Patented May 8, 1951 2,551,931

UNITED STATES PATENT OFFICE

2,551,931

POLYSILOXANE GREASE AND METHOD OF PREPARATION

Chester C. Currie, Midland, Mich., assignor to Dow Corning Corporation, Midland, Mich., a corporation of Michigan

No Drawing. Application September 29, 1948, Serial No. 51,861

8 Claims. (Cl. 252—38)

1

This invention relates to new compositions of matter and more particularly to greases prepared from polysiloxanes and salts of alicyclic substituted fatty acids.

The lubrication of moving parts which operate at high or low temperatures has always presented difficult or insoluble problems. With conventional hydrocarbon oils and greases the temperature at which effective lubrication may be obtained is limited by the inherent thermal instability of those compounds. Greases prepared from polysiloxanes and lithium stearate represent an improvement over the organic greases for high temperature lubrication, but they too have several undesirable properties.

It is an object of this invention to produce a heat stable, non-corrosive grease which will serve as a superior lubricant for operating at very high or low temperatures. Other objects and advantages will appear from the following description.

This invention relates to a grease comprising a liquid organo polysiloxane in which the organic radicals are methyl, phenyl, or tolyl radicals, said siloxane having a degree of substitution of from 1.9 to 2.5 organic radicals per silicon atom and a minor amount of a metallic salt of an alicyclic substituted fatty acid, which fatty acid has a chain length of from 2 to 6 carbon atoms. The metals of the salts are alkali metals or alkaline earth metals. These greases have desirable lubricating properties.

The siloxanes from which the greases of this invention are prepared, are polymers composed of alternate silicon and oxygen atoms wherein

2

the silicon atoms may be variously substituted with the indicated organic radicals. Preferably each silicon atom has from one to three of the herein defined organic radicals attached thereto. The proportions of the variously substituted silicon atoms should be such that there is an average of from 1.9 to 2.5 organic radicals per silicon. The viscosity of the siloxane polymer used to prepare the grease is in no way critical.

The above siloxanes may be prepared by any appropriate method. Methods known to the art include hydrolysis or co-hydrolysis of the corresponding hydrolyzable silanes, catalytic copolymerization of the desired siloxanes and the reaction of silicon halides with alkali metal salts of organo silanols.

The additives used to thicken the polysiloxane fluids to produce the greases of this invention are salts of alicyclic substituted fatty acids wherein the fatty acid chain is from 2 to 6 carbon atoms in length. Such acids include for example, cycloparaffin derivatives of straight chain fatty acids, such as cyclohexylacetic, cyclohexylbutyric and cyclopentylvaleric; alkyl substituted cycloparaffin derivates of fatty acids, such as alpha butylcyclohexylacetic, and alpha 4 diterbutylcyclohexylbutric; cyclo-olefine substituted fatty acids, such as 2 cyclohexenecaproic; and polycyclic substituted fatty acids such as pentalaneacetic.

In order that this invention may be better understood, the formulae of some of the acids which may be employed therein are given in Table I.

TABLE I

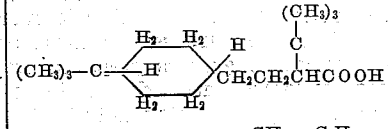
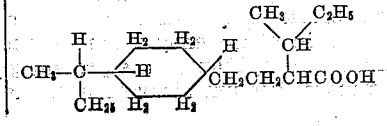
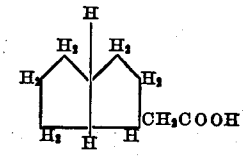
Name	Formula
Cyclohexylacetic	$C_6H_{11}CH_2COOH$
Cyclohexylpropionic	$C_6H_{11}(CH_2)_2COOH$
Cyclohexylbutyric	$C_6H_{11}(CH_2)_3COOH$
Cyclohexylvaleric	$C_6H_{11}(CH_2)_4COOH$
Cyclohexylcaproic	$C_6H_{11}(CH_2)_5COOH$
Alpha butylcyclohexylacetic	$(C_6H_{11})(C_4H_9)CHCOOH$
Gamma ethylcyclohexylbutyric	$(C_6H_{11})(C_2H_5)CH(CH_2)_2COOH$
Alpha 4 diterbutylcyclohexylbutyric	
Alpha 4 disecbutylcyclohexylbutyric	

TABLE I—Continued

Name	Formula
2 cyclohexenecaproic	$C_6H_9(CH_2)_4COOH$
Pentalaneacetic	
Cyclopentylvaleric	$C_5H_9(CH_2)_4COOH$

The salts employed herein are the alkali metal and alkaline earth metal salts of the above defined acids. These salts may be prepared by reacting the acid with the metallic hydroxide.

The greases of this invention may be prepared by any appropriate method. For example, the salt may be dispersed in the siloxane by dissolving both in a common solvent and then evaporating the latter, or the salt may be introduced directly into the siloxane and dissolved by heating and agitating the mixture, or the salt may be formed in situ by adding an aqueous solution of the metal hydroxide to a solution of the acid in the siloxane.

A preferred method of preparing the greases is to add an aqueous solution of the metal hydroxide to a solution of the acid in an equal weight of siloxane. The addition is preferably carried out at a temperature of about 80° C. The water is evaporated by heating at 100° C. and more siloxane is added to the residue. The product is then heated at a temperature up to 200° C., cooled and milled.

In the preparation of the grease, the amount of alkali added may be less than enough to neutralize the acid or it may be in amount equivalent to the acid or it may be in amount in excess of that required to react with the acid. Thus, the grease may be either acidic, neutral, or alkaline in character. It is preferred however, that the grease be alkaline with an alkaline number of at least 5. The alkaline number is determined by titrating a one gram sample of the material with standard acid and calculating the milligrams of KOH which are equivalent to the acid necessary to neutralize the sample. The number is always expressed in milligrams of potassium hydroxide regardless of the type of alkali present in the grease.

The greases of this invention are extremely stable at both high and low temperatures. They possess melting points in excess of 600° F. and exhibit a bleed of less than 1% when heated in a standard A. N. G.–5 test apparatus at 150° C. for 24 hours. Bearings lubricated with the products have been operated in excess of 2,000 hours at a speed of 1750 revolutions per minute and a temperature of 175° C. without showing any signs of failure. Samples of the material have been heated at 200° C. for 24 hours without showing any change.

The stability of the products herein defined are vastly superior as high-temperature lubricants to organic greases. They are also markedly superior to greases prepared from polysiloxanes thickened with lithium stearate. The latter carbonize at substantially lower temperatures and break down more readily, as shown by change in consistency when worked at elevated temperatures, than do the present greases. Furthermore, lithium stearate siloxane greases are erratic in their behavior in use. By contrast the present greases give reproducible results.

"Consisting essentially of" as used in the claims means that the composition is made up almost entirely of the ingredients recited and these ingredients are the main and characterizing ones, but this expression does not exclude the presence of minor amounts of other ingredients which are commonly employed in lubricating compositions or which are merely inert. Such added ingredients would not change the essential character of the composition.

In order that those skilled in the art may better understand this invention, recourse may be had to the following examples which should be considered only as illustrative thereof.

EXAMPLES

Example 1

The phenylmethylpolysiloxane employed in this run was composed of phenylmethylsiloxane units, dimethylsiloxane units and trimethylsiloxane units. The amount of trimethylsiloxane was such that the degree of substitution of the copolymer was between 2 and 2.1 organic radicals per silicon atom. A solution of 5 g. of $LiOH.H_2O$ in 20 g. of water was added with agitation to a solution of cyclohexylcaproic acid in 20 g. of a 100 c. s. phenylmethylpolysiloxane of the above composition. The addition of the hydroxide solution was carried out at a temperature of 80° C. After all the hydroxide had been added the temperature was raised to 100° C. to evaporate the water. 60 g. more of the phenylmethylsiloxane was added with stirring to the residue which was being maintained at a temperature between 100° and 120° C. The material was then heated at a temperature of about 200° C. for one hour, cooled and then milled on a three-roll mill. The grease so obtained melted above 315° C. and had an alkaline number of 8.96. This grease underwent no change after 24 hours heating at 200° C.

Example 2

A solution of 100 g. of cyclohexylcaproic acid and 100 g. of the 100 c. s. phenylmethylpolysiloxane fluid of Example 1 was heated to 80° C. The solution was agitated during the addition of 25.4 g. of $LiOH.H_2O$ in 120 g. of water. When the addition of the hydroxide solution was complete the temperature was raised to 100° C. to evaporate the water. The residue was maintained at 100° to 120° C. and agitated during the slow addition of 300 g. more of the phenylmethylpolysiloxane. After addition of the siloxane was complete, the mixture was heated to about 200° C. for one hour and allowed to cool. The resulting product was milled on a three-roll mill and the grease so obtained had a melting point greater than 600° F. with an alkaline num-

ber of 13.95. The grease was placed in a standard apparatus described in A. N. G.-5 and heated at 150° C. for 24 hours. The results were as follows: A bleed of 0.68 percent and a volatility of 1.60 percent. A bearing lubricated with this grease and operated at 1750 R. P. M. with no load at a temperature at 175° C. was still functioning after 1,666 hours.

Example 3

The procedure of Example 1 was employed to prepare greases using the Li salts of the acids shown in Table II.

TABLE II

Acid	M. P., °F., of grease	Alkaline No. of grease
Cyclohexyl acetic	600	6.56
cyclohexyl propionic	515	3.92
cyclohexyl butyric	487	3.76
cyclohexyl valeric	>600	15.9
alpha-butylcyclohexylacetic	>600	12.15
gamma ethylcyclohexylbutyric	>600	17.14
alpha-4-diterbutylcyclohexylbutyric	600	25.7
alpha-4 disecbutylcyclohexylbutyric	535	27.5
2 cyclohexenecaproic	455	4.54
pentalaneacetic	>600	7.82
cyclopentylvaleric	430	
20% cyclohexyl butyric 80% cyclohexyl caproic	460	1.61

Example 4

A suspension of 121 g. of $Ba(OH)_2 8H_2O$ in 200 g. of water was added with stirring to 100 g. of cyclohexylcaproic acid. The salt solution thus formed was heated to partially evaporate the water. A thick mass resulted to which 200 g. of the phenylmethylpolysiloxane of Example 1 was added slowly with stirring at about 100° C. When the addition was complete the temperature was raised gradually to 230° C. The resulting material was then cooled to room temperature and milled on a three roll mill. The milled product was a grease having a melting point >600° F. and an alkaline number of 44. This grease did not bleed after 16 hours at 150° C. and its volatility loss was 1.09 percent. The grease was essentially unchanged after heating 175 hours at 175° C.

Example 5

To a solution of 20 g. of cyclohexylcaproic acid and 20 g. of the phenylmethylpolysiloxane of Example 1, a solution of 4.2 g. of NaOH and 20 g. of water was added slowly with stirring. During the addition of the hydroxide solution the mixture was maintained at a temperature of 80° C. After all the hydroxide had been added the temperature was raised to 100° C. to evaporate the water. The resulting residue was heated at 100° to 120° C. as 40 g. more of the phenylmethylpolysiloxane was gradually added. The material was then heated at about 200° C. for one hour. After cooling the resulting material was milled on a three-roll mill to produce a grease.

Example 6

A solution of 20 g. of cyclohexylcaproic acid and 20 g. of the phenylmethylpolysiloxane fluid of Example 1, was warmed to 80° C. and agitated as a solution of 13.4 g. of $Sr(OH)_2 8H_2O$ and 30 g. of water was slowly added. The temperature of the mixture was raised to 100° C. to evaporate the water. The residue was maintained at 120° C. and agitated during the gradual addition of the phenylmethylpolysiloxane. The material was heated for one hour at 200° C. and allowed to cool. The resulting material was milled to produce a grease.

Example 7

A 20 g. sample of cyclohexylcaproic acid was neutralized with aqueous KOH. The resulting solution was maintained at a temperature of 100° C. and agitated as 20 g. of the phenylmethylpolysiloxane fluid of Example 1 was slowly added. The temperature was kept at 100° C. until the water evaporated. To the residue 60 g. of the phenylmethylpolysiloxane was added slowly with stirring at a temperature of about 120° C. The mixture was further heated to give a clear product which was then cooled and milled to produce a grease.

Example 8

A solution of 4.4 g. of $LiOH.H_2O$ and 20 g. of water was added slowly with stirring at a temperature of 80° C. to a solution of 20 g. of cyclohexylcaproic acid and 20 g. of 100 c. s. dimethylpolysiloxane fluid. The temperature was then raised to 100° C. to remove the water. The resulting mass was heated to 120° C. and 40 g. of the dimethylpolysiloxane fluid was slowly added. The product was heated at 200° C. for one hour, cooled, and milled on a three-roll mill to produce a grease.

Example 9

A solution of 10 g. of cyclohexylcaproic acid and 10 g. of tolylmethylpolysiloxane of 7,000 c. s. viscosity was heated to 60° C. and agitated during addition of a solution of 2.1 g. of $LiOH.H_2O$ and 15 g. of water. The temperature was raised to 100° C. to remove the water. The residue was maintained at a temperature of 120° C. during addition of 20 g. of the tolylmethylpolysiloxane. The resulting mixture was heated at 100° C. for one hour, cooled, and milled to produce a semi-clear grease.

Example 10

A solution comprising 100 g. of cyclohexylcaproic acid and 100 g. of a 500 c. s. polysiloxane having the composition of 90 mol percent phenylmethylsiloxane and 10 mol percent trimethylsiloxane, was prepared. To this solution 25.4 g. of $LiOH.H_2O$ in 120 g. of water was added slowly with stirring at a temperature of 180° C. The mixture was then heated at 100° C. to evaporate the water. The residue was maintained at about 120° C. as 300 g. of the copolymeric siloxane was slowly added. The resulting material was heated at 200° C. for one hour, cooled, and milled on a three-roll mill to produce a grease having an alkaline number of 12.15. This grease showed a weight loss of 0.67 percent after 24 hours at 150° C.

Example 11

A solution of 2.5 g. of $LiOH.H_2O$ in 20 g. of water was added to a solution of 10 g. of cyclohexylcaproic acid and 10 g. of the phenylmethylpolysiloxane fluid of Example 1, with agitation. During the addition of the hydroxide solution the temperature was maintained at 80° C. After all the lithium hydroxide was added the water was evaporated at 100° C. The residue was then heated to 120° C. as 70 g. of the phenylmethylsiloxane was slowly added with stirring. The material was then heated at 160° C. for one hour and allowed to cool. The resulting product was milled on a three-roll mill to produce a thin grease. This grease contained 10 percent by weight of the lithium salt of cyclohexylcaproic acid based on the weight of the grease.

Example 12

A solution of 8.75 g. of $LiOH.H_2O$ in water was added slowly with stirring to a solution of 35 g. of cyclohexylcaproic acid and 35 g. of the phenylmethylpolysiloxane fluid of Example 1. During the addition of the hydroxide solution the temperature of the solution was maintained at 80° C. After the addition was complete the water was evaporated at a temperature of 100° C. The residue was heated at 120° C. and agitated as 46 g. of the phenylmethylpolysiloxane fluid was slowly added. The resulting product was heated at 200° C. for one hour and then cooled. Upon milling on a three-roll mill a thick grease resulted. This material contained 35 percent by weight of the lithium salt of cyclohexylcaproic acid based on the weight of the grease.

The greases described in the above examples performed satisfactorily in the lubrication of bearings.

That which is claimed is:

1. A grease consisting essentially of a liquid organo polysiloxane having a degree of substitution of from 1.9 to 2.5 organic radicals per silicon atom, said radicals being selected from the group consisting of methyl, phenyl, and tolyl radicals and a minor amount of a metallic salt of an alicyclic substituted fatty acid in which fatty acid the chain length is from 2 to 6 carbon atoms, the metal of said salt being selected from the group consisting of alkali metals and alkaline earth metals, said salt being present in amount sufficient to form a grease.

2. A grease having an alkaline number of at least 5, said grease consisting essentially of a liquid organo polysiloxane having a degree of substitution of from 1.9 to 2.5 organic radicals per silicon atom, said radicals being selected from the group consisting of methyl, phenyl, and tolyl radicals and a minor amount of a metallic salt of an alicyclic substituted fatty acid in which fatty acid the chain length is from 2 to 6 carbon atoms, the metal of said salt being selected from the group consisting of alkali metals and alkaline earth metals, said salt being present in amount sufficient to form a grease.

3. A grease consisting essentially of a liquid organo polysiloxane having a degree of substitution of from 1.9 to 2.5 organic radicals per silicon atom, said radicals being selected from the group consisting of methyl, phenyl, and tolyl radicals and a minor amount of a barium salt of an alicyclic substituted fatty acid in which fatty acid the chain length is from 2 to 6 carbon atoms, said salt being present in amount sufficient to form a grease.

4. A grease having an alkaline number of at least 5, said grease consisting essentially of a liquid organo polysiloxane having a degree of substitution of from 1.9 to 2.5 organic radicals per silicon atom, said radicals being selected from the group consisting of methyl, phenyl, and tolyl radicals and a minor amount of a barium salt of an alicyclic substituted fatty acid in which fatty acid the chain length is from 2 to 6 carbon atoms, said salt being present in amount sufficient to form a grease.

5. A grease consisting essentially of a liquid organo polysiloxane having a degree of substitution of from 1.9 to 2.5 organic radicals per silicon atom, said radicals being selected from the group consisting of methyl, phenyl, and tolyl radicals and a minor amount of a lithium salt of an alicyclic substituted fatty acid in which fatty acid the chain length is from 2 to 6 carbon atoms, said salt being present in amount sufficient to form a grease.

6. A grease having an alkaline number of at least 5, said grease consisting essentially of a liquid organo polysiloxane having a degree of substitution of from 1.9 to 2.5 organic radicals per silicon atom, said radicals being selected from the group consisting of methyl, phenyl, and tolyl radicals and a minor amount of a lithium salt of an alicyclic substituted fatty acid in which fatty acid the chain length is from 2 to 6 carbon atoms, said salt being present in amount sufficient to form a grease.

7. A grease having an alkaline number of at least 5, said grease consisting essentially of a liquid polysiloxane having a degree of substitution of from 1.9 to 2.5 organic radicals per silicon atom in which siloxane the organic radicals are phenyl and methyl radicals and a minor amount of a lithium salt of an alicyclic substituted fatty acid in which fatty acid the chain length is from 2 to 6 carbon atoms, salt being present in amount sufficient to form a grease.

8. A grease having an alkaline number of at least 5, said grease consisting essentially of a liquid polysiloxane having a degree of substitution of from 1.9 to 2.5 organic radicals per silicon atom in which polysiloxane the organic radicals are tolyl and methyl radicals and a minor amount of a lithium salt of an alicyclic substituted fatty acid in which fatty acid the chain length is from 2 to 6 carbon atoms, salt being present in amount sufficient to form a grease.

CHESTER C. CURRIE.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,055,795	Kaufman	Sept. 29, 1936
2,379,245	Morway	June 26, 1945
2,409,950	Meyer	Oct. 22, 1946
2,446,177	Hain	Aug. 3, 1948
2,456,642	Merker	Dec. 21, 1948

OTHER REFERENCES

"Chemical Constituents of Petroleum," by Sachanen, Reinhold Pub. Co., 1945, pages 323 and 324.