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LUBRICATING GREASE CONTAINING BORON NITRIDE

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2 Claims. (Cl. 252-25)

This invention relates to lubricating grease containing boron nitride. Particularly, the invention relates to lubricating greases comprising a lubricating oil thickened with finely divided boron nitride.

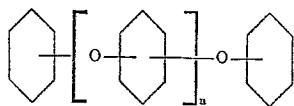
Finely divided boron nitride has been found effective in thickening both mineral lubricating oils and synthetic lubricating oils to a grease-like consistency. The finely divided boron nitride is not wettable by water, so that the greases formed with it are water-resistant. Boron nitride is very inert, has a very high melting and decomposition point, and will form lubricating greases having high dropping points and very long lubrication life at extremely high temperatures.

The finely divided boron nitride of the invention will generally have particle sizes of about 10 to 200, preferably 15 to 75 millimicrons, having an oleophilic surface. The boron nitride will have surface areas, as measured by nitrogen adsorption by the Perkin and Elmer Sorptometer technique, of about 150 to 650 sq. meters per gram. Boron nitride has the chemical formula: BN.

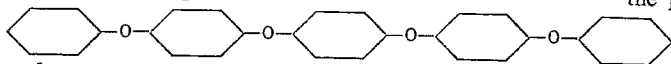
Boron nitride can be used in lubricating greases in amounts of about 2 to 20, preferably 4 to 10 wt. percent, as the sole thickener. Generally, amounts of about 5 to 7 wt. percent will be operable to thicken most lubricating oils to a normally solid grease-like consistency, having an ASTM unworked grease penetration of less than about 400 mm./10 at 77° F., although lesser amounts can be used to form solid greases when the boron nitride is used in conjunction with other thickeners.

The lubricating oil component of the grease can be mineral lubricating oil, or various synthetic lubricating oils such as esters of carboxylic acid and alcohol, polyoxyalkylene glycols (Ucon oils), polysilicone oils, polyphenyl ethers, etc. Where lubricants are to be used at very high temperatures, the lubricating oil is preferably a synthetic oil such as polyphenyl ether or ester.

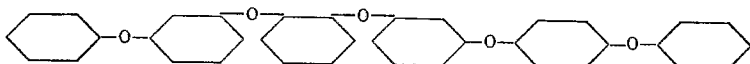
The polyphenyl ether oils for high temperature use are those normally liquid (at 77° F.) ethers represented by the general formula:



where n is about 3 to 6. Isomeric mixtures of polyphenyl ethers within the above formula are also included in the invention, as well as mixtures of polyphenyl ether molecules having different values for n . An oil of the above general formula wherein n was about 3, obtained from Monsanto Chemical Co. under the designation "High Temperature Functional Fluid and Lubricant OS-124," was used in a working example of the invention. Other specific examples of such polyphenyl ethers include the following:



and



etc.

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The ester lubricating oils generally comprise hydrocarbon chains interrupted with 2 to 10 ester linkages, which can be further interrupted with ether or thioether linkages. Included are diesters, polyesters, and complex esters.

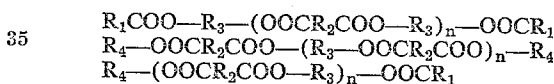
The diesters are generally prepared from dicarboxylic acids fully esterified with monohydric alcohols, or from glycols fully esterified with monocarboxylic acids. The total number of carbon atoms in the diester molecule is generally about 18 to 36, preferably 20 to 28. Preferred dicarboxylic diesters are those of the formula:



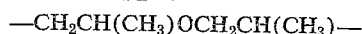
wherein each R may be the same or different, straight or branched chain alkyl radical of a monohydric alcohol having about 6 to 13 carbon atoms, while R' is a straight or branched chain C_2 to C_8 divalent saturated aliphatic hydrocarbon radical. Examples of dicarboxylic diesters include: di-2-ethylhexyl sebacate, di-nonyl sebacate, di-2-ethylhexyl azelate, di-2,2,4-trimethylpentyl azelate, di-nonyl adipate. Examples of glycol diester include dipropylene glycol dipelargonate and polyethylene glycol 200 dicaproate.

Useful polyesters are prepared by reacting polyhydric alcohols, such as trimethylolpropane and pentaerythritol, with monocarboxylic acids such as butyric acid, caproic acid, caprylic acid, pelargonic acid, etc. to give the corresponding tri- or tetraesters.

Useful complex esters are formed by esterification reactions between a dicarboxylic acid, a glycol, and an alcohol and/or a monocarboxylic acid. The more important complex esters may be represented by the following formulas:



wherein R_1 represents hydrocarbon radicals of a monocarboxylic acid; R_2 represents hydrocarbon radicals of dicarboxylic acids; R_3 represents divalent hydrocarbon or hydrocarbon-oxy radicals, such as $-\text{CH}_2(\text{CH}_2)_n-$, or $-\text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_n-$, or



derived from an alkylene glycol or polyalkylene glycol; and R_4 represents hydrocarbon radicals of a monohydric alcohol. n in the complex ester molecule will usually range from 1 to 6, depending upon the product viscosity desired, and is controlled by the relative molar ratio of the glycol or polyglycol to the dicarboxylic acid. In preparing the complex ester, there will usually be some simple mono or diester formed, i.e., $n=0$, but this will generally be a minor portion.

The boron nitride can be used in conjunction with other grease thickeners such as salts, soaps, mixed-salts, polymeric thickeners (e.g., polymers of C_2 to C_4 monoolefins of 10,000 to 200,000 molecular weight such as polyethylene), and inorganic thickeners (e.g., clay, carbon black, silica gel), etc.

When used with other thickeners, the boron nitride will generally improve the high temperature properties of the final grease, even though the bulk of the thickening power is supplied by lower cost conventional thickeners. The boron nitride is particularly useful in further improving the properties of calcium mixed salt greases, which are

high temperature greases in themselves. These mixed salt greases generally comprise a major amount of lubricating oil and within the range of about 5 to 40, e.g., 10 to 20 wt. percent of the mixed-salt thickener. This thickener, in turn, usually is a mixture of the calcium salt of acetic acid and calcium salt of C₇ to C₃₀ fatty acid. The calcium mixed salts are commercially prepared by using lime to neutralize a mixture of acetic acid or anhydride, and the higher fatty acid. Usually about 4 to 20, preferably 4 to 12, mole equivalent of acetic acid (or acetic anhydride) is used per mole equivalent of C₇ to C₃₀ fatty acid. The C₇ to C₃₀ fatty acids include C₇ to C₁₂ intermediate molecular weight fatty acids such as capric, caprylic, pelargonic acid, lauric acid, etc., and C₁₄ to C₃₀ fatty acids such as stearic, 12-hydroxy stearic, oleic, tallow, hydrogenated fish oil acids, etc.

Various other additives may also be added to the final lubricating grease composition (e.g., 0.1 to 10.0 weight percent, based on the total weight of the composition). Examples of such other additives include oxidation inhibitors such as phenyl-alpha-naphthylamine; corrosion inhibitors, such as sodium nitrite and sorbitan monooleate; stabilizers such as aluminum hydroxy stearate; and the like.

The greases of the invention containing boron nitride as the sole thickener can be simply prepared by merely dispersing the boron nitride in lubricating oil, e.g., at 77° F. Preferably, the lubricating oil is slowly added to the boron nitride, while stirring, until the desired grease consistency is obtained. When the boron nitride is to be used in conjunction with another grease thickener, the boron nitride can be added to a finished grease thickened with said other grease thickener, or the boron nitride can be added at any point during the manufacture of the grease.

The invention will be further understood by reference to the following examples which include a preferred embodiment of the invention.

Example I

5 wt. percent of boron nitride was added to a mixer,

appeared to have a length to diameter ratio of about 1, although they were somewhat irregular in form. The particle size ranged from about 5 to 75 millimicrons, and averaged about 15 millimicrons.

Example II

A grease was prepared in a manner similar to that of Example I, except that the oil was a polyphenyl ether (Monsanto OS-124 previously described), and the oxidation inhibitor was a commercial oxidation inhibitor obtained from Geigy Chemical Company under the designation RA-565.

Example III

A lubricating grease was prepared in a manner similar to that of Example I, except that the oil was di-ethylhexyl sebacate.

Example IV

All parts by weight.

A calcium mixed salt lubricating grease was prepared as follows: 4 parts of hydrated lime and 84.5 parts of mineral lubricating oil of 55 SUS viscosity at 210° F. were added to a fire heated kettle. Next, a blend consisting of 2.5 parts of Wecoline AAC acid and 5 parts of glacial acetic acid was slowly added to the kettle. Wecoline AAC acid is a commercial acid derived from coconut oil and consists of about 46 wt. percent capric acid, about 28 wt. percent caprylic acid and about 26 wt. percent lauric acid. External heating was next initiated to raise the contents of the kettle to 440° F. This temperature was maintained for about one hour in order to dehydrate the lubricant. Heating was then discontinued, and the mixture was cooled to 200° F. where 1 part of phenyl-alpha-naphthylamine and 3 parts of boron nitride were added and mixed into the lubricant. The grease was then further cooled to 100° F., homogenized by passing through a Charlotte mill, and subsequently deaerated in a Cornell homogenizer under reduced pressure.

The products of Examples I to IV along with their compositions and properties are summarized in the following table:

Formulation, (Wt. percent)	Examples			
Boron nitride	5.0	5.0	5.0	3.0
Phenyl α -naphthylamine	0.5		0.5	1.0
Mineral lubricating oil, 55 SUS at 210° F.	94.5			84.5
Inhibitor—RA-565		0.5		
Monsanto OS-124 (polyphenyl ether)		94.5		
Di-2-ethylhexyl sebacate			94.5	
Glacial acetic acid				5.0
Wecoline AAC acid				2.5
Hydrated lime				4.0
Properties:	Excellent, Smooth, Uniform Greases			
Appearance	500+	500+	500+	500+
Dropping point, ° F.	500+	500+	500+	500+
ASTM penetration, 77° F., mm./10—				
Unworked	300	290	325	
Worked 60 strokes	310	300	330	300
Worked 10,000 strokes	315	305	340	335
Water solubility	Insoluble	Insoluble	Insoluble	Insoluble
Wheel bearing test 1 hour at 220° F.	Pass	Pass		
Lubrication life,* hours—				
10,000 RPM—250° F.	2000+			2000+
10,000 RPM—300° F.			1895+	
10,000 RPM—400° F.		1200+		

*NLGI-ABEC spindle test—The 1200+ and 1895+ test results were still running at time of final preparation of this application. After 2,000 hours of test, the test is discontinued.

and then 94.5 wt. percent of a mineral lubricating oil of 55 SUS viscosity at 210° F. was slowly added to the boron nitride, while stirring, to form a smooth, homogeneous, firm grease structure. 0.5 wt. percent of phenyl-alpha-naphthylamine, as an oxidation inhibitor, was added. The resulting grease was then homogenized 450 sq. meters per gram. The boron nitride particles under high rates of shear in a Manton-Gaulin homogenizer operating at about 5,000 p.s.i.

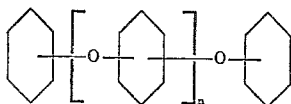
The boron nitride used above was in the form of a very finely divided powder having a surface area measured by the aforesaid nitrogen adsorption technique of

As seen by Examples I to III of the preceding table, boron nitride can be used as the sole thickening agent in either a mineral oil, a polyphenyl ether oil, or an ester oil, e.g., di-2-ethylhexyl sebacate, to give stable, high dropping point greases having good ASTM penetrations, which are insoluble in water, and have good lubricating properties as demonstrated by the Wheel Bearing Test and the NLGI-ABEC Spindle Test. At the same time, the boron nitride can be incorporated into a more conventional grease, e.g., the soap-salt grease of Example IV.

In sum, the present invention relates to greases containing boron nitride, which can be used in a wide variety of applications, particularly high temperature applications such as aviation greases, greases for various apparatus associated with missiles, rockets, etc., greases for lubricating apparatus subject to gamma radiation, etc. In this later instance, it is to be noted that the boron nitride is resistant to degradation by gamma radiation, although it is not resistant to neutron radiation.

What is claimed is:

1. A lubricating grease consisting essentially of a major amount of a normally liquid polyphenyl ether lubricating oil represented by the general formula:



wherein n is about 3 to 6, and as the sole grease thickening agent, about 4 to 10 wt. percent of finely divided boron

nitride having particle sizes ranging from about 10 to 200 millimicrons.

2. A lubricating grease according to claim 1, wherein said composition also contains about 0.5 wt. percent of an oxidation inhibitor.

References Cited by the Examiner

UNITED STATES PATENTS

2,093,454	9/37	Kistler	23—182
2,156,803	5/39	Cooper et al.	252—25
2,188,007	1/40	Kistler	252—317
2,260,625	10/41	Kistler	252—28
2,960,466	11/60	Saunders	252—25
2,967,151	1/61	Morway	252—18 X
3,012,856	12/61	Berry	252—25 X

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