(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 174 110**
A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **85305686.9**

(22) Date of filing: **12.08.85**

(51) Int. Cl.[4]: **C10M 169/06** , //C10N50:10,(C10M169/06,117:-04,139:00)

(30) Priority: **22.08.84 US 643344**

(43) Date of publication of application: **12.03.86 Bulletin 86/11**

(84) Designated Contracting States: **AT BE CH DE FR GB IT LI LU NL SE**

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(54) Grease composition.

(57) Grease compositions including borated alkoxylated alcohols as friction-reducing additives, are thickened with a proportion of metal hydroxy-containing soap grease thickener. Such compositions have unexpectedly high dropping points.

EP 0 174 110 A1

GREASE COMPOSITION

This invention relates to grease compositions comprising oil, hydroxy-containing soap thickener and borated alkoxylated alcohols and optionally, phosphorus and sulfur moieties.

Borated alkoxylated alcohols have been used in commercial lubricant formulations to provide improvements in lubricating properties. This is known from U.S. Patent 3,711,411, which describes hydraulic fluids containing such products.

It is known also that borated esters and related borates can be used in other areas. For example, U.S. Patent 3,740,358 describes a phenol-aldehyde foamable compositions containing boron compounds, for example a material formed by reacting boric acid or boric oxide with an aliphatic hydroxyl-containing compound. However, no effort has been made hitherto to employ borated alkoxylated alcohols in combination with a metal hydroxy-containing soap thickeners in grease compositions.

In accordance with the invention, there is provided a grease composition containing a major proportion of a grease and a minor amount of a compound prepared by reacting an alkoxylated alcohol or mixtures of such alcohols having the formula

$$RO(R^1O)_xH$$

in which R is a hydrocarbyl group containing from 7 to 30 carbon atoms, preferably 9 to 18 carbon atoms, R^1 is a hydrocarbylene group containing from 2 to 4 carbon atoms and x has a value from 1 to 10, with a boron compound selected from boric acid, boric oxide, metaborate and alkyl borate of the formula

$$(R^2O)_y\,B(OH)_z$$

in which y is 1, 2 or 3, z is 0, 1 or 2, the sum of y and z is 3, and the or each R^2 is an alkyl group containing from 1 to 6 carbon atoms, characterized in that the grease contains a thickener comprising a hydroxy-containing soap. Such compositions have been found to possess substantially higher dropping points compared to compositions thickened with other thickeners. The presence of phosphorus and sulfur moieties provides an even higher dropping point.

Preferably the alkoxylated alcohol is overborated, that is to say the borated product contains more than a stoichiometric amount of boron.

The hydrocarbyl group can be a cyclic or a straight or branched chain hydrocarbon group and can contain one or more unsaturated sites. The hydrocarbyl group is preferably an alkyl group, for example octyl, nonyl, decyl, dodecyl, isotridecyl, tetradecyl, pentadecyl, heptadecyl and octadecyl. Other possible hydrocarbyl groups include propylcyclohexyl, butylcyclohexyl, oleyl, stearyl, isostearyl, coco and mixtures thereof as well as similar groups. It may be preferable to use alkoxylated alcohols that have been prepared using a mixture of alcohols. The hydrocarbyl group can also be an aryl group, in which the aryl nucleus has 6 to l4 carbon atoms. The hydrocarbylene group is preferably an alkylene group, for example ethylene, propylene and butylene.

The alkoxylated alcohols are themselves well known, as are methods for preparing them. In general, they can be made by reacting, in the presence of a catalyst, an alcohol with an epoxide such as ethylene oxide or propylene oxide.

Boration of the alkoxylated alcohols is accomplished with the boron compound described above. The reaction can be carried out in the presence of a solvent and, in general, any relatively non-polar, unreactive solvent can be used, including benzene, toluene, xylene and 1,4-dioxane. Mixtures of such solvents can also be used. Reaction temperatures of from about 90 to about 280°C can be used. Reaction times can be from 1 to 24 hours or more. Up to a stoichiometric amount of boric acid or alkyl borate is preferably used to yield a product containing from about 0.1 to about 10% of boron. At least 5 to 10% of the available hydroxyl groups on the alcohol can be borated to derive substantial beneficial effect.

Conversely, a stoichiometric excess of boric acid (more than an equivalent amount of borating agent compared to alcohol hydroxyl groups) can also be used resulting in a product containing an even greater amount of boron.

The alkoxylated alcohols can also be borated with an alkyl borate such as mono-, di- or trimethyl borate, mono-, di- or triethyl borate, mono-, di- or tripropyl borate, mono-, di- or tributyl borate, mono-, di- or triaryl borate or mono-, di- or trihexyl borate, often in the presence of boric acid.

Preferred reaction temperatures for boration with boric acid are from about 110 to about 200°C and with the borate from about 160 to about 240°C. The temperature chosen will depend for the most part on the particular reactants and on whether or not a solvent is used. In carrying out this reaction, it is preferable that quantities of reactants are chosen such that the molar ratio of alkoxylated alcohol to boron compound is from about 6:1 to about 1:6, preferably from about 3:1 to about 2:1. As stated above, the alkoxylated alcohol can be reacted with an excess of the borating species to form a borate ester containing from about 0.1% by weight of boron to as much as 10% or more of boron.

While atmospheric pressure is generally preferred, the reaction can be carried out under a pressure of up to 500 kPa.

A particular class of thickening agents is used to make the grease compositions of the invention. The thickening agents are those containing at least a portion of alkali metal or alkaline earth metal or amine soaps of hydroxyl-containing fatty acids, fatty glycerides and fatty esters having from 12 to about 30 carbon atoms per molecule. The metals are typified by sodium, lithium, calcium and barium with lithium being the preferred metal. Preferred acids and fatty materials are 12-hydroxystearic acid and glycerides and esters containing 12-hydroxystearates, 14-hydroxystearic acid, 16-hydroxystearic acid and 6-hydroxystearic acid.

These thickeners need not constitute the total amount of thickeners in the grease compositions. Significant benefit can be attained using as little as about 15% by weight of these thickeners, based on the total thickeners. A complementary amount, that is up to about 85% by weight, of a wide variety of other thickening agents can be used in the grease compositions of the invention. Included among the other useful thickening agents are alkali metal and alkaline earth metal soaps of methyl-12-hydroxystearate, diesters of C_4 to C_{12} dicarboxylic acids and tall oil fatty acids. Other alkali or alkaline earth metal fatty acids containing from 12 to 30 carbon atoms and no free hydroxyl groups may be used. These include soaps of stearic and oleic acids.

Other thickening agents include salt and salt-soap complexes as calcium stearate-acetate (U.S. Patent 2,197,263), barium stearate acetate (U.S. Patent 2,564,561), calcium, stearate-caprylate-acetate complexes (U.S. Patent 2,999,065), calcium caprylate-acetate (U.S. Patent 2,999,066), and calcium salts and soaps of low-, intermediate- and high-molecular weight acids and of nut oil

acids. These thickening agents can be produced in open kettles, pressurized vessels or continuous manufacturing units. All of these production methods are commonly used for greases and have the necessary supporting equipment to process the grease during and after manufacture of the thickener.

Another group of thickening agents comprises substituted ureas, phthalocyamines, indanthrene, pigments such as perylimides, pyromellitdiimides, and ammeline, as well as certain hydrophobic clays. These thickening agents can be prepared from clays which are initially hydrophilic in character, but which have been converted into a hydrophobic

$$[(R^3O)_2PZ-]_nM$$

in which R^3 is a hydrocarbyl group containing 3 to 18 carbon atoms, M is a metal or non-metal, n is the valence of M and each Z is oxygen or sulfur with at least one Z being sulfur.

In this compound, R^3 is preferably an alkyl group and may be a propyl, butyl, pentyl, hexyl, octyl, decyl, dodecyl, tetradecyl or octadecyl group, but also includes those derived from isopropanol, butanol, isobutanol, sec-butanol, 4-methyl-2-pentanol, 2-ethylhexanol, oleyl alcohol, and mixtures thereof. Further included are alkaryl groups such as butylphenyl, octylphenyl, nonylphenyl and dodecylphenyl groups.

The metals covered by M include those in Groups IA, IB, IIA, IB, IIB, VIB and VIII of the Periodic Table. Some that may be mentioned are lithium, sodium, calcium, barium, zinc, cadmium, silver, molybdenum and gold. Non-metallic ions include organic groups derived from vinyl esters such as vinyl acetate, vinyl ethers such as butyl vinyl ether and epoxides such as propylene oxide and 1,2-epoxydodecane. Non-metallic ions also include compounds derived from hydrocarbylamines such as alkylamines, tertiaryalkylamines, alkyldiamines or arylamines, as well as those derived from oleylamine, N-oleyl-1,3-propylenediamine, imidazolines and oxazolines.

The phosphorus and sulfur moieties can also be supplied from the combination of two or more separate compounds, such as the combination of (1) a dihydrocarbyl phosphite having 2 to 10 carbon atoms in each hydrocarbyl group or mixtures of phosphites and (2) a sulfide such as sulfurized isobutylene, dibenzyl disulfide, sulfurized terpenes and sulfurized jojoba oil. The phosphites embrace the dibutyl, dihexyl, dioctyl, didecyl and similar phosphites. Hydrocarbyl phosphate esters containing 4 to 20 carbon atoms in each hydrocarbyl group, can also be used. These include esters such as tributyl phosphate, tridecyl phosphate, tricresyl phosphate and mixtures thereof. Mono- and dihydrocarbyl esters are also useful.

In accordance with the invention, the total thickener will contain at least about 15% by weight of a metal or non-metal hydroxy-containing soap and the grease will contain from about 3% to about 20% by weight of total thickener based on the grease composition.

The grease composition also contains from about 0.01% to about 10% by weight, preferably from about 0.1% to about 2%, of a borated alkoxylated alcohol which has been prepared by reacting an alkoxylated alcohol with preferably at least an equimolar amount of boron compound.

The composition may also contain from 0.01% to about 10% by weight, preferably from 0.2% to 2% by weight of phosphorus- and sulfur-containing compounds or a mixture of two or more compounds which together supply the phosphorus and sulfur moieties. If separate compounds are used, an amount of the mixture equivalent to the required concentration is used to supply desired amounts of phosphorus and sulfur.

It has been found that grease compositions according to the invention containing both the hydroxy-containing thickeners and the borated alkoxylated alcohols, have dropping points consistently and unexpectedly higher than those of greases derived from the same grease vehicles and the same borated alkoxylated alcohols, but with different thickeners, for example non-hydroxy-containing thickeners.

In general, the borated alkoxylated alcohols and the phosphorus and sulfur moieties may be employed in any amount which is effective for imparting the desired degree of friction reduction, antiwear activity, antioxidant activity, high temperature stability or antirust activity. In many applications, however, the borated alkoxylated alcohol and the phosphorus- and/or sulfur-containing compound(s) are effectively employed in combined amounts of from about 0.02% to about 20% by weight, and preferably from about 0.2% to about 4% by weight, based on the total composition.

The grease compositions of the invention can be made from either mineral oil or synthetic oil, or mixtures thereof. In general, mineral oils, both paraffinic, naphthenic and mixtures thereof, may be of any suitable lubricating viscosity range, as for example, from about 45 SSU at 38°C to about 6000 SSU at 38°C, and preferably from about 50 to about 250 SSU at 99°C. These oils may have viscosity indexes ranging to about 100 or higher. Viscosity indexes from about 70 to about 95 are preferred. The average molecular weights of these oils may range from about 250 to about 800. In making the grease, the lubricating oil from which it is prepared is generally employed in an amount sufficient to balance the total grease composition, after accounting for the desired quantity of the thickening agent and other additive components.

When synthetic oils are used in preference to mineral oils, various materials may be utilized. Typical synthetic vehicles include polyisobutylene, polybutenes, hydrogenated polydecenes, polypropylene glycol, polyethylene glycol, trimethylol propane esters, neopentyl and pentaerythritol esters, di(2-ethylhexyl) sebacate, di(2-ethylhexyl) adipate, dibutyl phthalate, fluorocarbons, silicate esters, silanes, esters of phosphorus-containing acids, liquid ureas, ferrocene derivatives, hydrogenated synthetic oils, chain-type polyphenyls, siloxanes and silicones (polysiloxanes), alkyl-substituted diphenyl ethers typified by a butyl-substituted bis(p-phenoxy phenyl) ether, phenoxy phenylethers. Other additives providing antirust, antioxidant antiwear/EP, anticorrosion, and other desired properties can be used with the greases of this invention.

condition by the introduction of long-chain hydrocarbon radicals into the surface of the clay particles prior to their use as a component of a grease composition, for example by being subjected to a preliminary treatment with an organic cationic surface active agent, such as an onium compound. Typical onium compounds are tetraalkylammonium chlorides, such as dimethyl dioctadecyl ammonium chloride, dimethyl dibenzyl ammonium chloride and mixtures thereof.

An optional component of the grease compositions are phosphorus and sulfur moieties. Both of these can be present in the same molecule, such as in a metal or non-metal phosphorodithioate of the formula

The grease compositions according to the invention possess the advantages of increased dropping point and improved grease consistency properties and exhibit antirust characteristics and potential antifatigue, antiwear and antioxidant benefits unavailable in any known grease. The grease compositions of the invention have the additional advantage that they can be manufactured simply by mixing additive quantities of the alkoxylated alcohol borates to the fully formed soap grease after completion of saponification.

The following Examples illustrated the invention.

EXAMPLE 1

BORATED ALCOHOL ETHOXYLATE

175g of commercial C_{12} to C_{15} alkanol triethoxylate having an average molecular weight of 338, containing approximately 3.0 ethylene oxide groups per molecule and having a hydroxyl number of 166, was charged to a 500 ml glass reactor equipped with agitator, Dean-Stark tube and slow nitrogen purge of vapor space. Approximately 13g of boric acid and about 50g of toluene were added and the reaction mixture was heated to 160°C and maintained for a period of 6 hours until azeotropic distillation of water ceased. Approximately 120g of water was collected. Solvent was removed by vacuum distillation and the product was filtered through diatomaceous earth to yield a clear, light-colored, oil-soluble fluid.

EXAMPLE 2

BORATED ALCOHOL ETHOXYLATE

Approximately 274g of commercial C_9 to C_{11} alcohol ethoxylate containing approximately 2.6 moles of ethylene oxide per molecule, having a molecular weight of approximately 274 and a hydroxyl number of 205, was charged to a 1000 ml reactor equipped as described in Example 1. Approximately 22g of boric acid and about 50g of toluene solvent were added. The reaction mixture was heated to 195°C and maintained for a period of 4 hours until azeotropic distillation of water ceased. The toluene was removed by vacuum distillation and the product was filtered over diatomaceous earth to yield a clear, light-colored, oil-soluble liquid.

EXAMPLE 3

A lithium hydroxystearate grease thickener was prepared by saponification of a mixture containing 12-hydroxystearic acid (8% by weight) and the glyceride thereof (9% by weight) with lithium hydroxide in a mineral oil vehicle at about 177°C in a closed vessel. After depressuring and dehydrating the thickener in an open kettle, sufficient mineral oil was added to reduce the thickener content to about 9.0%. After cooling to about 99°C, a typical grease additive package, consisting of an amine antioxidant, phenolic antioxidant, 1.5% zinc dithiophosphate derived from mixed C_3 secondary and C_6 primary alcohols, sulfur-containing metal deactivator and nitrogen containing antirust additives, was added.

EXAMPLE 4

Two percent by weight of the reaction product of Example 1 was added at 110 to 115°C, with vigorous stirring, to the base grease of Example 3.

EXAMPLE 5

Two percent by weight of the reaction product of Example 2 was added at 110 to 115°C, with vigorous stirring, to the base grease of Example 3.

The base grease of Example 3 and the compositions of Examples 4 and 5 were tested for dropping point characteristics in accordance with ASTM D2265. The results are summarized in the Table below. For comparison, the dropping points of the following compositions were determined also.

EXAMPLE 6

A base grease similar to that of Example 3 but thickened with the lithium soap of a 50/50 by weight mixture of stearic and palmitic acids.

EXAMPLE 7

A 50/50 by weight mixture of the base grease of Example 3 and the base grease of Example 6.

EXAMPLE 8

The base grease of Example 6 plus 2% by weight of the borated ethoxylate of Example 1.

TABLE

PRODUCT OF EXAMPLE	DROPPING POINT, °C
3	202
4	237
5	305
6	209
7	190
8	207

Claims

1. A grease composition comprising a major amount of a grease and from 0.01 to 10% by weight based on the total composition, of the reaction product of an alkoxylated alcohol of the formula

$$RO(R^IO)_xH$$

in which R is a hydrocarbyl group containing from 7 to 30 carbon atoms, R^I is a hydrocarbylene group containing from 2 to 4 carbon atoms and x has a value from 1 to 10, with a boron compound selected from boric acid, boric oxide, metaborate and alkyl borate of the formula

$$(R^2O)yB(OH)_z$$

in which y is 1, 2 or 3, z is 0, 1 or 2, the sum of y and z is 3, and the or each R^2 is an alkyl group having 1 to 6 carbon atoms, characterized in that the grease also comprises a thickener containing at least 15% by weight of a hydroxy-containing soap thickener.

2. A composition according to Claim 1, additionally containing from 0.01 to 10% by weight, based on the total composition, of a phosphorus and sulfur compound or a mixture of phosphorus-containing and sulfur-containing compounds to supply equivalent amounts of phosphorus and sulfur.

3. A composition according to Claim 1 or Claim 2, wherein the thickener is an alkali metal soap, alkaline earth metal soap or amine soap of a hydroxy-containing fatty acid, fatty glyceride or fatty ester containing 12 to 30 carbon atoms.

4. A composition according to Claim 3, wherein the soap is a sodium, lithium, calcium or barium soap.

5. A composition according to Claim 3, wherein the thickener is derived from 12-hydroxystearic acid, 14-hydroxystearic acid, 16-hydroxystearic acid, 6-hydroxystearic acid or ester or glyceride thereof.

6. A composition according to any one of Claims 1 to 5, wherein the grease vehicle is a mineral oil.

7. A composition according to any one of Claims 1 to 5, wherein the grease vehicle is a synthetic oil.

8. A composition according to any one of Claims 1 to 5, wherein the grease vehicle is a mixture of mineral and synthetic oils.

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EUROPEAN SEARCH REPORT

Application number

EP 85 30 5686

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-4 440 656 (A.G. HORODYSKY) * Claims 1-11; column 2, line 63 - column 3, line 35 * -----	1-8	C 10 M 169/06 // C 10 N 50/10 (C 10 M 169/06 C 10 M 117:04 C 10 M 139:00)

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 10 M 169

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22-11-1985	ROTSAERT L.D.C.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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