United States Patent

Curtis

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[54] EXTREME PRESSURE GREASES

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[73] Assignee: Esso Research and Engineering Company

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[52] U.S. Cl. 252/13, 252/28, 252/29, 252/30, 252/58

[51] Int. Cl. C10m 1/30, C10m 1/10

[58] Field of Search 252/13, 28, 29, 30, 58

[56] References Cited

UNITED STATES PATENTS

2,836,560	5/1958	Teale et al.	252/25
2,877,182	3/1959	May	252/28
2,890,170	6/1959	Ragborg	252/28
3,011,975	12/1961	Nitzsche et al.	252/28
3,159,577	12/1964	Ambrose et al.	252/28
3,248,326	4/1966	Swenson	252/49.6
3,288,710	11/1966	Hollitz	252/25
3,314,889	4/1967	Christian	252/49.6
3,350,307	10/1967	Brown et al.	252/28
3,424,678	1/1969	Morway et al.	252/13
3,437,593	4/1969	Bellavin	252/13

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[57] ABSTRACT

A lubricating grease having extreme pressure (e.p.) properties comprising a major amount of lubricating oil and minor amounts of colloidal asbestos, finely divided polymeric fluorocarbon powder having a melting point (m.p.) above 450° F. and a powdered inorganic grease thickener. The colloidal asbestos is characterized by its chrysolite configuration and by its separate distinct fibers. The polymeric fluorocarbon is selected from the group consisting of polytetrafluoroethylene and fluorinated ethylene propylene copolymer. The inorganic thickeners are selected from the group consisting of talc, graphite and Group I, II and IV metal oxides and carbonates.

10 Claims, No Drawings

EXTREME PRESSURE GREASES

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention is directed to lubricating grease compositions containing a combination of colloidal asbestos, finely divided, polymeric fluorocarbon having a melting point above 450° C. and inorganic thickeners, which combination results in an extreme pressure grease. More particularly, it is directed to a lubricating grease composition containing lubricating oil, such as mineral oil, polyphenylether oils and polysilicone oils, etc., colloidal asbestos, finely divided, solid polymeric fluorocarbons, such as polytetrafluoroethylene, and fluorinated ethylene propylene copolymer powder having an average particle size ranging from submicron (e.g., 0.1 micron) to 100-micron size, and inorganic thickeners, such as talc, graphite, and Group I, II and IV metal oxides and carbonates.

2. Description of the Prior Art

The use of natural asbestos as an ingredient in lubricating grease compositions is old in the art. A number of such grease formulations are taught in the book, "Lubricating Grease" by C. J. Boner, Second Edition, pages 687 et seq. These prior greases utilized conventional natural asbestos or asbestos floats, both of which are relatively long-fibered asbestos occurring in fibril bundles or agglomerates almost impossible to separate or deagglomerate. However, this prior art, fibered asbestos was always used in conjunction with other thickening agents, such as soaps, since the prior long-fibered asbestos fibrils or bundles (agglomerates) are too large and will not form a thickened, homogeneous stable grease gel by itself but, rather, rely upon other ingredients to form the grease or gel-like structure. In addition, these prior asbestos greases were often abrasive due to the large asbestos fibers.

Recently issued patent U.S. Pat. No. 3,424,678 discloses the use of colloidal asbestos in greases. This colloidal asbestos differs from the long-fibered conventional asbestos in that the asbestos fibers are separate and distinct, occuring in a small colloidal size, having a large surface area, and can be dispersed in oil to form a gel by themselves without settling out from the oil.

The use of fluorocarbon polymers in grease compositions has been described in U.S. Pat. No. 3,011,975 and U.S. Pat. No. 3,248,236. Similarly, the use of inorganic thickeners has also been taught. (See, e.g., U.S. Pat. No. 2,599,353, *Lubricating Greases*, C. J. Boner, pp. 677 etc., and *Lubricating Greases, their Manufacture and Use*, E. N. Klemgard, pp. 686 etc., [Reinhold 1937].) Thus, while colloidal asbestos, polymeric fluorocarbons and inorganic thickeners per se are known in the art, it has not heretofore been known that a mixture of three components exhibits an enhanced coaction in greases.

SUMMARY OF THE INVENTION

It has now been found, in accordance with this invention, that by incorporating in a lubricating oil the combination of (1) colloidal asbestos, (2) finely divided polymeric fluorocarbon powder having an m.p. above 450° F., and (3) an inorganic thickener, an improvement in the e.p. properties of the resultant grease over that provided by the incorporation of any one or two of these three components is obtained. More specifically, it has now been discovered that a grease having exceptional and unexpected extreme pressure properties can be prepared by adding about 1 to about 15 weight percent of a finely divided polymeric fluorocarbon powder selected from the group consisting of polytetrafluoroethylene and fluorinated ethylene propylene copolymer and about 1 to about 25 weight percent or an inorganic thickener selected from the group consisting of talc, graphite, Group I, II and IV metal oxides and carbonates, to a lubricating oil having about 1 to about 15 weight percent of colloidal asbestos as its primary thickener. It has further been found that, if the weight percent ratio of said inorganic thickener to the combined weight percent of the other two components is greater than 1:2, a further improvement in e.p. properties is achieved. Thus, it is

especially preferred that the ratio of weight percent of said inorganic thickener to the combined weight percent of the other two components, ranges from about 0.5:1 to about 3:1, and most preferred is a ratio of about 0.75:1 to about 1.25:1.

The colloidal asbestos of the present invention is chrysolite having the chemical formulation: $Mg_6(OH)_8Si_3O_{10}$. The usual mode of occurrence of chrysolite is a "cross-fiber" configuration in which agglomerates of chrysolite (i.e., bundles of fibers) are closely packed together and set at right angles to the walls of cracks and fissures that extend through the host rock of the ore body. However, in 1959, an unusual deposit of chrysolite asbestos, with properties and a mode of occurrence different from the previously known cross-fiber material was discovered in central California. The ore of this new deposit, instead of occurring in veins, occurs in randomly oriented, mattelike flakes of relatively deagglomerized, visible asbestos filaments which, in turn, are made up of many thousands of extremely small tubular fibers. The lengths of these small fibers vary from a few millimicrons to thousands of millimicrons, generally 2,000 to 30,000 millimicrons, while the diameters of the fibers vary much less and are usually in the range of 1 to 80, e.g., 10 to 30, millimicrons. The colloidal asbestos, because of its physical makeup, has thickening properties not demonstrated by conventional asbestos. A typical colloidal asbestos that was used in the working examples of the invention had the following characteristics:

PROPERTIES OF COLLOIDAL ASBESTOS FIBERS

Brightness (GE)	74–76
Refractive index	1.55
Dispersion in water	Fully/pH range 4–6
Surface area	47–50 sq. meters/gram
Oil absorption	14–16 cc./10 grams of fibers
Water retention	42 grams/20 grams of fibers
Dry bulk density	2–2.5 lbs./cu.ft.
Fiber dimension	Outer diameter 25.0 mμ
	Inner diameter 6.0 mμ
	Length 2500–25,000 mμ

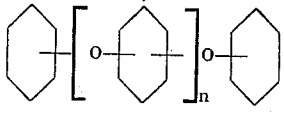
Any polymeric fully fluorinated fluorocarbon powder can be used in this invention provided it is characterized by a high melting point, i.e., above 450° F., and consists of finely divided particles whose average size ranges from submicron (e.g., 0.1) to 100-micron size. Preferably, these particles will have an average particle size of about 5 to about 25 microns. Preferred are the polymeric fluorocarbons selected from the group consisting of polytetrafluoroethylene and fluorinated ethylene propylene (FEP) copolymer. The polymer fluorocarbon compounds operable in this invention can be prepared by methods well known in the art, (See, e.g., U.S. Pat. Nos. 2,833,686; 2,946,763; 3,011,415 and 3,248,326.) or can be purchased as readily available commercial commodities under such trade names as "TFE Teflon" and d"FEP Teflon." The polytetrafluoroethylene is a polymer of a fully fluorinated hydrocarbon of the basic chemical formula $(-CF_2-CF_2-)_n$ containing 71 percent by weight of fluorine and having a melting point above 600° F. The fluorinated ethylene propylene copolymer is a fully fluorinated resin prepared by polymerization of tetrafluoroethylene and hexafluoropropylene to form a copolymer containing about 5 to about 50 weight percent hexafluoropropylene and about 95 to about 50 weight percent tetrafluoroethylene. These copolymers have melting points ranging from about 480° F. to about 560° F. Especially preferred for use in this invention is polytetrafluoroethylene.

The inorganic grease thickeners contemplated for use in the combination of this invention are those known in the art which do not, in their normally available particle size, form thick, homogeneous grease gels by themselves and which rely upon other ingredients to form the gellike structure. Among these are talc, graphite, and Group I, II and IV metal oxides such as zinc, titanium and magnesium oxides, and carbonates, such as calcium carbonate, sodium carbonate, e.g., Na_2CO_3, Na_2CO_3·

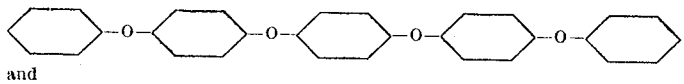
H_2O, zinc carbonate, e.g., $ZnCO_3$, $ZnCO_3 \cdot H_2O$, and magnesium carbonate etc. Among these inorganic secondary thickeners, talc and zinc oxide are preferred and talc is most preferred.

The lubricating oil used in the composition of the invention may be either a mineral lubricating oil or a synthetic lubricating oil. Synthetic lubricating oils which may be used include polyphenyl ether oils, polysilicone oils, esters of dibasic acids (e.g., di-2-ethylhexyl sebacate), esters of glycols (e.g., C_{13} Oxo acid diester of tetraethylene glycol, etc.), complex esters (e.g., the complex ester formed by reacting 1 mole of sebacic acid with 2 moles of tetraethylene glycol and 2 moles of 2-ethyl hexanoic acid, phosphoric acid, (e.g., the ester formed by contacting 3 moles of the monomethyl ether of ethylene glycol with 1 mole of phosphorus oxychloride, etc.) halocarbon oils (e.g., the polymer of chlorotrifluoroethylene containing 12 recurring units of chlorotrifluoroethylene), alkyl silicates (e.g., methyl polysiloxanes, ethyl polysiloxanes, methyl phenyl polysiloxanes, ethyl phenyl polysiloxanes, etc.), sulfite esters (e.g., ester formed by reacting 1 mole of sulfur oxychloride with 2 moles of the methyl ether of ethylene glycol, etc.), carbonates (e.g., the carbonate formed by reacting C_8 Oxo alcohol with ethyl carbonate to form a half ester and reacting this half ester with tetraethylene glycol), mercaptan with formaldehyde, formals (e.g., the formal formed by reacting C_{13} Oxo alcohol with formaldehyde), polyglycol-type synthetic oils (e.g., the compounds formed by condensing butyl alcohol with 14 units of propylene oxide, etc.), or mixtures of any of the above in any proportions.

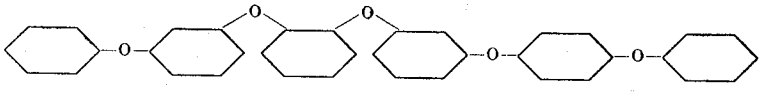
Preferred synthetic lubricating oils are the polyphenyl ether oils and the polysilicone oils, when the lubricant is designed for high temperature use since they are particularly stable at high temperature. The polyphenyl ether oils are those normally liquid (at 77° F.) ethers represented by the general formula:



wherein n is about 2 to 6. The oxygen atoms attached to the hydrocarbon rings intermediate the terminal phenyl groups, can be in an ortho, meta, or para position relative to each other. Isomeric mixtures of polyphenyl ethers within the above formula are also included 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 the working examples of this invention. Some other specific examples of these polyphenyl ethers include:



and



While the ratios of the colloidal asbestos, the polymer fluorocarbon and the inorganic thickener of this invention can vary in relation to each other, it is understood that an oil-thickening, grease-forming amount will be used. Thus, the combined amount of colloidal asbestos and inorganic thickener will range from about 5 to about 40 weight percent, preferably 6 to 30 weight percent, of the total composition and the polymeric fluorocarbon powder will form a minor amount, usually about 1.0 to about 15 weight percent, preferably 2 to 10 weight percent, of the total composition. Generally, the colloidal asbestos forms about 1.0 to about 15 weight percent, preferably about 3 to about 10 weight percent of the total composition, and the inorganic thickeners from about 1 to about 25 weight percent, preferably about 3 to about 20 weight percent, of the total composition.

Various other additives may also be added to the lubricating composition in amounts of 0.1 to 10.0 weight percent each. Such additives include lubricating oil sludge detergents and dispersants, oxidation inhibitors such as phenyl-alpha-naphthylamine, corrosion inhibitors, such as sorbitan monooleate and sodium nitrite, dyes, other grease thickeners, and the like.

The lubricating grease of the present invention can be prepared by methods known in the art. For example, the colloidal asbestos, the polymeric fluorocarbon, the inorganic thickener and a part of the lubricating oil to be used can be premixed at elevated temperatures below the melting point of the polymeric fluorocarbon, i.e., in the range of about 250° to 450° F., when free water and water of crystallization is felt to be above the desired level in order to drive off substantially all of said water, or can be premixed at ambient temperatures, e.g., 77° F. until the oil has wet the other components. Sufficient lubricating oil to obtain the desired consistency can then be added and the entire composition mixed until the homogeneous product is obtained. This product can then be milled to optimum smoothness by passage through a mill apparatus. Alternatively, the grease can just as readily be made by charging all of the components at essentially the same time to a Hobart mixer and then milling.

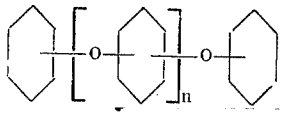
The nature of this invention will be further understood when reference is made to the following examples which include preferred embodiments, which are not to be construed as a limitation on the invention.

Series of greases were prepared by charging the ingredients to a Hobart mixer, heating to 450° F. for 5 minutes while mixing, and then roll milling to a uniform, homogeneous product. The compositions of the greases prepared and their penetration and load-carrying ability are summarized in the following table.

TABLE I

	Composition (grams)						Properties	
	Polyphenyl-ether [1]	Colloidal asbestos	Poly tetrafluoroethylene	Talc [2]	Zinc oxide	Phenyl-alpha-naphthylamine	ASTMD-217 penetration (mm./100) 77° F., 60 strokes	4-ball E.P. 1,800 r.p.m. (kg. weld)
Example 1	398	24.5	[3] 24.5	49	----	4	316	447
Comparative Grease A	398	24.5	----	49	----	4	316	158
Example 2	600	30	[3] 30	30	----	6.4	315	316
Comparative Grease B	600	30	----	30	----	6.4	315	158
Example 3	750	40	[4] 37.5	----	40	9	312	398
Comparative Grease C	750	40	----	----	40	9	312	158
Comparative Grease D	1,000	60	----	----	----	10.6	309	158
Comparative Grease E	1,000	60	[5] 50	----	----	10.6	309	251
Comparative Grease F	820	----	----	500	----	12.5	326	251
Comparative Grease G	820	----	[5] 65	500	----	12.5	326	251

1. An oil represented by the general formula:



where n is 3, obtained from Monsanto Chemical Co. under the designation, "High Temperature Functional Fluid and Lubricant OS-124."

2. Powdered talc obtained from Baker & Adams Co. and described as meeting USP standards.

3. DuPont TFE Teflon 7A having an average particle size of 20 microns, a specific gravity within the range of 2.12–2.14 (ASTM D-742) and an apparent bulk density of 470 g./l. (ASTM D-1457-62T).

4. Liquid Nitrogen Processing Co.'s TL-126 having an average particle size of about 5–10 microns, a specific gravity of about 2.16 and a softening point of 612° F.

5. Liquid Nitrogen Processing Co.'s TL-115 having an average particle size of 8–10 microns and a specific gravity within the range of 2.16–2.18.

The Shell 4-ball e.p. test is used to evaluate the e.p. characteristic of a grease. In this test three steel balls in a pot are locked in contact with one another on a horizontal base. A fourth ball is held on top in a vertical chuck which rotates at 1800 r.p.m. The points of contact are lubricated by the test grease. Initially, a 40-kilogram load applied to a lever arm presses the three stationary balls upward against the rotating ball. The machine is run at room temperature, e.g., 77° F., and increasing pressure is applied to the balls rotating in the machine until seizure is felt and finally until the balls weld. The higher the seize and weld values, the better the extreme pressure properties of the grease. A series of 10-second runs was made at preselected, successively higher loads until welding of the four balls occurred. The loads used were 40 kg., 50 kg., 63 kg., 79 kg., 100 kg., 126 kg., 158 kg., 200 kg., 251 kg., 316 kg., 398 kg., and 447 kg. A fresh grease sample and new steel balls were used with each load.

As can be seen from comparing the greases formed in examples 1, 2 and 3, which represent the invention, with those of comparative greases A, B and C, the greases containing a combination of the three components of this invention exhibit unexpectedly superior e.p. properties over those greases having the same consistency in which the polytetrafluoroethylene was not present.

Comparative Greases D through G serve to demonstrate that the observed synergistic effect was a result of the combination of the three components of this invention and was not the result of the combination of polytetrafluoroethylene with only one of the other two components or the result of merely additive e.p. properties. As can be seen by comparing grease G with grease F, polytetrafluoroethylene does not increase the e.p. properties of the product containing only talc and oil. Furthermore, a comparison of grease D with greases A and B shows that talc does not increase the e.p. properties of a grease containing only colloidal asbestos and oil.

Thus, while a comparison of greases D and E shows that polytetrafluoroethylene does increase the e.p. properties of a grease containing colloidal asbestos and oil, this, in view of the data on polytetrafluoroethylene, talc and oil, is far from suggesting that a combination of the three components of this invention would exhibit the clearly synergistic effect seen in examples 2, 3 and especially 1 of table I.

EXAMPLE 4

Extreme pressure greases are also obtained when fluorinated ethylene propylene copolymer[6]([6]Liquid Nitrogen Processing Co.'s TL-120 FEP, having an average particle size of 0.7 micron, a specific gravity within the range of 2.16–2.18 and a melting point of about 540° F.) is substituted for the polytetrafluoroethylene of examples 1, 2 and 3. When making these greases the components are heated to 400° F. for 5 minutes and then roll milled to a homogeneous product.

In light of the extreme pressure properties exhibited by the grease compositions of this invention, these greases are especially useful in the lubrication of relatively moving parts (e.g., gears, bearings, etc.) which are subject to high pressures in their operation.

While particular embodiments of this invention are shown in the examples, it will be understood that the invention is obviously subject to the variations and modifications disclosed above without departing from its broader aspects and, therefore, it is not intended that the invention be limited to the specific modifications which have been given above for the sake of illustration, but only by the appended claims.

What is claimed is:

1. A lubricating grease composition comprising:
   a. a major amount of lubricating oil;
   b. about 1 to about 15 weight percent of colloidal asbestos, characterized as having naturally occurring fibers with a particle outer diameter of about 1 to 80 millimicrons and a particle length of about 2,000 to 30,000 millimicrons;
   c. about 1 to about 15 weight percent of a finely divided polymeric fluorocarbon powder having an average particle size ranging from submicron to 100-micron size and having a melting point above 450° F.; and
   d. about 1 to about 25 weight percent of an inorganic grease thickener selected from the group consisting of talc and zinc oxide;
   said weight percents being based on the total composition, the combined amount of components (b) and (d) representing about 5 to about 40 weight percent of the total composition.

2. The lubricating composition of claim 1 wherein said polymeric fluorocarbon powder is selected from the group consisting of polytetrafluoroethylene and copolymer of tetrafluoroethylene and hexafluoropropylene.

3. A lubricating composition as in claim 1 wherein the inorganic thickener is zinc oxide.

4. A lubricating composition as in claim 1 wherein the inorganic thickener is talc.

5. A lubricating composition as in claim 1 wherein the combined amount of colloidal asbestos and inorganic thickener represents about 6 to about 30 weight percent of the total composition.

6. A lubricating composition as in claim 1 wherein the finely divided polymeric fluorocarbon powder is polytetrafluoroethylene.

7. A lubricating composition as in claim 1 wherein the finely divided polymeric fluorocarbon powder is characterized as having an average particle size ranging from about 5 to about 25 microns.

8. A lubricating composition as in claim 1 wherein the ratio of component (d) to the combined weight percent of components (b) and (c) ranges from about 0.5:1 to about 3:1.

9. A lubricating composition as in claim 1 wherein the colloidal asbestos forms about 3 to about 10 weight percent of the total lubricating grease composition, the finely divided polymeric fluorocarbon powder forms about 2 to about 10 weight percent of the total composition and the inorganic thickener forms about 3 to 20 weight percent of the total composition.

10. A method of improving the lubrication of relatively moving parts which comprises applying to said parts the grease composition defined by claim 1.

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