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POLY(SILOXYGLYCOL) GREASE COMPOSITION

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6 Claims. (Cl. 252—28)

This patent application is directed to grease compositions using as base oils liquid poly(siloxyglycols), some of which are new.

In recent years, careful studies have been made of numerous synthetic oils to replace in whole or in part the petroleum base oils used in the preparation of grease compositions. It has been realized that petroleum base oils have numerous deficiences, such as viscosity indices lower than desired for present operating conditions in high speed bearings. Thus, petroleum oils which are suitable at low temperatures are too volatile at high temperatures, and vice versa, petroleum oils having high viscosities at high temperatures become too stiff and too resistant to flow at low temperatures. Other disadvantages of petroleum base oils include high pour points, high volatility, etc.

Numerous synthetic oils have been prepared to satisfy certain requirements in the lubrication field. For example, polyether synthetic base oils normally are useful at temperatures lower and higher than can be had with mineral base oils. However, polyether oils inherently are readily susceptible to oxidation at high temperatures (e. g., 400° F.), and they become too viscous at such low temperatures as —100° F.

Other synthetic oils (e. g., poly(siloxane) base oils) have been prepared to rectify the disadvantages of such oils as exemplified hereinabove. Although the synthetic base oils such as poly(siloxane) base oils have high viscosity indices, low pour points, low volatility, high heat stability, etc., they are too expensive for general use in the lubrication field. The high cost of such base oils having these desirable properties has been a barrier for their use in the preparation of greases adaptable for general service lubrication.

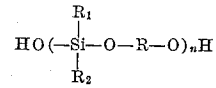
Present day greases must be able to lubricate effectively under conditions of high temperature, that is, temperatures considerably in excess of 400° F., and, in certain instances, in the range of 500° F., and under conditions of low temperature, such as —100° F. In the high temperature range greases, numerous military and industrial grease specifications describe greases having dropping points of about 400° F. as a minimum. This need for high temperature greases, for example, is the result of increased speeds of gears, bearings, and other moving parts.

The continuing trend to manufacture automobiles with lower centers of gravity has made it necessary to use smaller gears, particularly in such gear assemblies as the differentials and transmissions. The smaller gears thus used move at greater speeds and have considerably greater pressures exerted upon them per unit area than the older type gear assemblies. Thus, machines having higher loads on bearings and gears along with greater speeds, require grease compositions which will function at higher temperatures than heretofore.

It is a principal object of this invention to prepare grease compositions which are plastic at low temperatures and at high temperatures.

According to this invention, it has been discovered that highly useful grease compositions which are plastic at low temperatures, have excellent heat stability, have low volatility, etc. can be obtained at lower cost than heretofore possible. It has been discovered that such grease compositions are prepared by incorporating a grease thickening agent in a poly(siloxyglycol) base oil, which is a polymeric product obtained from a dihydric alcohol and a dialkyl dihalosilane. The grease compositions set forth herein comprise a major proportion of a poly(siloxyglycol) base oil, and a sufficient amount of a grease thickening agent to thicken the oil to the consistency of a grease. The grease composition may contain minor amounts of other base oils (e. g., synthetic ester type oils) blendable with the poly(siloxyglycol) oils.

The poly(siloxyglycol) base oils produced by the reaction of dihydric alcohols with dialkyl dihalosilanes are linear polymers of the formula:



wherein R_1 and R_2 represent monovalent organic radicals, R represents a divalent organic radical, and *n* represents the number of units in the polymeric compound.

R_1 and R_2, the monovalent organic radicals, each contain a total of from 1 to 6 aliphatic carbon atoms. Thus, R_1 and R_2 can be aliphatic radicals or alkyl-substituted aromatic radicals. Although R_1 and R_2 may be similar or dissimilar, it is preferred that at least one of these monovalent radicals is an aliphatic radical. Thus, R_1 and R_2 can both be similar or dissimilar aliphatic radicals. However, when one of these monovalent radicals is an aliphatic-substituted phenyl group, the other monovalent organic radical is preferably an aliphatic radical. Examples of R_1 and R_2 monovalent organic radicals include radicals derived from ethane, methane, propane, isopropane, butane, isobutane, tert-butane, pentane, isopentane, neopentane, hexane, isohexane, benzene, toluene, etc.

The R of the above formula is a divalent organic radical containing a total of from 2 to 12 carbon atoms; a total of 2 to 8 carbon atoms being preferred. The R divalent organic radical includes straight-chained and branch-chained aliphatic radicals. It is especially preferred that R be a branch-chained divalent organic radical containing from 3 to 8 carbon atoms. Examples of R radicals include the divalent radicals obtained by removing the hydroxy groups from the following dihydric alcohols: ethylene glycol; propylene glycol; 2,3-butanediol; 2,3-pentanediol; 2,4-pentanediol; 2-methyl-1,3-butanediol; 2-methyl-2,4-butanediol; 2-methyl-3,4-butanediol; 1,8-octanediol; 1,10-decanediol; 1,12-dodecanediol, etc.

As noted hereinabove, the *n* of the above formula represents the number of monomeric units which are present in the polymer. The number representing monomeric units is of such value that the molecular weight of the polymeric compound is from 240 to 5000; with the preferred molecular weight ranging from 350 to 3500.

Thickening agents which can be used to thicken the base oils set forth hereinabove include the following:

Metal soaps of fatty acids, such as the monovalent and polyvalent metal soaps of fatty acids containing from 8 to 30 carbon atoms, e. g., sodium stearate, sodium oleate, calcium oleate, aluminum oleate, barium stearate, strontium stearate, etc.;

Complex basic aluminum soaps, e. g., aluminum benzoate stearate, as described in Hotten U. S. Patent 2,599,553, issued June 10, 1952;

Phenylene diamides, e. g., N,N'-acetyl steroyl-p-

phenylene diamine, as described in Hotten patent application Serial No. 234,153, filed June 28, 1951, now Patent No. 2,698,300;

Acyl ureas, e. g., octadecanoyl urea, as described in Hotten patent application Serial No. 234,154, filed June 28, 1951, now Patent No. 2,709,157;

Polyamides, that is polyamides produced from amines and dibasic acid (e. g., from hexamethylene diamine and sebacic acid), as described in Dixon patent application Serial No. 305,290, filed August 19, 1952;

A metal salt of a polyamic acid (as described in Dixon patent application Serial No. 305,287, filed August 19, 1952);

Silica, and other thickening agents.

The thickening agents may be used in the polymeric base oil described hereinabove in amounts of from about 10% to about 30% by weight, 15% to about 25% being preferred. If it is desired to thicken oils to such consistency that they may be used as filter oils, the amount of thickening agents may be reduced to as low as 5% by weight.

The new base oils set forth herein are prepared by reacting a dialkyl dihalosilane (e. g., dimethyldichlorosilane) with a glycol (e. g., ethylene glycol) alone or in the presence of a base (e. g., pyridine).

The following examples illustrate the preparation of grease compositions of this invention, using the new poly(siloxyglycol) base oils.

Example 1.—Preparation of poly(dimethyl siloxy ethylene glycol)

227 grams of dimethyl dichlorosilane was added dropwise to a mixture of 109 grams of ethylene glycol in 715 grams of pyridine at 50° C. to 60° C. for a period of one hour. The reaction mixture was then distilled to 200° F. vapor temperature at an absolute pressure of 10 mm. of mercury to remove unreacted ethylene glycol, dimethyl dichlorosilane, and other low-boiling compounds. The remaining reaction mixture, which contained 33.9% silicon, had a pour point of —75 to —80° F., and viscosities of 769.6 centistokes at 100° F. and 319.2 centistokes at 210° F.

Example 2.—Preparation of poly(dimethyl siloxy-2-ethyl-1,3-hexanediol)

25.8 grams of dimethyl dichlorosilane was slowly added to a mixture of 2-ethyl-1,3-hexanediol (21.9 grams) and 6.5 grams of 2-ethyl hexanol in 16 grams of pyridine at temperatures ranging from 80 to 150° F. for a period of one hour. The reaction mixture contained 9.7% silicon (theoretical is 9.9%).

Example 3.—Preparation of poly(dimethyl siloxy-2-ethyl-1,3-hexanediol)

25.8 grams of dimethyl dichlorosilane was added to a mixture of 2-ethyl-1,3-hexanediol (29.2 grams). The reaction mixture was heated to a temperature of about 150° F. for a period of one hour. The reaction product, which contained 25.3% silicon, had viscosities of 29.9 centistokes at 100° F., and 6.6 centistokes at 210° F.

Example 4.—Preparation of poly(dimethyl siloxy propylene glycol)

130 grams of dimethyl dichlorosilane was slowly added to a mixture of 76 grams of propylene glycol in 158 grams of pyridine at temperatures ranging from 50–60° C. After the reaction mixture had been washed with water and dried, it was rectified to 300° F. at absolute pressure of 10 mm. of mercury. The reaction product remaining contained 34.2% silicon.

Example 5.—Grease preparation

32 grams of the reaction product distillation residue of Example 1 was thickened to the consistency of a grease (ASTM worked penetration of 264) with 8 grams of finely divided silica in a three-roll paint mill. After 500 hours in the thin film test described hereinbelow, this preparation still retained its grease characteristics.

Example 6.—Grease preparation

4.3 grams of the reaction product obtained from Example 4 was thickened to the consistency of the grease with 0.5 gram of silica. The product was a smooth, translucent grease which showed a wear of only 0.058 mm. in a 4-ball wear test machine over a period of 0.5 hour at a temperature of 200° F. and a pressure of 22 p. s. i.

The stability of the base oils herein in grease compositions was determined according to a thin film test procedure. This test measures the stability of grease compositions, particularly the retention of pliability and the resistance to deterioration under exposure of a thin film to high temperatures. The test also indicates other grease characteristics such as tendency to bleed, flake (some greases although soft and greasy, crack and flake) and tendency to become tacky. This test is performed as follows:

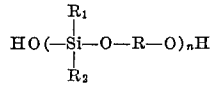
The grease to be tested is coated on a metal strip. The grease coating is of uniform dimension: 1/32 in. thick, 7/8 in. wide and 2½ in. long. This grease sample is then placed in an oven at 300° F. and observed at periodic intervals until the sample loses its grease-like characteristics.

When 0.1 gram of an organo selenide and 0.1 gram of N,N'-di-α-naphthyl-p-phenylenediamine had been added to the grease of Example 6 above, the grease composition still retained its grease characteristics after a test period of 900 hours, at which time the grease sample still had grease-like characteristics, that is, the test sample after this time had not become hard or brittle.

In addition to the components noted hereinabove, the grease compositions may contain extreme pressure agents, other oxidation inhibitors, rust inhibitors, oiliness agents, color agents, dispersing agents, etc.

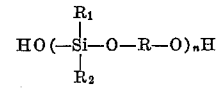
I claim:

1. A grease composition comprising a major proportion of a base oil of lubricating viscosity, and a grease-thickening agent in an amount sufficient to thicken said base oil to the consistency of a grease, said base oil consisting essentially of a poly(siloxyglycol) of the formula



wherein R_1 and R_2 are monovalent aliphatic radicals each containing from 1 to 6 carbon atoms, R is a divalent aliphatic radical derived from dihydric alcohols containing from 2 to 12 carbon atoms, and n is a number of such magnitude that the molecular weight of said poly (siloxyglycol) base oil is from 240 to 5000.

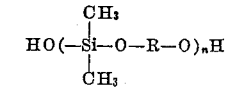
2. A grease composition comprising a major proportion of a base oil and a grease-thickening agent in an amount sufficient to thicken said base oil to the consistency of a grease, said base oil consisting essentially of a liquid poly(siloxyglycol) of the formula



wherein R_1 and R_2 is are monovalent aliphatic radicals containing from 1 to 6 carbon atoms, R is a divalent aliphatic radical derived from dihydric alcohols containing from 2 to 12 carbon atoms, and n represents the number of monomer units present in said poly(siloxyglycol), said monomer units being present in sufficient numbers such that the molecular weight of the poly(siloxyglycol) is from 240 to 5000.

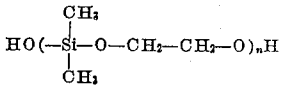
3. A grease composition comprising a major proportion of a base oil and from 10% to 30% of a grease thickening

agent, said base oil consisting essentially of a liquid poly (siloxyglycol) base oil of the formula



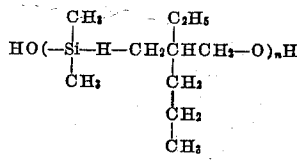
wherein R is a divalent aliphatic radical derived from dihydric alcohols containing from 2 to 12 carbon atoms, and *n* is a number of sufficient magnitude that the molecular weight of said poly(siloxyglycol) base oil is from 240 to 5000.

4. A grease composition comprising a major proportion of a base oil and from 10% to 30% of a grease thickening agent, said base oil consisting essentially of a poly(dimethyl siloxy ethylene glycol) of the formula:



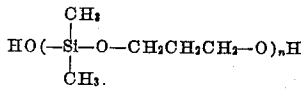
wherein *n* is a number of sufficient magnitude that the molecular weight of said poly(dimethyl siloxy ethylene glycol) is in the range of 240 to 5000.

5. A grease composition comprising a major proportion of a base oil and from about 10% to about 30% of a grease thickening agent, said base oil consisting essentially of a poly(dimethyl siloxy 2-ethyl-1,3-hexanediol) of the formula



wherein *n* is a number of sufficient magnitude that the molecular weight of said poly(dimethyl siloxy 2-ethyl-1,3-hexanediol) is in the range of 240 to 5000.

6. A grease composition comprising a major proportion of a base oil of lubricating viscosity and from about 10% to about 30% of a grease thickening agent, said base oil consisting essentially of a poly(dimethyl siloxy propylene glycol) of the formula



wherein *n* is a number of sufficient magnitude that the molecular weight of said poly(dimethyl siloxy propylene glycol) has a molecular weight in the range of 240 to 5000.

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