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2,815,325

**LITHIUM SOAP-BORIC ACID ESTER
CONTAINING GREASE**

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No Drawing. Application April 14, 1955,
Serial No. 501,432

8 Claims. (Cl. 252-42.1)

This invention relates to lithium base greases. More particularly, the invention relates to greases containing as a gelling agent a combination of a lithium soap and a boric acid ester.

The art has recognized that greases compounded with lithium soaps are characterized by superior properties. Economically, however, lithium base greases are comparatively expensive by virtue of the high cost of the lithium soaps which are contained therein.

It is, accordingly, an object of this invention to provide a novel grease characterized by the desirable properties of conventional lithium base greases but containing a smaller amount of lithium soap than is necessary to produce a grease of like physical properties by methods known to the prior art.

It is a further object of the invention to provide a means for minimizing the amount of lithium soap required to obtain a grease of desired physical characteristics, including penetration.

It is a further object of the invention to provide a grease containing a combination of a boric acid ester and a lithium soap.

It is a further object of the invention to provide a grease containing a mixture of a lithium soap and a boric acid ester, the amount of lithium soap present being less than that which would be required to produce a grease of like penetration in the absence of the boric acid ester.

In accordance with this invention, it has been discovered that the amount of lithium soap required to produce from an oleaginous vehicle a grease of a specified penetration can be substantially minimized by employing in conjunction with, and in addition to such lithium soap, from about 5% to about 20% by weight of a boric acid ester. Specifically, the invention embraces a grease composition comprising an oleaginous vehicle of lubricating viscosity containing from about 5% to about 25% by weight of lithium soap, and from about 5% to about 20% by weight of a boric acid ester, said grease being characterized by a substantially lower penetration than a similar grease containing a like amount of lithium soap but free of said boric acid ester. The particularly preferred grease composition contemplated by the invention comprises an oleaginous vehicle of lubricating viscosity containing from about 10% to about 20% by weight of a lithium soap and from about 10% to about 15% by weight of an orthoboric acid ester.

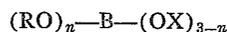
The oleaginous component of the grease composition to which the invention relates may be broadly described as any oleaginous vehicle and is inclusive of conventional mineral lubricating oils, synthetic lubricating oils prepared by cracking and polymerizing a product of the Fisher-Tropsch process, and the like. The synthetic oleaginous compositions which are contemplated include all those synthetic organic compounds and compositions which possess lubricating characteristics. Such compounds and compositions may be substituted in whole or in part for conventional lubricating oils in the greases of this invention. Representative of such synthetic oleagi-

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nous compounds are the aliphatic dicarboxylic acid esters of lubricating viscosity, such as the alkyl esters of sebacic acid and adipic acid, including di-2-ethyl hexyl sebacate and di-2-ethyl hexyl adipate, high molecular weight aliphatic ethers, such as polypropylene oxide materials. The particular oleaginous vehicle employed is not a critical factor of this invention, and all such vehicles of lubricating viscosity are contemplated.

The lithium soaps which are useful in the invention include all those lithium soaps which are useful in the preparation of lubricating greases. The art is well cognizant of the various lithium soaps which are or can be so utilized. Generally, such lithium soaps include lithium salts of higher fatty acids having about 10 or more carbon atoms. The lithium soaps may be derived from any source and produced in any way known to the art. Typical lithium soaps include the lithium soaps of stearic acid, oleic acid, linoleic acid, 12-hydroxy stearic acid, myristic acid, coconut oil fatty acids, lauric acid, and the like. Lithium soaps of higher fatty acids, both saturated and unsaturated, containing from 12 to 20 carbon atoms are preferred. The particular lithium soaps used do not constitute a critical factor of the invention. Reference is made to U. S. Patents Nos. 2,274,673 and 2,397,956 for representative lithium soaps useful in the invention and for methods for the production of such soaps.

All boric acid esters are useful in the invention. The preferred boric acid esters are orthoboric acid esters of aliphatic alcohols and phenols, which may be represented by the formula



in which R is an alkyl, aryl or alkaryl group, X represents either a hydrogen atom or alkyl, aryl or alkaryl group, and n is an integer not greater than 2. The specific nature of the R and X group is not critical. However, R and/or X is preferably an alkyl group containing from about 5 to about 25 carbon atoms. It is additionally preferred that the alkyl groups be of branched chain character, although straight chain alkyl groups are contemplated by the invention. The alkyl groups can be either saturated or unsaturated. Substituted or unsubstituted specific alkyl groups which can be represented by R include all the various pentyl, hexyl, isohexyl, octyl, iso-octyl, nonyl, decyl, isodecyl, undecyl, tetradecyl, pentadecyl, hexadecyl and octadecyl groups.

Representative aryl and alkaryl groups which may be represented by R are the phenyl, naphthyl, methyl phenyl, isohexyl phenyl, diethyl phenyl and like groups. Representative substituents for the R groups include the halogen substituents chlorine, bromine, iodine and fluorine, nitro groups, carbonyl groups, and carboxyl groups. Specific borate esters contemplated include monopentyl orthoborate, di-isohexyl orthoborate, trioctyl orthoborate, mono-, di-, and tridecyl orthoborate, mono-, di-, and tridodecyl orthoborate, mono-, di-, and tri-isododecyl orthoborate, mono-, di-, and tri-tetradecyl orthoborate, mono-, di-, and tri-isotetradecyl orthoborate, mono-, di-, and tri-hexadecyl orthoborate, mono-, di-, and tri-octadecyl orthoborate, mono-, di-, and triphenyl orthoborate, mono-, di-, and tri-naphthyl orthoborate, mono-, di-, and tritoyl orthoborate, mono-, di-, and tri-2-chlorohexadecyl orthoborate, mono-, di-, and tri-paranitrophenyl orthoborate, and the like.

A particularly preferred form of boric acid ester is that described in copending Lawrence et al. application Serial No. 313,851 filed October 9, 1952, now Patent 2,721,180 entitled "Organo-Boron Compositions and Method for Production Thereof." As described in that application, such boric acid esters are prepared by passing a free oxygen-containing gas through a normally liquid paraffin petroleum fraction having a boiling point of from about

350° to about 800° F. maintained at a temperature of from about 305° F. to about 385° F., there being provided for reaction in said fraction from about 1 to about 3 chemical equivalents of a boric acid, the gas being passed through the reaction mixture at a rate requisite to provide not more than about 0.6 cubic foot of oxygen per hour per gallon of petroleum fraction present. The disclosure of application Serial No. 313,851, now Patent 2,721,180, is incorporated into this application by reference.

The lithium soaps are incorporated in the grease compositions of the present invention in a concentration of from about 10% to about 20% by weight thereof. The boric acid esters are employed in any amount up to about 20% by weight of the grease composition. It has been discovered that the boric acid esters are effective in all concentrations to effect some reduction in the amount of lithium soap required to produce a grease of a specified consistency. Preferably, the borate esters are employed in an amount equal to from about 10% to about 20% by weight in the grease compositions.

The grease compositions which are contemplated by this invention are manufactured by conventional methods well known to the art. One such method is described in Patent No. 2,450,219. Specifically, as in the manufacture of a conventional lithium grease, a slurry of lithium soap, such as lithium stearate, may be either preformed or prepared in situ and blended with mineral oil heated to a temperature of around 350° to 500° F. until a homogeneous solution is produced. The boric acid ester is added to the mineral oil concurrently, before, or subsequently to the lithium soap and is likewise homogenized into the mixture. The composition so obtained is withdrawn from the kettle and allowed to cool statically until the gel structure is set up. The cooled gel may then be subjected to a milling operation wherein further homogenization occurs to produce a final homogeneous grease composition. Conventional grease additives, such as viscosity index improving agents, antioxidants, and the like, can be employed in the grease compositions of this invention in a manner well known to the prior art.

It is theorized that the success of the present invention is attributable, in part at least, to the acidic nature of the esters. Theoretically, lithium soap and borate ester complexes could be formed by means of ionic attraction, which complexes should have improved solubility in hydrocarbon oils and thereby facilitate grease formation. Lithium soaps, when complexed in such a manner, may be considered as having undergone transformation of their crystalline phase which permits greater ease of gelation. Further, by means of such ionic attractive forces, stronger gel structure may be formed, as evidenced by stiffer penetrations when employing the borate esters in combination with lithium soap, in accordance with the invention. Additionally, when a lithium soap of a hydroxy fatty acid, such as lithium 12-hydroxy stearate is employed, interaction between the borate ester and the hydroxyl group of the soap may be visualized as giving rise to complex formation of the type above referred to. Applicants, of course, will not be bound by the foregoing theory which is presented solely for the purpose of further informing the art concerning the theoretical aspects of the invention.

The examples which are presented herein for purposes of illustration will further demonstrate the preparation of grease compositions of the type contemplated by this invention, and represent the best mode presently known for the practice of the invention.

Example I

To a suitably heated reaction kettle provided with a stirrer, there is added 250 grams of lithium stearate and 375 grams of alkyl borate esters of the type hereinafter described. When a homogeneous slurry is formed, approximately 1875 grams of a bright stock oil fraction de-

rived from Pennsylvania paraffin base crude oil and characterized by a viscosity of 1522 SUS at 100° F., 117.1 SUS at 210° F., 101.6 V. I., a gravity of 28.0° API, 530° F. flash point, 592° F. fire point, and 0° F. pour point is added. The mixture so obtained is slowly heated, at a rate requisite to prevent excessive foaming, to a temperature of about 195-200° C. at which point gel formation is complete. The fluid mixture is poured from the kettle into a suitable container and allowed to cool to room temperature. The grease so produced need not be further homogenized.

A grease so compounded, which contains about 10% by weight of lithium stearate and 15% by weight of alkyl borates is tested for penetration by ASTM D217-52T. The unworked penetration of the grease is 256. The penetration after 60 strokes of working is 316. The dropping point, as determined by ASTM D566-42 is 368° F. Wheel bearing tests carried out pursuant to ASTM Proc. 48, 303-8, 1948 show no leakage and no structural or consistency change in the condition of the grease. The condition of the bearings shows no deposits and a good lubricant film.

The alkyl borate esters employed in this example were prepared as follows: approximately 1978.8 grams of paraffinic petroleum fraction, substantially free of aromatics and having an average molecular weight of about 235, a flash point of 275° F., a viscosity at 100° F. of 39.6 SUS, a viscosity at 210° F. of 31.0 SUS, a cloud point of 28° F., an actual pour point of 25° F., and a distillation range of from 523° F. to 642° F., with an end-point of 703° F., a density at 20° C. of 0.8014, and a refractive index of 1.4456, was placed in a reaction vessel and mixed with boric anhydride in an amount requisite to provide to the ultimate reaction about 2.0 equivalents of orthoboric acid per mole of hydrocarbon starting material. The mixture was heated in the reaction vessel to a temperature of about 385° F. whereupon air was passed through the reaction mixture at a rate of about 2.25 cubic feet per hour per gallon of paraffinic starting material for a period of about six hours. The boric acid composition employed in the grease formulation was obtained by distilling the reaction mixture at about 5 mm. pressure to a maximum temperature of about 175° C. and was characterized by a molecular weight of 624, a viscosity at 210° F. of 96.1 SUS and an acid number of 56.0.

Example II

For purposes of control, Example I is repeated precisely with the exception that the boric acid esters were omitted. The product so obtained is too soft to be tested pursuant to the penetration tests described in ASTM D566-42.

Example III

Example I is repeated with the exception that 15% by weight of lithium stearate is employed in the compounded grease which is characterized by a penetration (ASTM D217-52T) of 181.

Example IV

Example III is repeated with the exception that ditetradecyl orthoborate is utilized as the boric acid ester. A grease of satisfactory physical properties is obtained.

Example V

Example III is repeated with the exception that only 5% by weight of boric acid ester is employed. A grease of good penetration value results.

Example VI

Example I is repeated with the exception that di-2-ethyl hexyl adipate is employed as the oleaginous vehicle in lieu of the lubricating oil employed in Example I.

Example VII

Example III is repeated with the exception that trihexyl orthoborate is employed in an amount equal to 20% of the weight of the final grease.

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Example VIII

Example VII is repeated with the exception that triphenyl orthoborate is employed rather than trihexyl orthoborate.

Example IX

Example VIII is repeated with the exception that mono-octadecyl orthoborate is employed in an amount equal to about 10% of the weight of the final grease composition.

Example X

Example I is repeated with the exception that lithium 12-hydroxy stearate is employed rather than lithium oleate. A grease similar to that described in Example I is obtained.

Example XI

Example III is repeated with the exception that a polypropylene oxide of lubricating viscosity is employed as the oleaginous vehicle.

Example XII

Example I is repeated with the exception that lithium oleate is employed in an amount equal to about 15% of the weight of the final grease composition, and trioctadecylborate is utilized in an amount equal to about 15% of the weight of the final grease composition.

We claim:

1. A grease composition comprising an oil of lubricating viscosity containing from about 5% to about 25% by weight of lithium soap and from about 5% to about 20% by weight of an orthoboric acid ester, said grease being characterized by a substantially lower penetration than a similar grease containing a like amount of lithium soap but free of said boric acid ester.

2. A grease composition comprising an oil of lubricating viscosity containing from about 5% to about 25% by weight of a lithium soap of a fatty acid containing from about 10 to about 20 carbon atoms, and from about 5% to about 20% by weight of an orthoboric acid ester having at least one alkyl group which contains from 5 to 25 carbon atoms, said grease being characterized by a substantially lower penetration than a similar grease containing a like amount of lithium soap but free of said boric acid ester.

3. A grease composition comprising a mineral oil of lubricating viscosity and from about 10% to about 20% by weight of a lithium soap of a higher fatty acid con-

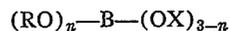
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taining from about 12 to about 20 carbon atoms and from about 10% to about 15% by weight of an orthoboric acid ester, said grease being characterized by a substantially lower penetration than a similar grease containing a like amount of lithium soap but free of said boric acid ester.

4. A grease composition comprising a mineral oil of lubricating viscosity containing from about 5% to about 25% by weight of a lithium soap and from about 5% to about 20% by weight of an orthoboric acid ester, said grease being characterized by a substantially lower penetration than a similar grease containing a like amount of lithium soap but free of said boric acid ester.

5. The grease composition of claim 4 wherein said boric acid ester is an orthoboric acid ester having at least one alkyl group which contains from about 5 to about 25 carbon atoms.

6. The grease composition of claim 4 wherein said boric acid ester is that represented by the formula



in which R is a group selected from the alkyl, aryl and alkaryl groups, and in which X is selected from the group consisting of hydrogen, alkyl, aryl, and alkaryl groups, and in which n is an integer not greater than 2.

7. A grease comprising a synthetic oil of lubricating viscosity containing from about 5% to about 25% by weight of a lithium soap and from about 5% to about 20% by weight of an orthoboric acid ester, said grease being characterized by a substantially lower penetration than a similar grease containing a like amount of lithium soap but free of said boric acid ester.

8. The grease composition of claim 7 wherein the boric acid ester is prepared by passing a free oxygen-containing gas through a normally liquid paraffin petroleum fraction having a boiling point of from about 350° F. to about 800° F. maintained at a temperature of from about 305° F. to about 385° F., there being provided for reaction in said fraction from about 1 to about 3 chemical equivalents of a boric acid, the gas being passed through the reaction mixture at a rate requisite to provide not more than about 0.6 cubic foot of oxygen per hour per gallon of petroleum fraction present.

References Cited in the file of this patent

UNITED STATES PATENTS

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