Corp.) (BN 448 mg KOH/g)

Method of preparation

[0047] The grease compositions of Examples of Embodiment 1 to 7 and Comparative Examples 1 to 3 were obtained by methods of the known art.

Tests

[0048] Tests were carried on the examples of embodiment and comparative examples, by the above mentioned test methods, in respect of dropping point, worked penetration, roll stability test and water-resistant lubrication life. The properties of the various greases of the examples of embodiment and comparative examples obtained are shown in Table 1. The worked penetration of the greases of the examples of embodiment and comparative examples was in every case No. 2 or No. 2.5 penetration. The dropping point for all the greases was not less than 220°C, values not at all inferior for urea greases. As to the criterion of water resistance, an evaluation was made on the basis of the results of a roll stability test, performed with samples mixed with 10% water in the grease, and a water-resistant lubrication life test.

[0049] These results demonstrated superior lubricity in all cases for the greases of the examples of embodiment over the greases of the comparative examples. Specifically, all the greases in the examples of embodiment had a long water-resistant lubrication life of over 400 minutes. In addition, in the water-resistant lubrication wear resistance test, the amount of bearing wear was substantially below 20 mg. According to verification tests within the same framework, the results were that "Example of Embodiment 6" containing an alkyl organic acid or alkyl organic acid ester and containing both a calcium sulphonate and a zinc naphthenate had the best water-resistant lubrication wear resistance, followed by "Example of Embodiment 5" containing both a calcium sulphonate and a zinc naphthenate, then came "Example of Embodiment 1" and "Example of Embodiment 4" containing either a calcium sulphonate or a zinc naphthenate. On the other hand, the greases of the comparative examples had inferior results in respect of either or both of water-resistant lubrication life and water-resistant lubrication wear resistance.

Table 1

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Comp Ex. 1	Comp Ex. 2	Comp. Ex. 3
Thickener	Urea A	10		10	10	10	10		10	10	Own company's commercial product, tetraurea grease
	Urea B		10								
	Urea C							13.5			
Base oil	Base oil A	87	87	87	87	87	87	83.5	87	87	
First additive	Additive A		1.5					1.5			
	Additive B	1.5			1.5	1.5	1.5		1.5	1.5	
	Additive E			1.5							
Second additive	Additive G		1					1			
	Additive H	1		1	1	1	1		1.5	1	
Third additive	Additive M					0.10		0.5			
	Additive N	0.5	0.5	0.5		0.20					
	Additive O				0.5	0.20					
	Additive P						0.5				
	Additive Q									0.5	
Additives total (mass%)		3	3	3	3	3	3	3	3	3	
Total (mass%)		100	100	100	100	100	100	100	100	100	
Worked penetration		279	269	277	276	274	278	286	269	270	263
NLGI viscosity grade No.		2	2	2	2	2	2	2	2	2	2.5
Dropping point °C		238	232	237	241	242	234	265	230	228	243
Roll stability test 10% water content, 40°C, 24 hrs	Worked penetration after test	342	333	335	331	333	332	351	316	357	422
	Difference in worked penetration before and after test	63	64	58	55	59	54	65	47	87	159
Water-resistant lubrication life test - Life, min		>400	>400	>400	>400	>400	>400	>400	>400	<400	<400
Water-resistant lubrication wear resistance test (running for 120 min) – Bearing wear mg		14.7	12.6	16.9	15.4	12.8	12.3	14.3	23.7	19.4	112.5[1]

[1] value after stopping at 58 minutes.

Claims

1. Grease composition containing, a urea compound as a thickener, a base oil, an alkaline earth metal salicylate and/or an alkaline earth metal phenate as a first additive constituent, a metal soap, being a stearic acid metal salt, as a second additive constituent, and a calcium sulphonate and/or a zinc naphthenate as a third additive constituent, wherein the blended amount of the aforementioned urea compound is 0.5 to 50 parts by mass, wherein the blended amount of the aforementioned first constituent is 0.1 to 10 parts by mass, wherein the blended amount of the aforementioned second constituent is 0.1 to 10 parts by mass, and the blended amount of the aforementioned third constituent is 0.1 to 10 parts by mass, taking the total grease composition as 100 parts by mass.

2. Grease composition in accordance with Claim 1 containing both a calcium sulphonate and a zinc naphthenate as

the aforementioned third constituent.

3. Grease composition in accordance with Claim 1 or 2 further containing an alkyl organic acid and/or an alkyl organic acid ester.

4. Grease composition in accordance with any of Claims 1 to 3 wherein the thickener is a diurea or a tetraurea.

5. Grease composition in accordance with any of Claims 1 to 4 wherein the BN of the aforementioned first constituent is 5 to 600 mg KOH/g.

Patentansprüche

1. Schmierfettzusammensetzung, die Folgendes enthält: eine Harnstoffverbindung als ein Verdickungsmittel, ein Grundöl, ein Erdalkalimetallsalicylat und/oder ein Erdalkalimetallphenat als einen ersten Additivbestandteil, eine Metallseife, die ein Stearinsäuremetallsalz ist, als einen zweiten Additivbestandteil und ein Calciumsulfonat und/oder ein Zinknaphthenat als einen dritten Additivbestandteil, wobei die gemischte Menge der vorgenannten Harnstoffverbindung 0,5 bis 50 Masse-% beträgt, wobei die gemischte Menge des vorgenannten ersten Bestandteils 0,1 bis 10 Masse-% beträgt, wobei die gemischte Menge des vorgenannten zweiten Bestandteils 0,1 bis 10 Masse-% beträgt und die gemischte Menge des vorgenannten dritten Bestandteils 0,1 bis 10 Masse-% beträgt, wobei die gesamte Schmierfettzusammensetzung als 100 Masse-% angenommen wird.

2. Schmierfettzusammensetzung nach Anspruch 1, die als den vorgenannten dritten Bestandteil sowohl ein Calciumsulfonat als auch ein Zinknaphthenat enthält.

3. Schmierfettzusammensetzung nach Anspruch 1 oder 2, die ferner eine organische Alkylsäure und/oder einen organischen Alkylsäureester enthält.

4. Schmierfettzusammensetzung nach einem der Ansprüche 1 bis 3, wobei das Verdickungsmittel ein Diharnstoff oder ein Tetraharnstoff ist.

5. Schmierfettzusammensetzung nach einem der Ansprüche 1 bis 4, wobei die BN des vorgenannten ersten Bestandteils 5 bis 600 mg KOH/g beträgt.

Revendications

1. Composition de graisse contenant, un composé d'urée comme épaississant, une huile de base, un salicylate de métal alcalinoterreux et/ou un phénate de métal alcalinoterreux comme premier constituant additif, un savon métallique, étant un sel métallique de l'acide stéarique, comme deuxième constituant additif, et un sulfonate de calcium et/ou un naphténate de zinc en tant que troisième constituant additif, dans lequel la quantité mélangée du composé d'urée susmentionné est de 0,5 à 50 parties en masse, dans laquelle la quantité mélangée du premier constituant susmentionné est de 0,1 à 10 parties en masse, dans laquelle la quantité mélangée du deuxième constituant susmentionné est de 0,1 à 10 parties en masse, et la quantité mélangée du troisième constituant susmentionné est de 0,1 à 10 parties en masse, en prenant la composition totale de graisse comme 100 parties en masse.

2. Composition de graisse selon la revendication 1, contenant à la fois un sulfonate de calcium et un naphténate de zinc comme troisième constituant susmentionné.

3. Composition de graisse selon la revendication 1 ou 2, contenant en outre un acide alkyle organique et/ou un ester d'acide alkyle organique.

4. Composition de graisse selon l'une quelconque des revendications 1 à 3, dans laquelle l'épaississant est une diurée ou une tétraurée.

5. Composition de graisse selon l'une quelconque des revendications 1 à 4, dans laquelle le BN du premier constituant susmentionné est de 5 à 600 mg de KOH/g.

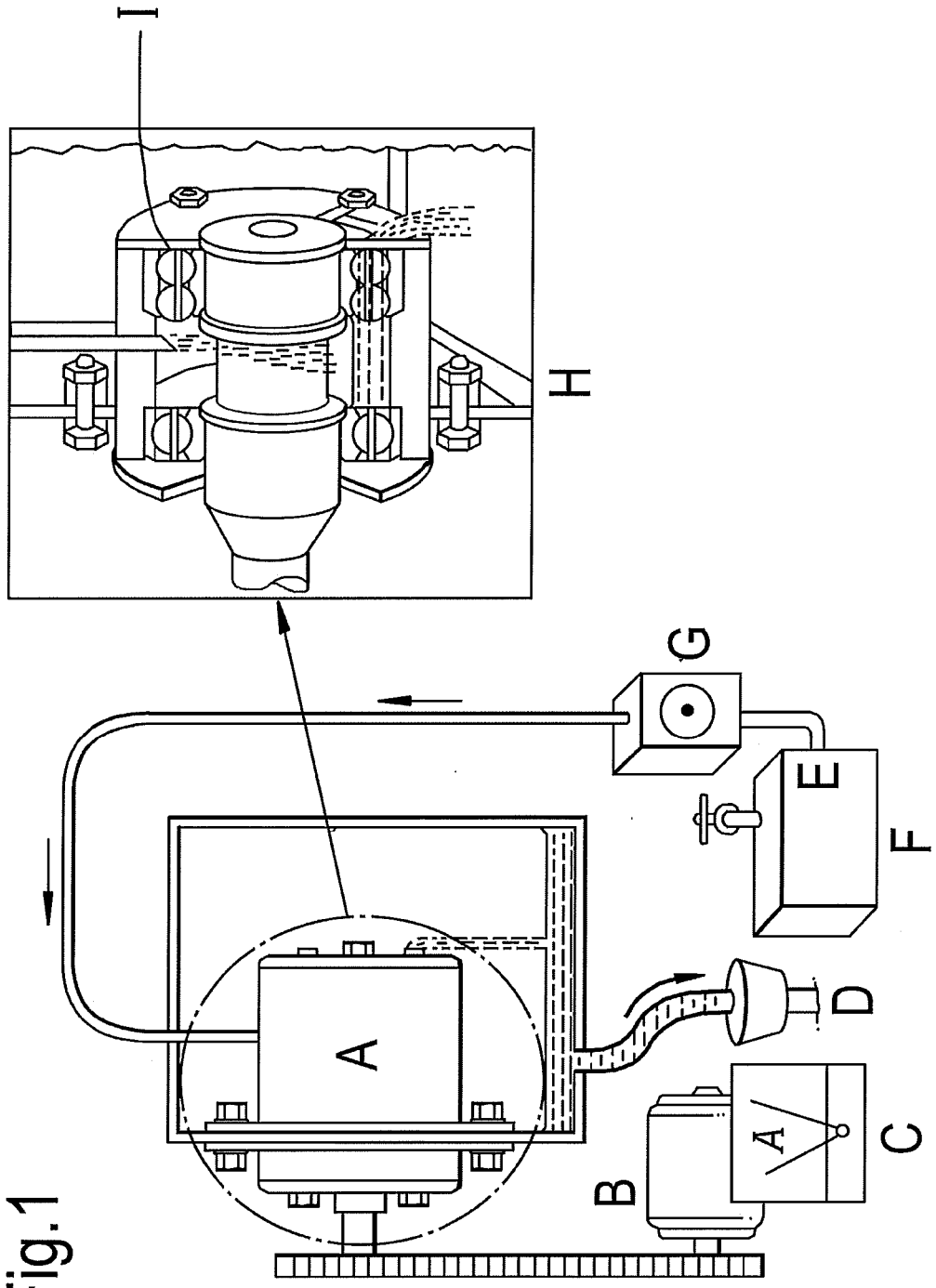

Fig.1

REFERENCES CITED IN THE DESCRIPTION

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