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[54] **METHYL SILICONE GREASE COMPOSITION AND METHOD OF MAKING SAME**
4 Claims, No Drawings

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[56] **References Cited**
UNITED STATES PATENTS
2,680,095 6/1954 Hotten et al. 252/42.1
2,684,944 7/1954 Zajac 252/42.1

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ABSTRACT: A grease composition contains a polysiloxane, the organic substituents of which are methyl radicals, a higher fatty acid soap of lithium, an amount of a polyether which is sufficient to cause the lithium soap of the fatty acid to disperse into the polysiloxane, but insufficient to deleteriously affect the high-temperature properties of the grease, and a sufficient amount of a base to render the grease alkaline. The grease is made by heating together the polysiloxane, the polyether, the lithium soap of the higher fatty acid and the base to a temperature of about 400° to 500° F., after which the grease composition is cooled to room temperature, then milled. The grease composition is used in the journal bearings of starter motors having high-current capacity and which run hot but are subjected to extremely low temperatures when not running.

METHYL SILICONE GREASE COMPOSITION AND METHOD OF MAKING SAME

This invention relates to improved methylpolysiloxane grease compositions and an improved process for making the same. More particularly, the present invention is concerned with organopolysiloxane grease compositions, the organic substituents of which are all methyl, and a method for making the same which eliminates the formation of soap lumps in the finished grease.

Organopolysiloxane greases and grease compositions are well known in the art and have been used as lubricants, dielectric compounds, sealing compounds and high-vacuum greases. These organopolysiloxane greases have been particularly valuable because of their high degree of heat stability, their water repellency, their low- and high-temperature viscosity characteristics and dielectric properties.

In the past it has been extremely difficult to prepare greases containing a silicone fluid all of the substituents of which are methyl in combination with a higher fatty acid soap by means of a melt process. The soap and the silicone fluid are incompatible because the soap and the silicone fluid are incompatible because the soap does not absorb the fluid and soap lumps are formed in the grease. This interferes with the mechanical processing of the grease and results in a final product which has poor bleed characteristics and poor stability at higher temperatures and during storage.

To solve this problem of lump formation in silicone greases, it has been found that long chain alkyl groups and aryl radicals could be used to replace the methyl radicals on the polysiloxane and thus give better compatibility with metal soaps of higher fatty acids. The proposed theoretical reason for the compatibility is that the large organic radicals on the polysiloxanes are adsorbed on or dissolved in the long alkyl groups on the fatty acid soap. While the substitution of higher alkyl radicals and aromatic radicals for the methyl radicals on the polysiloxane used to make greases have served their purpose so far as compatibility is concerned, some of the radicals added have had an adverse affect on the desirable characteristics, particularly the thermal breakdown characteristics of the organopolysiloxane component of the grease composition. Other radicals have resulted in good high-temperature lubricating properties at the sacrifice of low-temperature properties.

It is an object of the present invention to provide improved organopolysiloxane grease compositions which retain most of the beneficial properties of heretofore known polysiloxane grease compositions and which, in addition, are easy to make and inexpensive.

This and other objects of my invention are accomplished by an improved methylpolysiloxane grease composition containing a minor amount of a polyether. It has been found that the presence of a minor amount of a polyether in a methylpolysiloxane grease composition containing a lithium soap of a higher fatty acid provides markedly improved compatibility between the lithium soap of a higher fatty acid and the polysiloxane component. This prevents the formation of large agglomerates of soap during the manufacturing of the grease and allows the preparation of a grease with desirable properties. The grease compositions of the present invention consist essentially of, on a weight basis:

1. from 61 to 98 percent of a polysiloxane fluid, the organic substituents of which are methyl groups;
2. from 2 to 35 percent of a lithium soap of a higher fatty acid having from 10 to 22 carbon atoms such as a lithium soap of lauric, myristic, palmitic or stearic acid, preferably myristic or stearic acid;
3. from 0.01 to 5.0 percent of a polyether;
4. a base such as lithium hydroxide in an amount sufficient to maintain the grease on the alkaline side.

The fluid methylpolysiloxanes employed in the practice of the present invention are well known in the art. These fluids are described generally in U.S. Pat. Nos. 2,469,888 and 2,469,890 - Patnode. This type of methylpolysiloxane can be characterized as having the average unit formula:

$$(CH_3)_nSiO_{\frac{4-n}{2}} \qquad (1)$$

where n has a value of from 2.002 to 2.2. Although any methylpolysiloxane fluid within the scope of formula (1) is applicable in the process of the present invention, it is preferred that the fluid have a viscosity of from about 10 centistokes to about 100,000 centistokes when measured at 25° C.

It should be understood that methylpolysiloxane fluids of formula (1) can include siloxane units of varied types and formulation such as trimethylsiloxane units and dimethylsiloxane units alone or in combination with monomethylsiloxane units. The only requirement is that the ratio of the various siloxane units employed be selected so that the average composition of the copolymeric fluid is within the scope of formula (1).

One component of the grease compositions of the present invention is the grease-thickening agents which are well known in the art. This invention contemplates the use of the lithium soaps of any of the higher fatty acids having from 10 to 22 noncarboxyl carbon atoms to form a grease composition of the desired consistency. The term grease as employed in the present application is intended to refer to greaselike materials which may have consistencies varying from readily flowable materials to materials which exhibit essentially no flow. The consistency of the greases of the present invention depend on the amount of thickening agent employed, the particular thickening agent employed and the particular polysiloxane fluids in the grease. Examples of suitable thickening agents include the lithium soaps of higher fatty acids of 10 to 22 noncarboxyl carbon atoms such as lauric, myristic, palmitic, stearic, and preferably the myristic and stearic soaps of lithium.

While, as explained above, the amounts of thickening agent employed in the grease compositions of the present invention are not critical and may vary within wide limits depending on the particular consistency desired in the final product, it has been found that the amount of thickening agent usually varies from about 2 percent to 35 percent and preferably from about 5 percent to 25 percent by weight based on the weight of the grease composition.

One critical feature, however, of the grease composition of the present invention is the amount of the polyether present. For satisfactory dispersion of the thickening agent in the polysiloxane, it has been found that the polyether must be present in an amount equal to from about 0.01 to 5.0 percent by weight based upon the weight of the grease, and preferably from 0.1 to 2.0 percent by weight. When less than 0.01 percent by weight of the polyether is present, it is found that it is very difficult to disperse the thickening agent into the grease and, in addition, there is a tendency for a higher bleed of the polysiloxane fluid from the grease composition. When the amount of polyether in the grease composition is in excess of 5.0 percent by weight, it is found that the weight loss of the grease at temperatures in excess of 300° F. is so excessive that the grease is unsuitable for use in many applications.

The polyethers which are used herein in combination with the polysiloxane oils according to this invention are polymeric alkylene oxides and/or polymeric alkylene glycols, and may be represented by the following formulas:

$$A{-}O{-}(C_xH_{2x}O)_nB$$

and

$A{-}O{-}[(C_xH_{2x}O)_n]_y(Q)_z$ wherein A and B represent radicals selected from the class comprising hydrogen, alkyl radicals containing from one to 12 carbon atoms, cycloalkyl radicals containing five to seven carbon atoms in the ring, mononuclear and binuclear aryl radicals and mononuclear aryl lower alkyl radicals wherein the alkyl groups attached to the aromatic nucleus contain a total of no more than five carbon atoms; A and B also represent ester-forming groups containing from two to 12 carbon atoms; A and B may or may not be alike. When there is more than one A radical per molecule, the A radicals may or may not be the same. Q is a residue of a polyhydric initiator radical containing at least two hydroxyl radicals such as ethylene glycol, glycerol, trimethylolpropane, and other polyhydric alcohols having from two to six hydroxyl groups; x is a number having a value of 2 to 4; n is a number having a value of from 4 to 2,000, y has a value of from 2 to 10 and z has a value of 1 to 5.

More specifically, A and B represent radicals selected from the class comprising hydrogen; alkyl radicals having from one to 12 carbon atoms, e.g., methyl, ethyl, propyl, butyl, octyl, etc. radicals; cycloalkyl radicals having five to seven carbon atoms in the ring, e.g., cyclopentyl, cyclohexyl, cycloheptyl, etc. radicals; mononuclear and binuclear aryl radicals, e.g., phenyl, naphthyl, biphenyl, etc. radicals; mononuclear aryl lower alkyl radicals wherein the alkyl groups attached to the aromatic nucleus contain a total of no more than five carbon atoms, e.g., benzyl, phenylethyl, phenylpropyl, etc.; and ester groups having from one to 12 carbon atoms such as the residues formed by the removal of a carboxyl hydrogen from a fatty acid, e.g., an acetate, propionate, octoate, etc.; hydroxyether groups derived from glycols such as butylene glycol, octylene glycol, etc.; and groups formed by esterification with a hydroxyl group of a nonfatty acid, e.g., propyl phosphate, octyl sulfonate, butyl sulfate, etc.

The polyethers may be prepared from the various alkylene oxides (e.g., ethylene oxide), the higher 1,2-epoxides (such as 1,2-propylene oxide), the alkylene glycols (e.g., ethylene glycol) and mixtures of these. The resulting products may be polyoxalkylene diols or polyalkylene glycol derivatives; that is, the terminal hydroxyl groups can remain as such, or one or both of the terminal hydroxyl groups can be removed during the polymerization reaction or subsequent thereto, as by etherification or esterification to yield mono- or di-ether or mono- or di-ester groups or a combination of such terminal groups whereby certain desirable properties are imparted to the final polymeric mixtures. For example, in the above formula A and/or B may be: alkyl radicals, forming a di-alkyl polyether (e.g., dibutyl heptaoxypropylene diether); ester forming radicals, forming alkyl oxyalkylene esters (e.g., butyl pentaoxypropylene acetate); hydrogen, forming polyglycols (e.g., polyethylene glycol), etc.

To further exemplify the polyethers which can be used, the polyether oil, that is, the $-Cx(H_{2x}O)_n-$ section of the above formula, can be derived from such basic units as the following oxides:

$$\text{sec-propylene oxide}\ -(CH_2-\underset{}{\overset{\displaystyle CH_3}{\overset{|}{C}H}}-O)-$$

$$\text{sec-butylene oxide}\ -(CH_2-\underset{\underset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_2}{|}}}}{CH}-O)-$$

$$\text{tert-butylene oxide}\ -(CH_2-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-O)-\text{, etc.}$$

or basic units obtained by the dehydration of alkylene glycols, resulting in the formation of the following:

ethylene oxide $-(CH_2-CH_2-O)-$,

propylene oxide $-(CH_2-CH_2-CH_2-O)-$,

butylene oxide $-(CH_2-CH_2-CH_2-CH_2-O)-$,

etc.

Polyethers containing combinations of the above-described basic units have been found to be quite useful in the practice of the present invention. A composition containing two different alkylene oxide groups can be prepared, e.g., by reacting a polypropylene glycol with ethylene oxide in the presence of boron trifluoride. This mixed polyalkylene glycol, if desired, can then be reacted with an alkanol such as butanol to form the monobutoxyether of the mixed polyalkylene glycol. A number of these polyalkylene oxide materials are commercially available including the materials sold under the trade name "Ucon" by Union Carbide Corporation, and the materials sold under the name of "Pluracol" by the Wyandotte Chemicals Corporation.

The molecular weight of the polyether oils used according to this invention can range from 300 to 200,000; from 400 to 20,000 being preferred.

In addition to the above-described components, additives normally present in silicone greases can be present in the composition of the present invention. Examples of additives include antioxidants such as the amines, e.g., N-phenyl-alpha-naphthyl amine; corrosion inhibitors, e.g., zinc naphthanate; and extreme pressure additives such as selenium disulfide, molybdenum disulfide, etc.

There are a number of methods for forming the compositions of the present invention. In the preferred method, the polysiloxane fluid, the lithium soap-thickening agent, the polyether dispersing agent and a small amount of a finely ground base such as lithium hydroxide are heated to a temperature of about 400° to 500° F. after which the grease composition is cooled to room temperature, then milled.

The following examples are illustrative of the practice of the present invention and are not intended for purposes of limitation.

EXAMPLE 1

In this example a grease composition was prepared employing a trimethylsilyl chain-stopped polydimethylsiloxane having a viscosity of 350 centistokes when measured at 25° C. as a base fluid. To 540 grams of lithium myristate and 30 grams of a polyoxalkylene polyol of the formula:

$$\begin{array}{l} \qquad\qquad\qquad\qquad\qquad\quad\ CH_2(OC_3H_6)_8(OC_2H_4)_{24}OH \\ \qquad\qquad\qquad\qquad\qquad\quad\ | \\ HO(C_2H_4O)_{24}(C_3H_6O)_8CH_2-C-CH_2(OC_3H_6)_8(OC_2H_4)_{24}OH \\ \qquad\qquad\qquad\qquad\qquad\quad\ | \\ \qquad\qquad\qquad\qquad\qquad\quad\ CH_3(OC_3H_6)_8(OC_2H_4)_{24}OH \end{array}$$

were added 1,080 grams of the base fluid and 0.9 grams of finely divided lithium hydroxide. The components were thoroughly mixed and then heated to 470° F. The mixture was slowly cooled (1.4° F. per minute) to 345° F. at which point 15 grams of N-phenyl-alpha-naphthylamine and 1,365 grams of the base oil were added with continuous stirring. The slow cooling was continued and at 210° F. 1.5 gram of finely divided lithium hydroxide was added and the grease was cooled to room temperature still with continuous stirring. The grease formed was milled through a Morehouse mill three times. Processing was very smooth and very few lumps were formed due to the lithium myristate conglomerating during mixing.

A comparison grease was formed to determine the effect of the addition of the polyether on the ease of processing. The grease was prepared in exactly the same manner as that prepared earlier in the example except that no polyether was added. The processing was very difficult due to the formation of lithium myristate lumps during the mixing operation. The lumps would not pass through the mill with the rest of the ingredients. A comparison of the two greases showed that the grease containing the polyether was a thicker, smoother grease and there was much less tendency for the silicone oil to separate from the grease.

EXAMPLE 2

To 540 grams of a mixture containing 60 percent of lithium stearate and 40 percent of lithium palmitate were mixed 1,080 grams of the base oil described in example 1, 0.9 grams of lithium hydroxide which had been preground on a three roll mill with a small portion of the lithium stearate—lithium palmitate—base oil mixture and then with continued stirring was added 30 grams of a polyoxyalkylene polyol of the formula:

$$\begin{array}{l} \qquad\qquad\qquad\qquad\qquad\quad\ CH_2(OC_3H_6)_8(OC_2H_4)_{24}OH \\ \qquad\qquad\qquad\qquad\qquad\quad\ | \\ HO(C_2H_4O)_{24}(C_3H_6O)_8CH_2-C-CH_2(OC_3H_6)_8(OC_2H_4)_{24}OH \\ \qquad\qquad\qquad\qquad\qquad\quad\ | \\ \qquad\qquad\qquad\qquad\qquad\quad\ CH_3(OC_3H_6)_8(OC_2H_4)_{24}OH \end{array}$$

The mixture was heated to 475° F. with continued stirring. The mixture was then slowly cooled (1.4° F. per minute) to

345° F. at which point 15 grams of N-phenyl-alpha-naphthylamine and 1,365 grams of the base oil were added, still with continued stirring. The slow cooling was continued and at 212° F. an additional 1.5 grams of lithium hydroxide, which had been preground as described above, was added and the grease formed was cooled to room temperature, still with continuous stirring. The grease formed was milled through a Morehouse mill three times. Processing was very smooth and few lumps were present due to lithium soap conglomerating.

For comparison purposes a grease identical in all respects except that the polyoxyalkylene polyol was omitted from the formulation. The processing of the comparison grease was very difficult and the grease was quite lumpy upon completion of the mixing operation due to the conglomeration of particles of lithium stearate and palmitate. Many of the larger, harder lumps remained in the mill reservoir, resulting in a thinner grease. The grease produced containing the polyoxyalkylene polyol was much less prone to bleeding than the comparison grease especially at high temperatures.

EXAMPLE 3

In this example a grease composition was prepared employing a trimethylsilyl chain-stopped polydimethylsiloxane having a viscosity of 100 centistokes when measured at 25° C. as a base fluid. To 540 grams of lithium myristate and 30 grams of polyoxyalkylene polyol of the formula:

$$HO(C_2H_4O)_{24}(C_3H_6O)_8CH_2-\underset{\displaystyle CH_3(OC_3H_6)_8(OC_2H_4)_{24}OH}{\overset{\displaystyle CH_2(OC_3H_6)_8(OC_2H_4)_{24}OH}{\underset{|}{\overset{|}{C}}}}-CH_2(OC_3H_6)_8(OC_2H_4)_{24}OH$$

were added 1,080 grams of the base fluid and 0.9 grams of finely divided lithium hydroxide. The components were thoroughly mixed and then heated to 470° F. The mixture was slowly cooled (1.4° F. per minute) to 345° F. at which point 15 grams of N-phenyl-alpha-naphthylamine and 1,365 grams of the base oil were added with continuous stirring. The slow cooling was continued and at 210° F. 1.5 gram of finely divided lithium hydroxide was added and the grease was cooled to room temperature still with continuous stirring. The grease formed was milled through a Morehouse mill three times. Processing was very smooth and very few lumps were formed due to the lithium myristate conglomerating during mixing. A comparison grease was formed to determine the effect of the addition of the polyether on the ease of processing. The grease was prepared in exactly the same manner as that prepared earlier in the example except that no polyether was added. The processing was very difficult due to the formation of lithium myristate lumps during mixing. A comparison of the two greases showed that the grease containing the polyether was thick and smooth whereas the comparison grease was thinner and the mill reservoir had little round balls like buckshot in it, formed from the lithium myristate. The balls would not pass through the mill. The balls were so hard that a treatment more severe than that conventionally used would be required to break them up.

EXAMPLE 4

In this example a grease composition was prepared employing a trimethylsilyl chain-stopped polydimethylsiloxane having a viscosity of 350 centistokes, when measured at 25° C. as a base fluid. To 560 grams of lithium myristate and 31.2 grams of a polyether of the formula:

$$HO(\underset{\displaystyle CH_3}{\underset{|}{C}}H_2CH_2O)_{26}-(CH_2)_3CH_3$$

were added 1,200 grams of the base fluid and 1.0 grams of finely divided lithium hydroxide. The components were thoroughly mixed and then heated to 470° F. The mixture was slowly cooled (1.4° F. per minute) to 345° F. at which point 20 grams of N-phenyl-alpha-naphthylamine and 1,740 grams of the base oil were added with continuous stirring. The slow cooling was continued and at 210° F. 1.0 gram of finely divided lithium hydroxide and 440 grams of lithium myristate were added and the grease was cooled to room temperature still with continuous stirring. The grease formed was milled through a Morehouse mill three times. Processing was very smooth as there were very few lumps formed due to the lithium myristate conglomerating during mixing.

A comparison grease was formed to determine the effect of the addition of the polyether on the ease of processing. The grease was prepared in exactly the same manner as that prepared earlier in the example except that no polyether was added. The milling was very difficult due to the presence of lithium myristate lumps which had formed earlier in the process clogging the inlet to the mill. A comparison of the two greases showed that the grease containing the polyether was a thicker, smoother grease and there was much less tendency for the silicone oil to separate from the lithium myristate especially at high temperature. The comparison grease was deficient in soap due to the impossibility of getting many of the larger soap lumps through the mill. The grease containing the polyether had the following properties:

Penetration (worked 60x)	245
Bleed, 24 hours 0 150° C.	1.68%
Evaporation, 24 hours 0 150° C.	1.62%

While the foregoing examples have illustrated certain embodiments of the present invention, it should be understood that our invention is broadly applicable to grease compositions containing polysiloxanes, the substituents of which are all methyl groups in combination with a lithium soap of a higher fatty acid, from 0.01 to 5.0 percent of a polyether and a sufficient amount of base to maintain the composition on the alkaline side.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A grease composition consisting essentially of on a weight basis:

1. from about 61 percent to about 98 percent by weight based upon the weight of the grease of a fluid methyl polysiloxane having a viscosity of from about 10 to about 100,000 centistokes having the average unit formula:

$$(CH_3)_nSiO_{\frac{4-n}{2}}$$

where n has a value of from 2.002 to 2.2;

2. from about 2 percent to about 35 percent by weight based upon the weight of the grease of a grease-thickening lithium soap of a fatty acid having from 10 to 22 non-carboxyl carbon atoms;

3. from 0.01 percent to 5.0 percent by weight based upon the weight of the grease of a polyether selected from the group consisting of

$$A-O-(C_xH_{2x}0)_nay-B \text{ and}$$
$$(A-O-(C_xH_{2x}O)-n-_y(Q)_z$$

wherein A and B represent radicals selected from the class consisting of hydrogen, alkyl radicals containing one to 12 carbon atoms, cycloalkyl radicals containing five to seven carbon atoms in the ring, mononuclear and binuclear aryl radicals and mononuclear aryl lower alkyl radicals wherein the alkyl groups attached to the aromatic nucleus contain a total of no more than five carbon atoms; Q is a residue of a polyhydric initiator radical containing at least two hydroxyl radicals selected from the class consisting of ethylene glycol, glycerol, trimethylolpropane, and other polyhydric alcohols having from 2 to 6 hydroxyl groups; n is a number having a value of from 4 to 2,000; x is a number having a value of 2 to 4; y has a value of from 2 to 10; and z has a value of from 1 **to** 5; the polyether having a molecular weight of from about 300 to about 200,000;

4. a metal base in an amount sufficient to maintain the

grease on the alkaline side.

2. The grease composition of claim 1, wherein:

1. the grease-thickening lithium soap is selected from the class consisting of lithium myristate and lithium stearate;
2. the polyether is present in an amount constituting from 0.1 percent to 2.0 percent by weight of the grease composition;
3. the metal base used to maintain the grease on the alkaline side is lithium hydroxide.

3. The grease composition of claim 1, wherein the grease-thickening lithium soap is lithium myristate.

4. The grease composition of claim 1, wherein the polyether is present in an amount constituting from 0.1 percent to 2.0 percent of the grease composition.

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