Description

The present invention relates to a grease composition which contains a base fluid and a thickening agent, and is free from potentially hazardous additives.

Grease compositions are generally used in environments where water, in minute or substantial quantity, is present. While the compositions provide lubrication they may fail to protect the metal parts with which they are in contact, from rust formation. Required are grease compositions that provide excellent lubrication and inhibit rust formation. To achieve this goal it has been proposed to add anti-rust additives to the grease composition. Particularly effective in this regard is sodium nitrite. Although this compound adds slightly to the oxidation stability of the composition, an antioxidant is included as well. Suitable and effective antioxidants are amines and products derived from amines. However, it is known that a combination of nitrites and amines may produce nitrosamines, some of which are believed to be carcinogenic. This problem is acknowledged by the persons skilled in the art and efforts have been undertaken to prevent the formation of nitrosamines. For example, in United States patent specification No. 4,200,542 it is described that the inhibition of nitrosamine formation can be obtained by adding to the grease composition a combination of an ascorbate or iso-ascorbate with alpha tocopherol. Although the latter combination is claimed to be effective, it is evident that only grease compositions that do not contain nitrites and/or amine derivatives can adequately solve the problem of nitrosamine formation.

US-A-2 714 092 discloses a lithium base grease which incorporates about 0.25 to 5 per cent, and preferably about 1 to 3 per cent, by weight of an oil-soluble metal alkyl salicylate whereof the benzene nucleus of the salicylate bears 1 to 3 C_{5-30} alkyl radicals, provided that the total number of carbon atoms in the alkyl substitution on each benzene nucleus is at least 10, and preferably about 18 to 30 or more, the metal being a divalent metal selected from the group consisting of zinc, magnesium, barium, calcium and strontium.

FR-A-974 374 discloses lubricant compositions containing minor amounts of at least two organic salts with dissimilar cations, the acid radicals of these salts being other than an aliphatic carboxylic acid and at least one of the acid radicals being a hydroxy aromatic acid radical.

Surprisingly it has been found that calcium alkyl salicylate when added to a grease composition shows excellent anti-rust properties, so that addition of sodium nitrite is no longer required. However, the dropping point of the grease composition, i.e. the temperature at which the grease passes from a semi-solid to a liquid phase, is lowered by the addition of calcium alkyl salicylate. It has now surprisingly been found that grease compositions containing a combination of calcium alkyl salicylate and magnesium alkyl salicylate show excellent anti-rust properties and have satisfactory dropping points.

Accordingly, the present invention provides a grease composition comprising a base fluid, a thickening agent, calcium alkyl salicylate and magnesium alkyl salicylate. It appears that grease compositions according to the invention not only have excellent anti-rust properties and satisfactory dropping points, but also water washout characteristics which are superior to sodium nitrite-containing grease compositions.

The base fluid can be any lubricating agent known in the art. This includes mineral hydrocarbon oils, synthetic hydrocarbon oils, polymeric compounds such as polyolefins and polyglycols, esters such as dialkylsebacate, polysiloxanes, phenoxy phenyl ethers, and other lubricants, or mixtures thereof. Preferred are mineral and synthetic hydrocarbon oils. These oils may have been subjected to certain treatments, in particular a hydrotreatment. Suitably the viscosity of the lubricating agent is between 2 and 60mm^2/s at 100°C, preferably between 3 and 50mm^2/s at this temperature.

Thickening agents can be selected from a wide range of compounds which include substituted ureas, phthalocyanines, clays modified by treatment with a surface-active agent, which clays can be chosen from for example montmorillonites, in particular bentonite or attapulgite, zeolites or other complex inorganic silicates which occur naturally. Preferably the thickening agent is selected from alkali and alkaline earth metal soaps of fatty acids having from 6 to 30 carbon atoms. The metal salts applied in the soap are preferably lithium and/or calcium salts. When alkali metal and alkaline earth metal salts are used in combination the weight ratio of alkali metal : alkaline earth metal is suitably from 1 : 2 to 20 : 1. Suitable fatty acids are stearic acid, hydroxystearic acid, oleic acid, palmitic acid, myristic acid or hydrogenated natural oil fatty acids, in particular hydrogenated castor oil fatty acid. These soaps may be used in combination with an alkali metal salt, in particular lithium salt, selected from the di alkali metal salt of C_{4-12} aliphatic dicarboxylic acid, the alkali metal salt of aromatic hydroxy carboxylic acids and alkali metal salts of boric acids, such as lithium metaborate, lithium tetraborate, lithium perborate or the monolithium salt of orthoboric acid or with phosphate, phosphite or thiophosphate esters.

The alkyl salicylates may be neutral calcium and magnesium salts. Preferably, at least one of the alkyl salicylates is overbased ; particularly preferred is the case when both alkyl salicylates are overbased. The preparation of overbased metal alkyl salicylates is known in the art. A suitable method is described in UK

patent application No. 2,097,417. The overbased metal alkyl salicylates are usually complexes of the metal hydroxide and/or carbonate and alkyl salicylate. The degree of overbasing is expressed as the basicity index (BI) defined as the equivalent ratio of metal : alkyl salicylic acid. The calcium alkyl salicylate suitably has a basicity index of from 1 to 15, preferably from 2 to 10, and the magnesium alkyl salicylate has suitably a basicity index of from 1 to 15, preferably from 2 to 8. The advantage of using overbased alkyl salicylates resides in that they now can neutralise acid compounds which may be formed when the grease compostion is actually being used, so that a corrosive attack of metal parts by these acid compounds is prevented.

The length of the alkyl chain of the alkyl salicylate plays an important role in the uniformity of the distribution thereof in the grease composition. Generally the chain length may vary between 5 and 50 carbon atoms, preferably from 10 to 35 carbon atoms. The chains may be branched, but suitably are straight. The amount of calcium alkyl salicylate is preferably between 0.1 and 10%w, in particular between 0.5 and 5%w, and the amount of magnesium alkyl salicylate in suitably from 0,05 to 5, in particular from 0.1 to 3%w, all percentages being based on the weight of the total composition.

The composition according to the invention may further contain several other compounds and additives. These include alcohols like glycol, glycerol, trimethylolpropane, pentaerythritol, linseed or castor oil ; anti-wear and extreme pressure additives such as triphenylphosphorothionate, zinc dialkyl dithio phosphate, lead naphthenate or sulphurized fatty oils ; antioxidants such as diaryl amines, e.g. diphenylamines phenyl-naphthylamines, or alkylated derivatives thereof and other conventional additives.

The composition can be prepared by any of the techniques known in the art to be useful for the preparation of greases. For the preparation of a soap-containing grease these techniques include processes in which the desired fatty acid or acids are incorporated in a suitable base fluid, e. g. a mineral base stock oil, and the resulting mixture is neutralized with suitable alkali metal or alkaline earth metal compounds, and also processes in which the desired soap is prepared separately and thereafter is incorporated in the base fluid. The alkyl salicylates are suitably mixed with the composition obtained, i.e. a mixture of the soap and the base fluid. Another suitable method for preparing the composition according to the invention comprises saponifying an ester from which the suitable fatty acid is to be obtained in the presence of alkali or alkaline earth metal compounds and of base fluid at elevated temperature, e.g. from 120 to 250°C, dehydrating the mixture obtained, adding additional base fluid to the dehydrated mixture and cooling the grease obtained. The metal alkyl salicylates are suitably mixed BK37.005 with the grease composition during the cooling stage. The preparations can be carried out batchwise or in a continuous manner.

The invention is illustrated by means of the following Examples.

EXAMPLE 1

To show the effect of calcium and magnesium alkyl salicylates on the dropping point and anti-rust properties of a grease composition a number of greases were prepared having various amounts of calcium alkyl salicylate and magnesium alkyl salicylate.

The base grease composition tested comprised

11.0%w of the lithium and calcium soaps of hydrogenated castor oil fatty acid, with a Li : Ca weight ratio of 6 ;

4.5%w of a package of conventional anti-oxidant, anti-corrosion and extreme pressure/anti-wear additives.

84.5%w mineral hydrocarbon oil having a kinematic viscosity of 100mm²/s at 40°C and a viscosity index of 90 (corresponding to a kinematic viscosity of 10.2mm²/s at 100°C).

To this base grease overbased calcium C_{14-18} alkylsalicylate (Ca-AS) having a BI of 3.0 and overbased magnesium C_{14-18} alkyl salicylate (Mg-AS) having a BI of 7.5 were added in amounts as indicated in Table I. The weight percentages are based on the weight of the above base grease composition.

The compositions were subjected to a dropping point test (IP 132) and an anti-rust test (IP 220, using salt water). The rating of the latter test ranges from 0 (= no rust) to 5 (= rusty areas covering more than 10% of the surface). The results are shown in Table I.

TABLE I

Composition No.	Ca-AS %w	Mg-AS %w	Dropping point (IP 132), °C	Anti-rust (IP 220)
1	-	-	198	5
2	2	-	179	2
3	3	-	177	0
4	2	1	188	2
5	3	1	187	0

From the results it is apparent that Ca-AS improves the anti-rust properties considerably and that the co-addition of Mg-AS effectively counteracts a dropping point decrease caused by the addition of Ca-AS.

EXAMPLE 2

In this Example grease compositions containing sodium nitrite and Ca-AS and Mg-AS are compared.
Grease composition 6 contained
11.0%w hydrogenated castor oil fatty acid
1.6%w lithium hydroxide monohydrate
2.0%w sodium nitrite
5.3%w of a package of conventional anti-oxidant and extreme pressure/anti-wear additives.
80.1%w hydrocarbon oil used in Example 1
Grease composition 7 contained

12.0%w hydrogenated castor oil fatty acid
1.5%w lithium hydroxide monohydrate
0.2%w calcium hydroxide
4.3%w of a package of conventional anti-oxidant, anti-corrosion and extreme pressure/anti-wear additives.
3.0%w Ca-AS, as used in Example 1
1.0%w Mg-AS, as used in Example
78.0%w hydrocarbon oil used in Example 1
A number of characteristics of the compositions was determined. These are indicated in Table II.

TABLE II

Composition No.		6	7
Penetration unworked/worked (IP 50),	dmm	239/243	238/248
Dropping point (IP 132),	°C	186	185
Water wash-out (ASTM D 1264),	%w	50	1.3
Anti-rust (ASTM D1743),	rating	1	1
Copper corrosion (IP 112)		slight tarnish	Negative
Oil separation (IP 121) 18 hr/7d,	%w	0.41/1.68	0.39/1.72
Roll test (ASTM D1831, modified such that penetration difference is determined after 100 h):			
at ambient temperature,	dmm	112	29
at 100°C	dmm	122	94

From the above results it is apparent that the grease composition according to the present invention has similar or better characteristics than the prior art composition. In particular the water resistance is improved considerably.

Claims

1. Grease composition comprising a base fluid, a thickening agent, calcium alkyl salicylate and magnesium alkyl salicylate.

2. Grease composition according to claim 1, in which the thickening agent is an alkali or alkaline earth metal soap of a fatty acid having from 9 to 30 carbon atoms per molecule.

3. Grease composition according to claim 2, in which as the fatty acid hydrogenated castor oil fatty acid is used.

4. Grease composition according to claim 2 or 3, in which the metals are lithium and/or calcium.

5. Grease composition according to any one of claims 1-4, in which the calcium alkyl salicylate has a basicity index of from 1 to 15, and the magnesium alkyl salicylate has a basicity index of from 1 to 15.

6. Grease composition according to anyone of claims 1-5, in which the metal alkyl salicylates have an alkyl moiety of from 5 to 50 carbon atoms.

7. Grease composition according to any one of claims 1-6, in which the amount of calcium alkyl salicylate is from 0.1 to 10%w and the amount of magnesium alkyl salicylate is from 0.05 to 5%w, based on the weight of the total composition.

8. A grease composition according to claim 1 comprising a base fluid, a thickening agent and from 0.1 to 10.0 per cent weight of an over-based calcium alkyl salicylate based on the weight of the total grease composition having a basicity of from 1 to 15, wherein said alkyl moiety has from 5 to 50 carbon atoms and from 0.05 to 5.0 weight per cent of an over-based magnesium alkyl salicylate based on the weight of the total grease composition having a basicity index of from 1 to 8, wherein said alkyl moiety has from 5 to 50 carbon atoms.

9. Process for the preparation of a grease composition comprising mixing calcium alkyl salicylate and magnesium alkyl salicylate with a mixture containing a fatty acid soap and a base fluid.

10. Process according to claim 9, in which the mixture containing a fatty acid soap and a base fluid has been prepared by

(i) incorporating the fatty acid or acids in the base fluid and neutralizing the resulting mixture with alkali metal and/or alkaline earth metal compounds ; or

(ii) preparing the fatty acid soap separately and incorporating it in the base fluid ; or

TABLE II

Composition No.		6	7
Penetration unworked/worked (IP 50),	dmm	239/243	238/248
Dropping point (IP 132),	°C	186	185
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Oil separation (IP 121) 18 hr/7d,	%w	0.41/1.68	0.39/1.72
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Claims

1. Grease composition comprising a base fluid, a thickening agent, calcium alkyl salicylate and magnesium alkyl salicylate.

2. Grease composition according to claim 1, in which the thickening agent is an alkali or alkaline earth metal soap of a fatty acid having from 9 to 30 carbon atoms per molecule.

3. Grease composition according to claim 2, in which as the fatty acid hydrogenated castor oil fatty acid is used.

4. Grease composition according to claim 2 or 3, in which the metals are lithium and/or calcium.

5. Grease composition according to any one of claims 1-4, in which the calcium alkyl salicylate has a basicity index of from 1 to 15, and the magnesium alkyl salicylate has a basicity index of from 1 to 15.

6. Grease composition according to anyone of claims 1-5, in which the metal alkyl salicylates have an alkyl moiety of from 5 to 50 carbon atoms.

7. Grease composition according to any one of claims 1-6, in which the amount of calcium alkyl salicylate is from 0.1 to 10%w and the amount of magnesium alkyl salicylate is from 0.05 to 5%w, based on the weight of the total composition.

8. A grease composition according to claim 1 comprising a base fluid, a thickening agent and from 0.1 to 10.0 per cent weight of an over-based calcium alkyl salicylate based on the weight of the total grease composition having a basicity of from 1 to 15, wherein said alkyl moiety has from 5 to 50 carbon atoms and from 0.05 to 5.0 weight per cent of an over-based magnesium alkyl salicylate based on the weight of the total grease composition having a basicity index of from 1 to 8, wherein said alkyl moiety has from 5 to 50 carbon atoms.

9. Process for the preparation of a grease composition comprising mixing calcium alkyl salicylate and magnesium alkyl salicylate with a mixture containing a fatty acid soap and a base fluid.

10. Process according to claim 9, in which the mixture containing a fatty acid soap and a base fluid has been prepared by

(i) incorporating the fatty acid or acids in the base fluid and neutralizing the resulting mixture with alkali metal and/or alkaline earth metal compounds ; or

(ii) preparing the fatty acid soap separately and incorporating it in the base fluid ; or

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(iii) saponifying an ester from which the fatty acid is to be obtained in the presence of alkali or alkaline earth metal compounds and of base fluid at elevated temperature, dehydrating the mixture obtained, adding additional base fluid to the dehydrated mixture and cooling the grease obtained.

Ansprüche

1. Fettzusammensetzung, umfassend ein Grundfluid, ein Verdickungsmittel, Kalziumalkylsalicylat und Magnesiumalkylsalicylat.

2. Fettzusammensetzung nach Anspruch 1, worin das Verdickungsmittel eine Alkali- oder Erdalkalimetallseife einer Fettsäure mit 9 bis 30 Kohlenstoffatomen je Molekül ist.

3. Fettzusammensetzung nach Anspruch 2, worin hydrierte Rizinusölfett-säure als Fettsäure verwendet wird.

4. Fettzusammensetzung nach Anspruch 2 oder 3, worin die Metalle Lithium und/oder Kalzium sind.

5. Fettzusammensetzung nach einem der Ansprüche 1 bis 4, worin das Kalziumalkylsalicylat einen Basizitätsindex von 1 bis 15 aufweist und das Magnesiumalkylsalicylat einen Basizitätsindex von 1 bis 15 hat.

6. Fettzusammensetzung nach einem der Ansprüche 1 bis 5, worin die Metallalkylsalicylate einen Alkylrest mit 5 bis 50 Kohlenstoffatomen aufweisen.

7. Fettzusammensetzung nach einem der Ansprüche 1 bis 6, worin der Anteil an Kalziumalkylsalicylat von 0,1 bis 10 Gew.-% und der Anteil an Magnesiumalkylsalicylat von 0,05 bis 5 Gew.-% beträgt, bezogen auf das Gewicht der gesamten Zusammensetzung.

8. Fettzusammensetzung nach Anspruch 1, umfassend ein Grundfluid, ein Verdickungsmittel un von 0,1 bis 10,0 Gew.-% eines überbasischen Kalziumalkylsalicylats, bezogen auf das Gewicht der Gesamtfettzu-sammensetzung, mit einem Basizitätsindex von 1 bis 15, worin der Alkylrest 5 bis 50 Kohlenstoffatome aufweist, und 0,05 bis 5,0 Gew.-% eines überbasischen Magnesiumalkylsalicylats, bezogen auf das Gewicht der Gesamtfettzusammensetzung, mit einem Basizitätsindex von 1 bis 8, worin der Alkylrest 5 bis 50 Kohlenstoffatome aufweist.

9. Verfahren zur Herstellung einer Fettzusammensetzung, umfassend das Vermischen von Kalziumalkylsalicylat und Magnesiumalkylsalicylat mit einem eine Fettsäureseife und ein Grundfluid enthaltenden Gemisch.

10. Verfahren nach Anspruch 9, worin das eine Fettsäureseife und ein Grundfluid enthaltende Gemisch durch

(i) Einarbeiten der Fettsäure oder der Fettsäuren in das Grund-fluid und Neutralisieren des gebildeten Gemisches mit Alkali-metall- und/oder Erdalkalimetallverbindungen ; oder

(ii) gesondertes Bereiten der Fettsäureseife und Einarbeiten der-selben in das Grundfluid ; oder

(iii) Verseifen eines Esters, aus dem die Fettsäure erhalten werden soll, in Arwesenheit von Alkali- oder Erdalkalimentallverbin-dungen und eines Grundfluids bei erhöhter Temperatur, Ent-wässern des erhaltenen Gemisches, Zusetzen von weiterem Grund-fluid zu dem entwässerten Gemisch und Abkühlen des erhaltenen Fettes hergestellt worden ist.

Revendications

1. Composition de graisse comprenant un fluide de base, un agent épaississant, un alcoyl salicylate de calcium et un alcoyl salicylate de magnésium.

2. Composition de graisse selon la revendication 1, dans laquelle l'agent épaississant est un savon de métal alcalin ou alcalino-terreux d'un acide gras ayant de 9 à 30 atomes de carbone par molécule.

3. Composition de graisse selon la revendication 2, dans laquelle on utilise l'acide gras d'huile de ricin hydrogénée.

4. Composition de graisse selon la revendication 2 ou 3, dans laquelle les métaux sont du lithium et/ou du calcium.

5. Composition de graisse selon l'une quelconque des revendications 1-4, dans laquelle l'alcoyl salicylate de calcium a un indice de basicité de 1 à 15 et l'alcoyl salicylate de magnésium a un indice de basicité de 1 à 15.

6. Composition de graisse selon l'une quelconque des revendications 1-5, dans laquelle les alcoyl salicylates de métaux ont une portion alcoyle ayant de 5 à 50 atomes de carbone.

7. Composition de graisse selon l'une quelconque des revendications 1-6, dans laquelle la quantité

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d'alcoyl salicylate de calcium est comprise entre 0,1 et 10% en poids et la quantité d'alcoyl salicylate de magnésium est comprise entre 0,05 et 5% en poids, par rapport au poids de la composition totale.

8. Composition de graisse selon la revendication 1 comprenant un fluide de base, un agent épaississant et de 0,1 à 10,0 pour cent en poids d'un alcoyl salicylate de calcium hyperbasique par rapport au poids de la composition de graisse totale ayant un indice de basicité compris entre 1 et 15, dont la portion alcoyle a de 5 à 50 atomes de carbone, et de 0,05 à 5,0 pour cent en poids d'un alcoyl salicylaté de magnésium hyperbasique par rapport à la composition de graisse totale ayant un indice de basicité compris entre 1 et 8, dont la portion alcoyle a de 5 à 50 atomes de carbone.

9. Procédé pour la préparation d'une composition de graisse comprenant l'opération de mélange d'un alcoyl salicylate de calcium et d'un alcoyl salicylate de magnésium avec un mélange contenant un savon d'acide gras et un fluide de base.

10. Procédé selon la revendication 9, dans lequel le mélange contenant un savon d'acide gras et un fluide de base a été préparé

(i) en incorporant l'acide gras ou les acides gras dans un fluide de base et en neutralisant le mélange résultant avec des composés de métaux alcalins et/ou de métaux alcalino-terreux ; ou

(ii) en préparant le savon d'acide gras séparément et en l'incorporant dans le fluide de base ; ou

(iii) en saponifiant un ester à partir duquel l'acide gras sera obtenu en présence de composés de métaux alcalins ou alcalino-terreux et de fluide de base à température élevée, en déshydratant le mélange obtenu, en ajoutant du fluide de base supplémentaire au mélange déshydraté et en refroidissant la graisse obtenue.