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(54) Grease composition.

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

EP 0 176 202 A1

GREASE COMPOSITION

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

Borated diols have been used in commercial lubricant formulations to provide improvements in lubricating properties. They have also, on occasion, been used in brake fluid formulations.

The grease compositions containing one or more of hydroxy-containing soaps, one or more of the disclosed borated diols and one or more of the sulfur- and phosphorus-containing compositions described herein provide advantages in increased dropping point, improved grease consistency properties, antirust characteristics and potential antifatigue, antiwear and antioxidant benefits unavailable in any prior grease. In addition, unlike any of such prior art greases, the high dropping point extended temperature range metallic soap greases of this invention are preferably manufactured by mixing additive quantities of the diol borates to the fully formed soap grease after completion of saponification.

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 a diol, preferably vicinal, of the formula

$$R(OH)_2$$

in which R is a C_8 to C_{30} hydrocarbyl group, with a boron compound, for example boric acid, boric oxide, metaborate or alkyl borate of the formula

$$(R^1O)_yB(OH)_z$$

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^1 is an alkyl group containing from 1 to 6 carbon atoms, characterized in that the grease comprises a thickener containing a hydroxy-containing soap thickener. Such compositions have been foiund to possess substantially higher dropping points compared to compositions thickened with other thickeners. The presence of phosphorus and sulfur moieties provides an even higher drop point.

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

The borated product used in the compositions of this invention can be made using a single diol or two or more diols. A mixture of diols can contain from about 5% to about 95% by weight of any one diol, the other diol or diols being selected such that it or they together comprise from about 95% to about 5% by weight of the mixture. Such mixtures are often preferred to a single diol.

The hydrocarbyl vicinal diols can be linear, branched or cyclic, saturated or unsaturated, with linear saturated vicinal diols being preferred to maximize friction reduction. The two hydroxyl groups can be anywhere along the hydrocarbyl chain, and they are preferably on adjacent carbon atoms (vicinal), but the terminal diols are especially preferred.

The preferred vicinal diols can be synthesized using several known methods, such as the method described in , J. Am. Chem. Soc.,68, 1504 (1946), which involves the hydroxylation of 1-olefins with peracids. Vicinal diols can be prepared also by the peroxytrifluoroacetic acid method for the hydroxylation of olefins as described in J. Am. Chem. Soc.,76, 3472 (1954). Similar procedures are described in U.S. Patents 2,411,762, 2,457,329 and 2,455,892. Vicinal diols can also be prepared via catalytic epoxidation of appropriate olefins followed by hydrolysis.

The preferred borated vicinal diols contain 12 to 20 carbon atoms. Below a carbon number of 12, friction-reducing properties begin to diminish. Preferred are the C_{14}-C_{18} hydrocarbyl groups in which solubility, frictional characteristics and other properties are maximized.

Among the preferred diols there may be mentioned 1,2-octanediol, 1,2-decanediol, 1,2-dodecanediol, 1,2-tetradecanediol, 1,2-pentadecanediol, 1,2-octanedecanediol, 1,2-eicosanediol, 1,2-triacontanediol, 1,2-mixed C_{15} to C_{18}-alkanediols, as well as diols derived from epoxide derivatives of propylene oligomers such as the trimers and tetramer and from butylene oligomers such as the trimers, and mixtures of any two or more such compounds.

Reaction of the diol with the boron compound can be preformed at reaction temperatures of 90 to 260°C or more, but 110 to 200°C is preferred. Up to a stoichiometric amount of boric acid or other boron compound can be used, or an excess can be used to yield a product containing from about 0.1 to about 10% of boron. At least 5% to 10% of the available hydroxy groups of the diol should be borated to derive substantial beneficial effect. The alkyl borates that can be used include mono-, di- and trialkyl borates, such as mono-, di- and trimethyl, triethyl, tripropyl, tributyl, triamyl and trihexyl borates, often in the presence of boric acid. Times for boration using any of these boron compounds can be from about 2 to about 12 hours or more.

While atmospheric pressure is generally preferred when using any of these borating agents, the reaction can be advantageously carried out under a pressure of up to 500 kPa. Furthermore, where boration conditions warrant it, a solvent may be used. In general, any relatively non-polar, unreactive solvent can be used, including benzene, toluene, xylene and 1,4-dioxane. Other hydrocarbon and alcoholic solvents, which include propanol and butanol, can be used. Mixtures of alcoholic and hydrocarbon solvents can be used also.

A particular class of thickening agents is used to make the grease compositions of the invention. These thickening agents are those containing at least a portion of alkali metal or alkaline earth metal or amine or hydrocarbylamine soaps of hydroxy-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. Preferred is lithium. Preferred members among these acids and fatty materials are those derived from 12-hydroxystearic acid and glycerides 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 thereof as about 15% by weight of the hydroxy-containing thickener, 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 and alkaline earth metal soaps of methyl-12-hydroxystearate, diesters of a 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 hydroxy 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 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

$$[(R^2O)_2\overset{\overset{Z}{\|}}{P}Z-]_nM$$

in which R^2 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^2 is preferably an alkyl group and may be a propyl, butyl, pentyl, hexyl, octyl, decyl, dodecyl, tetradecyl or octadecyl group, including 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, 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 organic amine moieties such as hydrocarbylamines, e.g., mono- and diamines. Such amines embrace oleylamine as well as the imidazolines and the oxazolines.

The phosphorus and sulfur can also be supplied from the combination of two 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. Phosphate esters containing 4 to 20 carbon atoms in each hydrocarbyl group, such as tributyl phosphate, tridecyl phosphate, tricresyl phosphate and mixtures of such phosphates, can also be used.

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 present from about 3% to about 20% by weight of thickener, based on the grease composition.

The grease composition also contains from about 0.01% to about 10% by weight, preferably about 0.1% to about 2%, of a borated diol, preferably prepared by reacting the diol with at least an equimolar amount of boron.

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 separately 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 diols, have dropping points consistently and unexpectedly higher than those of greases derived from the same grease vehicles and the same borated diols, but with different thickeners, for example non-hydroxy-containing thickeners.

In general, the borated diols 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 diol and the phosphorus- and/or sulfur-containing compound(s) are effectively employed in combined amounts 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 I00 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 compounds of this type 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.

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 antixodiant 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 diol borates to the fully formed soap grease after completion of saponification.

The following Examples illustrate the invention.

EXAMPLE 1

Approximately 1500 g of 1,2-mixed C_{15}-C_{18} diols (containing approximately 28% 1,2-pentadecane-diol, 28% 1,2-hexadecanediol, 28% 1,2-heptadecanediol and 16% 1,2-octadecanediol), 600 g of toluene and 235 g of boric acid where charged to a 5 liter reactor equipped with agitator, heater, Dean-Stark tube with a condenser and provision for blanketing vapor space with nitrogen. The reactor contents were heated to about 155°C and kept there until water evolution ceased. The solvent was removed by vacuum topping at 150°C and the product was filtered through diatomaceous earth at about 120°C.

EXAMPLE 2

A lithium hydroxystearate grease thickener was prepared by saponification of a mixture containing 12-hydroxystearic acid (8% by weight) and glyceride thereof (9% by weight) with lithium hydroxide in a mineral oil vehicle at about 174°C in a closed vessel. After depressuring and dehydration of the thickener in an open·kettle, sufficient mineral oil was added to reduce the thickener content to about 9.0%. After cooling to about 74°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 3

After dehydrating the thickener in an open kettle, 2.0% by weight of the boron ester of Example 1 was added to the grease concentrate of Example 2. The concentrate was heated at 110 - 116°C.

EXAMPLE 4

A base grease was thickened with the lithium soap of a 50/50 by weight mixture of stearic and palmitic acids, containing only non-hydroxy soap thickeners.

EXAMPLE 5

The base grease of Example 2 and the base grease of Example 4 were mixed to form a 50/50 by weight mixture of hydroxy and non-hydroxy thickeners..

EXAMPLE 6

The base grease of Example 4 was mixed with 2% by weight of the borated diol product of Example 1.

The grease compositions of Examples 2 to 6 were tested in the ASTM D2265 Dropping Point Test. The result as shown in the following Table.

TABLE

PRODUCT OF EXAMPLE	DROPPING POINT, °C
2	201
3	305
4	209
5	190
6	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 a diol of the formula

$$R(OH)_2$$

in which R is a hydrocarbyl group containing from 8 to 30 carbon atoms and a boron compound, selected from boric acid, boric oxide, metaborated and alkyl borate of the formula

$$R^1O_yB(OH)_z$$

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^1 is an alkyl group having 1 to 6 carbon atoms, characterized in that the grease also comprises thickener containing 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 in an amount sufficient to supply an 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 or 16-hydroxystearic acid or 6-hydroxystearic acid or ester or glyceride thereof.

6. A composition according to 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.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 85 30 5688

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	EP-A-0 075 478 (MOBIL OIL) * Claims 1-4,8-11; page 4, paragraph 2 - page 5, paragraph 1 *	1,3-8	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)
A	GB-A-2 103 651 (CHEVRON) * Claims 1,4,5 *	1,2	
A	GB-A-2 107 734 (CHEVRON) * Claims 1-7; page 3,lines 41-61 *	1,2	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 10 M

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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A : technological background
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