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LUBRICATING GREASE CONTAINING COLLOIDAL ASBESTOS

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ABSTRACT OF THE DISCLOSURE

5 to 40 wt. percent of colloidal asbestos in the form of small tubular fibers having outer diameters of 1 to 80.0 millimicrons and particle lengths of 2,000 to 30,000 millimicrons will thicken a major amount of lubricating oil to form a lubricating grease. Optionally, 0.5 to 15 wt. percent of carboxylic acid such as C_{12} to C_{30} fatty acids, dimers or trimers of said fatty acids, can be reacted by mixing and heating with the colloidal asbestos, during the grease making process, which makes the grease water-insoluble.

BACKGROUND OF THE INVENTION

Field of the invention

Lubricating oil is thickened to form a lubricating grease by colloidal asbestos. Optionally, carboxylic acid can be added to the composition and is believed to interact with the asbestos. This invention, therefore, relates to lubricating grease containing colloidal asbestos as a thickener, wherein the colloidal asbestos can be the sole thickener for the grease, or wherein it can be used in conjunction with various carboxylic acids.

Description of the prior art

The use of natural asbestos as a prior ingredient of lubricating compositions is old in the art and a number of various grease formulations are taught in the book "Lubricating Grease," by C. J. Boner, 2nd edition, pp. 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 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 relies 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.

SUMMARY OF THE INVENTION

The asbestos of the present invention differs from the aforesaid prior long fibered conventional asbestos in that this new asbestos is colloidal asbestos, i.e. the particles are in a very small colloidal size, having a large surface

area. This colloidal asbestos can be dispersed in the oil to form a gel by itself, without soap, and without settling out from the oil. This colloidal asbestos is chrysotile having the chemical formulation $Mg_6(OH)8Si_3O_{10}$. The usual mode of occurrence of chrysotile is a "cross-fiber" configuration in which filaments of chrysotile (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 chrysotile 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, matte-like flakes and agglomerates of 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 80.0, e.g. 10 to 40.0 millimicrons. While the diameters of the fibers cannot be reduced, their lengths can be further reduced by milling or homogenization during grease manufacture. A typical colloidal asbestos that was used in the working examples of the invention had the following characteristics:

Properties of colloidal asbestos used in the working examples

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	O.D. 25.0 millimicrons. I.D. 6.0 millimicrons. Length 2,500–25,000 millimicrons.

While the colloidal asbestos can be used per se, as the sole grease thickener, it has been further found that the asbestos grease can be even further improved by the addition of a high molecular weight fatty acid which acts to make the grease water-insoluble. It is believed that the asbestos neutralizes the fatty acid either by reacting with the fatty acid to form a magnesium soap and/or by physical combining to the asbestos. In any event the acid imparts water insolubility to the grease.

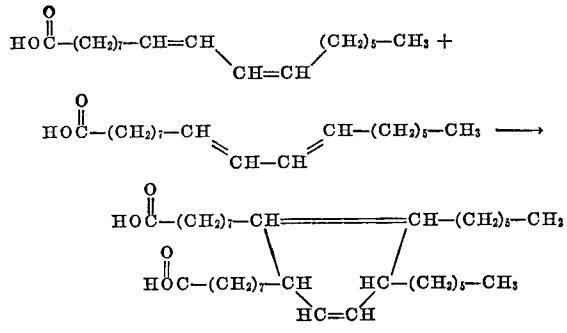
The lubricating oil used in making the lubricating grease compositions of the invention may be either a mineral lubricating oil or a synthetic lubricating oil. Synthetic lubricating oils which may be used include esters of dibasic acids (e.g. di-2-ethylhexyl sebacate), esters of glycols (e.g. C_{13} Oxo acid diester of tetraethylene glycol), complex esters (e.g. the complex ester formed by reacting one mole of sebacic acid with two moles of tetra-

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ethylene glycol and two moles of 2-ethyl-hexanoic acid), halocarbon oils, alkyl silicates, sulfate esters, mercaptals, formals, polyglycol type synthetic oils, etc.

If a fatty acid is used to react with the asbestos, it will generally be a C_{12} to C_{30}, preferably C_{14} to C_{20}, monocarboxylic fatty acid of any of the types generally used in grease making, e.g. substituted or unsubstituted, such as hydroxy substituted, saturated or unsaturated, either synthetic or naturally occuring, or the acid can be dimers or trimers of the C_{12} to C_{30} unsaturated fatty acids. Examples of such monocarboxylic acids include capric, caproic, lauric, coconut oil acids (mixtures of capric, caproic and lauric acids), tallow fatty acids, oleic, palmitoleic, gadoleic, erucic, stearic, linoleic, 12-hydroxy stearic, etc. The 12-hydroxy stearic acid is particularly preferred since it gives a good grease structure at low temperatures.

The aforementioned dimer and trimer acids are polycarboxylic acids having the general formula: $R(COOH)_n$ wherein n is 2 or 3, and wherein R is a hydrocarbon radical within the range of 24 to 90 carbon atoms, usually 36 to 54 carbon atoms, and may be either saturated or unsaturated. While some of the higher molecular weight acids will be solid, they can be dispersed in the oil by heating the acid in the oil sufficiently to melt the acid, while stirring. Dimers and trimers of linoleic acid are commercially readily available. Linoleic dimer acid is formed by reaction of two molecules of linoleic acid in a typical Diels-Alder reaction. This dimer acid is described in U.S. Patent 2,424,588. Its formation and structure is believed to be as follows:



Linoleic trimer acid is tricarboxylic acid formed by polymerization of three molecules of linoleic acid which are linked together by their unsaturation.

Further description of these linoleic dimer and trimer acids are given in the catalog "Empol Dimer Acids" by Emery Industries, Inc., copyright 1963.

The grease compositions of the invention will comprise a major amount of lubricating oil and about 5.0 to 40.0 wt. percent, preferably 8 to 30 wt. percent of colloidal asbestos. The composition may also contain about 0.5 to 15, preferably 2 to 5 wt. percent of fatty acid to make the grease water-insoluble, all of said wt. percent being based on the weight of the total composition. The amount of fatty acid can be such as to be substantially neutralized by the colloidal asbestos, although either more or less than a neutralizing amount of acid can be used. In other words, using less acid in any amount will result in a mixture of neutralized asbestos and unneutralized asbestos, while an excess of acid will result in some free acid, which free acid will generally improve the lubricity of the grease.

Various additives can be added to the finished grease lubricant in amounts of 0.1 to 10.0 wt. percent, based on the weight of the finished grease. Among additives that can be added are: corrosion inhibitors such as sodium nitrite, lanolin, wool grease stearine; antioxidants such as phenyl-α-naphthylamine; load carrying agents such as sulfurized sperm oil, lead naphthenate; dyes; etc.

The compositions of the invention can be readily formed by simply stirring the colloidal asbestos into the oil while at room temperatures. In the event that fatty acid is also used, it too can be simply added to the oil, following which the mixture of oil, asbestos and acid is preferably heated to temperatures of about 250 to 600° F., preferably 320 to 450° F., in order to facilitate the interaction and neutralization of the asbestos. The higher temperatures will result in dehydrating the grease, or the water of reaction from the neutralization can be left in to form a cold set grease. Upon cooling, the other additives can be added to the composition, following which the grease can be homogenized, e.g. in a Charlotte colloidal mill, or a Manton-Gaulin homogenizer, etc.

The invention will be further understood by reference to the following preferred embodiments wherein all parts are by weight.

Description of the preferred embodiments

EXAMPLE I

10 parts of the aforesaid colloidal asbestos was mixed with 90 parts of mineral lubricating oil having a viscosity of 80 SUS at 210° F. in a grease kettle, while at room temperature of about 77° F. After thoroughly mixing, the resultant composition was then passed through a Charlotte colloidal mill having a .003" opening. The milled product was a homogeneous solid grease structure.

EXAMPLE II

76 parts of mineral lubricating oil having a viscosity of 55 SUS at 210° F. and 3 parts of 12-hydroxy stearic acid were added to an electrically heated jacketed grease kettle and stirred while warming to a temperature of about 125° F. Then 20 parts of the colloidal asbestos was added and stirred into the reaction mass. Heating was continued to a temperature of about 420° F. in order to complete the reaction of acid and asbestos and to dehydrate the grease. Upon reaching 420° F., heating was discontinued and the grease was rapidly cooled while stirring and passing cold water through the kettle jacket so that in about 15 minutes the grease temperature had dropped to about 250° F., where one part of phenyl-alpha-naphthylamine was stirred into the grease as an antioxidant. The grease was further cooled to 100° F., and then homogenized by passage through a Morehouse mill having a .032 inch opening to form the finished grease product.

EXAMPLE III

92 parts of the grease product of Example II was mixed with 6 parts of sulfurized sperm oil having a sulfur content of 12 wt. percent and 2 parts of a lead naphthenate concentrate consisting of 30% of lead naphthenate dispersed in 70 wt. percent of a mineral lubricating oil. The resulting mixture was then stirred while at a temperature of 120° F. until a smooth homogeneous product was obtained.

EXAMPLE IV

Following the general procedure of Example I, a grease was prepared using a linoleic trimer acid having three carboxylic acid groups in place of the 12-hydroxy stearic acid and using different proportions of materials.

The compositions prepared and their properties are summarized in the following table.

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TABLE I

Formulation (Parts by Weight)	I	II	III	IV
Colloidal tubular asbestos [1] ($Mg_6OH_8Si_4O$)	10.0	20.0	18.40	15.0
12-hydroxy stearic acid		3.0	2.76	
Linoleic trimer acid				2.0
Phenyl-α-naphthylamine		1.0	.92	1.0
Sulfurized sperm oil (12% S)			6.00	
Lead naphthenate (30%)			2.00	
Mineral lubricating oil, 80 SUS at 100° F	90			
Mineral lubricating oil, 55 SUS at 210° F		76.0	69.92	84.0
ASTM Free acidity or alkalinity	[2]	[2]		[2]
Properties:				
Appearance	[5]	[5]	[6]	[5]
Dropping point, ° F	400	400+	400+	400+
ASTM Penetration, 77° F., mm/10:				
Unworked	305	272	302	285
Worked 60 strokes	310	284	302	296
Worked 10,000 strokes	320	298	310	350
Water solubility (boiling water)	[7]	[8]	[8]	[8]
Lubrication Life, NLGI-ABEC Test at 10,000 r.p.m. and 250° F., Hours	950	1,200		1,800
Wheel bearing test, 220° F		Pass	Pass	
Slump		None	None	
Leakage, grams		3.0	None	
Timken Test (lbs. load)		[9]	[10]	[10]

[1] O.D., 25 millimicrons; I.D., 6 millimicrons, length, 2,500 to 25,000 millimicrons.
[2] Neutral.
[3] 0.54% acid calculated as oleic acid.
[4] 0.5% acid calculated as oleic acid.
[5] Excellent.
[6] Smooth.
[7] Unstable.
[8] Insoluble.
[9] Pass 35 lbs.
[10] Pass 40 lbs.

As seen by the preceding table, the product of Example I consisting of the mineral oil thickened with colloidal asbestos as the thickener formed an excellent appearing grease having a dropping point of 400° F. Example II shows that by adding hydroxy stearic acid, the grease was converted into a water insoluble, stable grease. Example III shows that the grease of the invention is compatible with conventional load carrying additives, namely, sulfurized sperm oil and the lead naphthenate. Example IV shows the use of a high molecular weight linoleic trimer acid also resulted in an insoluble grease having a long lubrication life and good load carrying ability, even without load carrying agents, as indicated by the Timken Test. On the other hand, without the acid present, the load carrying ability would have been much lower, i.e. about 10 to 15 pounds in the Timken Test.

What is claimed is:

1. A water-insoluble lubricating grease comprising a major amount of a lubricating oil and as a thickener about 5 to 40 wt. percent of colloidal asbestos having particle outer diameters of about 1 to 80 millimicrons and particle lengths of about 2,000 to 30,000 millimicrons reacted with 0.5 to 15 wt. percent of a carboxylic acid selected from the group consisting of C_{12} to C_{30} fatty acids, dimers and trimers of said fatty acids.

2. A lubricating grease according to claim 1, wherein said asbestos has particle outer diameters of 10 to 40.0 millimicrons, and said fatty acid is 12-hydroxy stearic acid.

3. A lubricating grease according to claim 1, wherein said asbestos has particle outer diameters of 10 to 40.0 millimicrons, and said fatty acid is a trimer of linoleic acid.

4. A lubricating grease comprising a major amount of mineral lubricating oil, about 8 to 30 wt. percent of colloidal asbestos having particle outer diameters of about 10 to 40.0 millimicrons and particle lengths of about 2,000 to 30,000 millimicrons reacted with about 2 to 5 wt. percent of C_{12} to C_{30} fatty acid.

5. A method of preparing the lubricating grease of claim 1, which comprises heating said acid and said asbestos together in lubricating oil to 250 to 600° F. and cooling.

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