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(54) **Grease composition.**

(57) Grease compositions, wherein the grease is thickened with a metal hydroxyl-containing soap grease thickener are provided. Other essential ingredients of the compositions include borated hydrocarbyl epoxides and phosphorus and sulfur moieties.

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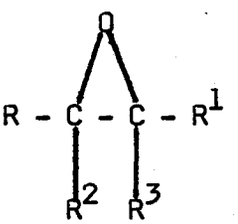
GREASE COMPOSITION

The invention is concerned with a novel group of compositions. It more particularly relates to a synergistic grease composition comprising grease, metal hydroxy-containing soap thickener, borated epoxide and phosphorus and sulfur moities.

U.S. Patent No. 4,410,438 relates to lubricant compositions, including greases, comprising borated epoxides in which boron is present in excess. Also, certain other forms of epoxides have been used in lubricants. For example, U. S. 4,244,829 describes the use of epoxidized fatty acid esters as lubricity agents in lubricating oils.

In accordance with the invention, there is provided a grease composition containing (1) a metal hydroxyl-containing soap thickener, (2) a compound prepared by reacting an epoxide of the formula



wherein R, R^1, R^2 and R^3 are hydrogen or a C_8 to C_{30} hydrocarbyl group, at least one of which is hydrocarbyl, with at least a molar amount of boric acid, boric oxide or an alkyl borate of the formula

$$(R^4O)_xB(OH)_y$$

wherein x is 1 to 3, y is 0 to 2, their sum being 3, and R^4 is an alkyl group containing from 1 to 6 carbon atoms and (3) phosphorus and sulfur moieties.

Preferably the borated product contains more than a stoichiometric amount of boron..

The borated epoxides of the invention can be made by reacting an epoxide with boron compound, such as boric oxide, boric acid or an alkyl borate, or mixtures thereof. The resulting products are

primarily monoborate esters, but other possible products present ar the products of reaction between epoxide dimers, or higher oligomer and a boron compound to form the corresponding borate esters. Included within the scope of the epoxides as set forth above, are 1,2-epoxyoctane, 1,2-epoxydecane, 1,2-epoxydodecane, 1,2-epoxytetradecane, 1,2-epoxypentadecane, 1,2-epoxyhexadecane, 1,2-epoxyheptadecane, 1,2-epoxyoctadecane, 1,2-epoxyeicosane and mixtures of such epoxides, as well as mixtures of other epoxides. These include epoxides of mixtures of C_{22} to C_{30} olefins and of mixtures of C_{24} to C_{28} olefins. Also included are epoxides from dimers of octene, dimers of decene, dimers of mixed octene and decer epoxides from decene trimers and the like. Hydrocarbyl is meant to include alkyl, aryl, cycloalkyl or cycolalkenyl groups containing fr 8 to 30 carbon atoms, preferably 10 to 22 carbon atoms. Preferably, hydrocarbyl is an alkyl group.

As noted hereinabove, the boron compound used is boric acic boric oxide or an alkyl borate, preferably boric acid. The alkyl borates include the mono-, di- and trialkyl borates, such as the mono-, di- and triethyl borates.

The reaction to form the borate ester can be carried out at from 80°C to 260°C, preferably from 110°C to 180°C. The temperature chosen will depend for the most part on the particular reactants anc on whether or not a solvent is used. In carrying out this reaction, it is preferable that quantities of reactants be chosen such that th molar ratio of epoxide to boron compound be from 0.2 to 1, preferabl from 0.5 to 0.9. The epoxide can be reacted with an excess of the borating species to form a borate ester containing from 0.1% by weig of boron to more than 10% of boron.

While atmospheric pressure is generally preferred, the reaction can be advantageously run at from 1 to 5 atmospheres. Furthermore, where 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 hydrocarb and alcoholic soluents, which include propanol and butanol can be used. Mixtures of alcoholic and hydrocarbon solvents can be used al

The times for the reactions are not critical. Thus, any phase of the process can be carried out in from 1 to 20 hours.

A narrow class of thickening agents is preferred to make the grease of this invention. Included among the preferred thickening agents are those containing at least a portion of alkali and alkaline earth metal 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. Preferred is lithium. Preferred members among these acids and fatty materials are 12-hydroxystearic acid and glycerides containing 12-hydroxystearates.

The entire amount of thickener need not be derived from the aforementioned preferred members. Significant benefit can be attained using as little thereof as about 15% by weight of the total thickener. A complementary amount, such as up to about 85% by weight of a wide variety of thickening agents, can be used in the grease of this 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 acid and tall oil fatty acids. Other alkali or alkaline earth metal fatty acids containing from 12 to 30 carbon atoms and no free hydroxyl 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 No. 2,197,263), barium stearate acetate (U.S. Patent No. 2,564,561), calcium, stearate-caprylate-acetate complexes (U.S. Patent No. 2,999,065), calcium caprylate-acetate (U.S. Patent No. 2,999,066), and calcium salts and soaps of low-, intermediate- and high-molecular weight acids and of nut oil acids.

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 hydrocaron

radicals into the surface of the clay particles prior to their use as a component of a grease composition, as, 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. This method of conversion, being well known to those skilled in the art, is believed to require no further discussion.

The third member(s) of the grease composition of the instant invention are the 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

$$\left[(R^5O)_2\overset{X}{\overset{\|}{P}}S\right]_n M$$

wherein R^5 is a hydrocarbyl group containing 3 to 18 carbon atoms, M is a metal or non-metal, n is the valence of M and X is oxygen or sulfur.

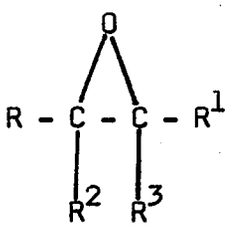
In this compound, R^5 is preferably an alkyl group and may be a propyl, butyl, pentyl, hexyl, octyl, decyl, dodecyl, tetradecyl or octadecyl group, including those derived from isopropanol, butanol, isobutanol, sec-butanol, 4-methyl-2-pentanol, 2-ethylhexanol, oleyl alcohol, and mixtures thereof. Further included are alkaryl groups such as butylphenyl, octylphenyl, nonylphenyl and dodecylphenyl groups.

The metals covered by M include those in Groups IA, IIA, IIB and VIII of the Periodic Table. Some that may be mentioned are lithium, sodium, calcium, zinc, cadmium, silver 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.

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,

Claims:

1. A grease composition consisting essentially of (1) a major amount of a grease and at least about 15% by weight of a hydroxyl-containing soap thickener (2) from 0.01% to 10% by weight of a reaction product made by reacting an epoxide of the formula



wherein R, R^1, R^2 and R^3 are hydrogen or a hydrocarbyl group containing from 8 to 30 carbon atoms at least 1 of which is hydrocarbyl, with at least a molar amount of a boron compound selected from boric acid, boric oxide and an alkyl borate of the formula

$$(R^4O)_xB(OH)_y$$

wherein x is 1 to 3, y is 0 to 2, their sum being 3, and R^4 is an alkyl group having 1 to 6 carbon atoms and (3) from about 0.01% to about 10% by weight of a phosphorus and sulfur compound or a mixture of phosphorus-containing and sulfur-containing compounds to supply a like amount of phosphorus and sulfur.

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

3. The composition of Claim 2 wherein the metal is sodium, lithium, calcium or barium.

4. The composition of Claim 2 wherein the thickener is derived from 12-hydroxystearic acid.

5. The composition of Claim 1 wherein the epoxide is 1,2-epoxyoctane, 1,2-epoxydecane, 1,2-epoxydodecane, 1,2-epoxytetradecane, 1,2-epoxypentadecane, 1,2-epoxyhexadecane, 1,2-epoxyoctadecane, 1,2-epoxyeicosane, epoxides of mixtures of C_{22} to C_{30} olefins, epoxides of mixtures of C_{24} to C_{28} olefins, epoxides from decene trimers or epoxides from: dimers of octene; dimers of decene; or dimers of mixed octene and decene.

6. The composition of Claim 1 wherein the phosphorus and sulfur moieties are supplied by a phosphorothioate of the formula

$$\left[(R^5O)_2\overset{X}{\overset{\|}{P}}S\right]_n M$$

wherein R^5 is a hydrocarbyl group containing 3 to 18 carbon atoms, M is a metal or non-metal, n is the valence of M and X is oxygen or sulfur.

7. The composition of Claim 6 wherein R^5 is an alkyl group.

8. The composition of Claim 7 wherein R^5 is a propyl, butyl, pentyl, hexyl, octyl, dodecyl, tetradecyl, octadecyl or oleyl group or mixtures thereof.

9. The composition of Claim 8 wherein R^5 is derived from isopropanol, butanol, isobutanol, sec-butanol, 4-methyl-2-pentanol, 2-ethylhexanol or mixtures thereof.

10. The composition of Claim 6 wherein M is a metal from Group IA, IIA, IIB or VIII of the Periodic Table.

11. The composition of Claim 10 wherein the metal is lithium, sodium, calcium, zinc, cadmium or gold.

12. The composition of Claim 6 wherein M is derived from vinyl acetate, butyl vinyl ether, propylene oxide or 1,2-epoxydodecane.

13. The composition of Claim 1 wherein the phosphorus and sulfur moieties are supplied by a combination of (1) a dihydrocarbyl phosphite having 2 to 6 carbon atoms in each hydrocarbyl group, mixtures of such phosphites, or a phosphate ester having 4 to 20 carbon atoms in each hydrocarbyl group and (2) a sulfide selected from sulfurized isobutylene, dibenzyl disulfide, sulfurized terpenes, phosphorodithionyl disulfide and sulfurized jojoba oil.

14. The composition of Claim 13 wherein the phosphite is a dibutyl, dihexyl, dioctyl or didecyl phosphite or mixtures thereof.

15. The composition of Claim 13 wherein the phosphate ester is a tributyl, tridecyl or tricresyl phosphate or mixtures thereof.

16. The composition of Claim 13 wherein the epoxide is 1,2-epoxyhexadecane, the boron compound is boric acid and the phosphorus- and sulfur-containing compound is zinc dialkyl phosphorodithioate wherein the alkyl group is derived from mixed C_3 secondary and C_6 primary alcohols.

17. The composition of Claim 1 wherein the grease vehicle is a mineral oil, synthetic oil or mixtures thereof.