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2,623,019

LUBRICATING OILS

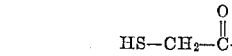
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9 Claims. (Cl. 252—48.4)

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The present invention relates to improvements in liquid organo-substituted polysiloxanes employed for lubricating purposes. More particularly the invention is concerned with a lubricating oil exhibiting improved load-bearing properties which oil comprises (1) a liquid polymeric organo-substituted polysiloxane and (2) a minor proportion, preferably a small amount, of a mixture of ingredients comprising (*a*) a chlorinated compound selected from the class consisting of chlorinated aliphatic hydrocarbons, more specifically, chlorinated saturated aliphatic hydrocarbons and chlorinated saturated cycloaliphatic hydrocarbons, and chlorinated saturated aliphatic monohydric alcohol esters of lower saturated aliphatic fatty acids and (*b*) a thioglycollic acid ester corresponding to the general formula



where R is an alkyl group containing from 2 to 8 carbon groups.

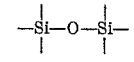
Liquid organo-substituted polysiloxanes, for example, liquid hydrocarbon-substituted polysiloxanes, because of their outstanding resistance to heat and to oxidation at elevated temperatures, because of their low viscosity-temperature coefficients, and because of their low pour points, are ideal fluids for lubrication under hydrodynamic or fluid film conditions. However, such materials when employed for lubricating purposes, under certain lubricating conditions where a fluid film cannot be formed or if formed has broken down, may not afford the protection against bearing seizure or "freezing" of the revolving member or shaft supported by the bearings that has come to be expected from certain petroleum-base oils of like viscosity. This disparity in lubrication properties is particularly pronounced where both rubbing surfaces are steel. This difficulty is believed due to the inability of the liquid polysiloxanes to maintain a continuous lubricating film on the steel bearing surfaces when the load on the bearings has been increased above a certain critical point.

The primary object of this invention is to provide liquid lubricants capable of adequately lubricating the bearing surfaces of relatively moving metallic bodies, even under increased loads, said liquids being characterized by high resistance to oxidation, little change of viscosity with temperature and low pour points. Other objects and advantages of the present invention will become apparent from the following description and claims.

The liquid organo-substituted polysiloxanes with which this invention is concerned are compositions comprising essentially silicon atoms connected to one another by oxygen atoms as

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illustrated by the following structure called a siloxane structure:



wherein a preponderant number of the valences of the silicon atoms are satisfied by the substitution thereon of organic radicals, for example, aliphatic radicals. These compositions of matter may be prepared, e. g., by hydrolysis hydrolyzable aliphatic-substituted silanes, for instance, dialiphatic dihalogenosilanes, for example, dimethyl dichlorosilane, followed by complete or partial condensation of the hydrolysis product. They may also be prepared, for example, by hydrolyzing mixtures of hydrolyzable diorgano-substituted silanes either among themselves or with hydrolyzable silanes containing, for example, three organic radicals substituted on the silicon atom, for instance, trimethylchlorosilane.

A further method for preparing the liquid organo-substituted polysiloxanes comprises hydrolyzing a diorgano-substituted dihalogenosilane, isolating the hydrolysis product and effecting reaction between the hydrolyzed product and, e. g., hexamethyl disiloxane in the presence of sulfuric acid. More specific directions for the hydrolysis of hydrolyzable organo-substituted silanes to form liquid organo-substituted polysiloxanes may be found, for example, in patents and literature now available in the art.

By the term "hydrolyzable organo-substituted silanes" is intended to mean derivatives of SiH_4 which contain hydrolyzable groups or radicals, for example, halogens, amino groups, alkoxy, aryloxy, and acyloxy radicals, etc., in addition to the organic groups substituted directly on the silicon atom that are joined to the silicon through carbon-silicon linkages. Examples of such organic radicals are aliphatic radicals including alkyl radicals, for example, methyl, ethyl, propyl, isopropyl, butyl, etc.; alicyclic radicals, for example, cyclopentyl, cyclohexyl, etc.; aryl radicals, for example, phenyl, diphenyl, naphthyl, anthracyl, etc.; aralkyl radicals, for example, benzyl, phenylethyl, etc.; alkaryl radicals, for example, tolyl, xylyl, etc.; heterocyclic radicals, etc.; as well as hydrolyzable silanes containing two different organic radicals, for example, methyl and phenyl radicals, etc., attached to the silicon atom. If desired, the above-mentioned radicals may also contain substituents substituted thereon, for instance, halogens.

Hydrolysis of the above silanes or mixtures of silanes results in the formation of silanols, i. e., organo-substituted silanes containing hydroxy groups substituted directly on the silicon, which hydroxy groups almost immediately condense intermolecularly (intercondense) splitting out water to give the siloxane linkages mentioned

previously. Such intercondensations are accelerated by acidic materials, for example, sulfuric acid, hydrochloric acid, ferric chloride, etc., as well as by basic materials, for example, sodium hydroxide, potassium hydroxide, etc. As a result of the hydrolysis and condensation, liquid organo-substituted polysiloxanes may be produced which are partially or completely condensed and which may have on the average up to as high as three organic radicals substituted per silicon atom. The liquid organopolysiloxanes prepared in this manner consist essentially of silicon atoms joined together by oxygen atoms through silicon-oxygen linkages and organic radicals attached to silicon through carbon-silicon linkages, the remaining valences, if any, of the silicon atoms being satisfied by hydroxyl radicals and/or by residual unhydrolyzed radicals such as the hydrolyzable radicals listed previously.

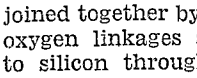
We have now found that the frictional properties of liquid organo-substituted polysiloxanes, especially liquid hydrocarbon-substituted polysiloxanes containing an average of from about 1.9 to 2.67, more particularly, from approximately 1.95 to 2.3, hydrocarbon groups per silicon atom, may be greatly improved by incorporating in the said liquid polysiloxane a minor proportion, preferably a small amount, of a mixture of ingredients comprising (*a*) a chlorinated compound selected from the class consisting of chlorinated aliphatic hydrocarbons, chlorinated cycloaliphatic hydrocarbons and chlorinated saturated aliphatic monohydric alcohol esters of lower saturated aliphatic acids and (*b*) a compound corresponding to the general formula

This result was quite surprising and unexpected since only minor improvements in frictional properties are obtained when either of the ingredients described under (*a*) and (*b*) above are added separately to the liquid organopolysiloxane. However, by mixing the ingredients and adding the same to the liquid polysiloxane, a marked and totally unpredictable increase in the load-bearing properties of bearings lubricated with the aforementioned polysiloxanes was obtained.

Among the chlorinated compounds of the foregoing class, which may be employed in our invention, there may be mentioned the following: chlorinated aliphatic compounds, for example, 1,1,2-trichloroethane, hexachloroethane, acetylene tetrachloride, 1,2-dichloropentane, dichloro tertiary butyl chloride, tertiary amyl chloride, pentachloropropane, etc.; chlorinated cycloaliphatic hydrocarbons, for example chlorinated cyclohexanes and chlorinated methyl cyclohexanes in various degrees of chlorination, chlorinated cycloheptanes, etc.

Examples of chlorinated saturated aliphatic monohydric alcohol esters of lower saturated aliphatic fatty acids which may be employed in the practice of our invention are chlorinated and unchlorinated saturated aliphatic monohydric alcohol esters of chlorinated lower saturated aliphatic fatty acids, for example, monochloroethyl trichloroacetate, dichloropropyl monochloroacetate, ethyl monochloroacetate, butyl dichloroacetate, propyl 3,3,3-trichlorobutyrate, 1,3-dichloro-2-propyl-trichloroacetate, [di-(monochloromethyl) methyl trichloroacetate], butyl 2,2,3-trichlorobutyrate, etc.; chlorinated saturated aliphatic monohydric alcohol esters of unchlorinated lower saturated aliphatic fatty acids, for example, dichloroethyl acetate (2,2-dichloroethyl acetate), 2-chloropropyl butyrate, trichloroethyl propionate (2,2,2-trichloroethyl propionate), 3,4,4,4-tetrachlorobutyl butyrate, 1,3-dichloropropyl pentanoate, etc. Preferably, the chlorinated compounds, many examples of which have been given above, should have boiling points above 100° C. and should be miscible with the liquid organo-substituted polysiloxane in the desired proportions.

Included among the various compounds corresponding to the general formula



where R is an alkyl group containing from 2 to 8 carbon atoms, which may be added to the liquid organopolysiloxane are, for example, ethyl thioglycollate, propyl thioglycollate, butyl thioglycollate, hexyl thioglycollate, 2-ethylbutyl thioglycollate, 2-ethylhexyl thioglycollate, etc.

The amount of additives which may be employed to effectively increase the load-bearing properties of the liquid organopolysiloxane lubricants should not be more than is necessary for the required purpose, since too much of either the chlorinated compound or the thioglycollic acid ester adversely affects certain physical properties of the lubricant, e. g., its flat temperature-viscosity characteristics, its pour point, low volatility, etc. We have found that, based on the weight of the liquid organo-substituted polysiloxanes, good results are obtained when the total mixture of the chlorinated compound and the thioglycollic acid ester comprises not more than 15 percent, by weight, preferably from about 3 to 12 percent, by weight, of the liquid organo-substituted polysiloxane. As regards the ratio of the weight of the chlorinated compound to the thioglycollic acid ester, good results are obtained if each of the two ingredients comprising the mixture constitutes from approximately 30 to 70 percent, by weight, based on the total weight of the mixture of the chlorinated compound and the thioglycollic acid ester. In many cases, optimum results are obtained when the chlorinated compound and the thioglycollic acid ester are present in approximately equal proportions, by weight.

In order that those skilled in the art may better understand how the present invention may be practiced, the following examples are given by way of illustration and not by way of limitation. All parts and percentages are by weight.

A liquid methyl-substituted polysiloxane containing an average of slightly more than two methyl groups per silicon atom was prepared by hydrolyzing substantially pure dimethyl dichlorosilane and thereafter effecting rearrangement of the siloxane units in the hydrolyzed product with hexamethyl disiloxane in the presence of concentrated sulfuric acid in accordance with the procedure disclosed in the aforementioned Patnode application, Serial No. 463,814, now U. S. Patent 2,469,888, issued May 10, 1949. The viscosity of the oily liquid obtained was approximately 42 centistokes at about 100° F. The load-bearing properties of this oily methyl polysiloxane were tested in an Almen extreme-pressure lubricant-testing machine (for a more complete description of this machine, see "Lubricants and Lubrication" by James I. Clower, pages 145–147, published by McGraw-Hill Book Co., 1939) which comprises a steel bearing split into two equal halves which are adjusted and positioned around a rotating steel journal or shaft. The com-

plete assembly was immersed in the test oil and as the steel shaft revolved (at about 600 R. P. M.), the halves of the bearing were squeezed increasingly tighter around the shaft until the pressure of the bearing on the said shaft caused seizure of the shaft by the bearing. The average pressure in pounds per square inch exerted at the time of seizure is called the "seizure bearing pressure."

In the case of the above-described liquid methyl polysiloxane containing no additives, seizure of the shaft occurred when a pressure of about 300 p. s. i. was exerted by the journal on the bearing. In the following table are found the results of using various mixtures of chlorinated compounds and thioglycollic acid esters. For comparison purposes, tests were conducted (the results being shown in the same table) using each of the additives separately. Unless stated otherwise, the thioglycollic acid ester employed in each case was ethyl thioglycollate.

Table

Additive	Percent Added		Seizure Bearing Pressure, p. s. i.
	Chlorinated Compound	Thioglycollic Acid Ester	
Ethyl thioglycollate		5	390
Do		10	3,190
2-ethylbutyl thioglycollate		10	605
Acetylene tetrachloride ($C_2H_2Cl_4$)	10		1,010
Acetylene Tetrachloride	20		7,420
Do	5	5	21,700
Do	5	[a] 5	12,330
Hexachloroethane	10		840
Do	5	5	4,700
Ethyl monochloroacetate	10		1,170
Do	5	5	13,100
Ethyl trichloroacetate	10		345
Do	15		730
Do	5	5	12,900
Do	5	[a] 5	27,500
$Cl_3CCOOCH(CH_2Cl)_2$ (1,3-dichloro-2-propyltrichloroacetate)	10		1,790
$Cl_3CCOOCH(CH_2Cl)_2$	2.5	5	4,310
Do	5	5	16,000
Do	4	10	16,350
Do	5	[b] 5	605
Butyl 2, 2, 3-trichlorobutyrate	15		605
Do	20		950
Do	25		1,730
Do	5	5	8,250
Chlorinated cyclohexane (71% chlorine)	5		775
Do	5	5	22,700
Chlorinated methyl cyclohexane (55.6% chlorine)	5	5	18,100
Do	5	[a] 5	9,000

[a] The thioglycollic acid ester employed was 2-ethylbutyl thioglycollate.

[b] In this case, ethyl glycollate was employed in place of ethyl thioglycollate.

It will, of course, be understood by those skilled in the art that other chlorinated compounds and thioglycollic acid esters falling within our classes of compounds, many examples of which have been given previously, may be employed in place of the additives employed in the above examples.

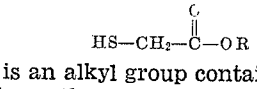
In addition, it will be apparent that the mixture of chlorinated compound and thioglycollic acid ester may be added to organo-substituted polysiloxanes other than the liquid methyl polysiloxane disclosed above to improve their lubricating properties. These include, for instance, liquid alkyl-substituted polysiloxanes, for example, liquid ethyl-, propyl, butyl-, isopropyl-substituted polysiloxanes, etc; liquid aryl-substituted polysiloxanes, for example, liquid phenyl-substituted polysiloxanes, etc.; liquid organopolysiloxanes containing different hydrocarbons substituted on the silicon atom or atoms, for example, liquid methyl and phenyl substituted polysiloxanes, etc., as well as liquid organopolysiloxanes containing both alkyl and aryl hydrocarbons substituted on different silicon atoms, for example, liquid organopolysiloxanes obtained by hydrolyzing a mixture comprising substantially dimethyl dichlorosilane and diphenyl dichlorosilane and effecting rearrangement of the siloxane units with hexamethyl disiloxane in the presence of sulfuric acid, which products are more particularly disclosed and claimed in our copending application Serial No. 702,590, filed October 11, 1946, now U. S. Patent 2,483,153, issued September 27, 1949, and assigned to the same assignee as the present invention.

Our invention is particularly suitable for improving the load-bearing and frictional properties of liquid methyl polysiloxanes containing an average of from about 1.9 to 2.67 methyl groups per silicon atom, especially where the average ratio of methyl groups to silicon atoms is from about 1.95 to 2.3 methyl groups per silicon. Although, certain liquid organo-substituted polysiloxanes containing, e. g., both a phenyl and a lower alkyl group, for instance, a methyl group, on the same silicon atom have better frictional and load-bearing properties than the liquid methyl polysiloxanes, their load-bearing properties may be still further improved in accordance with the teachings and disclosures of our claimed invention.

Still greater improvements are obtainable if liquid organo-substituted polysiloxanes are employed which contain chlorine atoms substituted on the organic radical. An example of such a polysiloxane is one prepared, for example, by cohydrolyzing a mixture of chlorosilanes comprising dimethyl dichlorosilane and a minor proportion (approximately 5 mol per cent) of di-(monochlorophenyl) dichlorosilane, and thereafter effecting rearrangement of the siloxane units with hexamethyl disiloxane in the presence of sulfuric acid.

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

1. A lubricating oil consisting essentially of (1) a liquid polymeric hydrocarbon-substituted polysiloxane containing an average of from 1.9 to 2.67 hydrocarbon groups per silicon atom and (2) from 3 to 15 per cent, by weight, based on the weight of (1) of a mixture of ingredients comprising (*a*) a chlorinated compound having a boiling point above 100° C. and selected from the class consisting of chlorinated aliphatic hydrocarbons and chlorinated cycloaliphatic hydrocarbons and, (*b*) a compound corresponding to the general formula

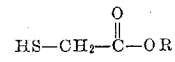


where R is an alkyl group containing from 2 to 8 carbon atoms, the compound (*b*) comprising from 30 to 70 per cent, by weight, of the total weight of (*a*) and (*b*).

2. A lubricating oil exhibiting good load-bearing properties which consists essentially of (1) a liquid polymeric hydrocarbon-substituted polysiloxane containing an average of from 1.9 to 2.67 hydrocarbon groups per silicon atom and (2) from 3 to 15 per cent, by weight, based on the weight of (1) of a mixture of ingredients comprising (*a*) a chlorinated compound having a boiling point above 100° C. and selected from the class consisting of chlorinated aliphatic hydrocarbons and chlorinated cycloaliphatic hydrocarbons, and (*b*)

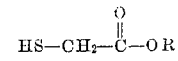
ethyl thioglycollate, the compound (*b*) comprising from 30 to 70 per cent, by weight, of the total weight of (*a*) and (*b*).

3. A lubricating oil consisting essentially of (1) a liquid polymeric hydrocarbon-substituted polysiloxane containing an average of from 1.9 to 2.67 hydrocarbon groups per silicon atom and (2) from 3 to 15 per cent, by weight, based on the weight of (1) of a mixture of ingredients comprising (*a*) a chlorinated aliphatic hydrocarbon having a boiling point above 100° C. and (*b*) a compound corresponding to the general formula



where R is an alkyl group containing from 2 to 8 carbon atoms, the compound (*b*) comprising from 30 to 70 per cent, by weight, of the total weight of (*a*) and (*b*).

4. A lubricating oil consisting essentially of (1) a liquid polymeric hydrocarbon-substituted polysiloxane containing an average of from 1.9 to 2.67 hydrocarbon groups per silicon atom and (2) from 3 to 15 per cent, by weight, based on the weight of (1) of a mixture of ingredients comprising (*a*) a chlorinated cycloaliphatic hydrocarbon having a boiling point above 100° C. and (*b*) a compound corresponding to the general formula

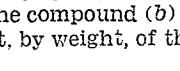


where R is an alkyl radical containing from 2 to 8 carbon atoms, the compound (*b*) comprising from 30 to 70 per cent, by weight, of the total weight of (*a*) and (*b*).

5. A lubricating oil consisting essentially of (1) a liquid hydrocarbon-substituted polysiloxane containing an average of from about 1.9 to 2.67 hydrocarbon groups per silicon atom and (2) from 3 to 15 per cent, by weight, based on the weight of (1) of a mixture of ingredients comprising (*a*) a chlorinated aliphatic hydrocarbon having a boiling point above 100° C. and (*b*) ethyl thioglycollate, the compound (*b*) comprising from 30 to 70 per cent of the total weight of (*a*) and (*b*).

6. A lubricating oil consisting essentially of (1) a liquid hydrocarbon-substituted polysiloxane containing an average from about 1.9 to 2.67 hydrocarbon groups per silicon atom and (2) from 3 to 15 per cent, by weight, based on the weight of (1) of a mixture of ingredients comprising (*a*) a chlorinated cycloaliphatic hydrocarbon having a boiling point above 100° C. and (*b*) ethyl thioglycollate, the compound (*b*) comprising from 30 to 70 per cent, by weight, of the total weight of (*a*) and (*b*).

7. A lubricating oil consisting essentially of (1) a liquid methyl polysiloxane containing an average of from 1.9 to 2.67 methyl groups per silicon atom and (2) from 3 to 15 per cent, by weight, based on the weight of (1) of a mixture of ingredients comprising (*a*) a chlorinated compound having a boiling point above 100° C. and selected from the class consisting of chlorinated aliphatic hydrocarbons and chlorinated cycloaliphatic hydrocarbons, and (*b*) a compound corresponding to the general formula



where R is an alkyl radical containing from 2 to 8 carbon atoms, the compound (*b*) comprising from 30 to 70 per cent, by weight, of the total weight of (*a*) and (*b*).

8. A lubricating oil consisting essentially of (1) a liquid methyl polysiloxane containing from about 1.95 to 2.3 methyl groups per silicon atom and (2) from 3 to 12 per cent, by weight, based on the weight of (1) of a mixture of ingredients comprising (*a*) acetylene tetrachloride and (*b*) ethyl thioglycollate, the compound (*b*) comprising from 30 to 70 per cent, by weight, of the total weight of (*a*) and (*b*).

9. A lubricating oil consisting essentially of (1) a liquid methyl polysiloxane containing from about 1.95 to 2.3 methyl groups per silicon atom and (2) from 3 to 12 per cent, by weight, based on the weight of (1) of a mixture of ingredients comprising (*a*) a chlorinated cyclohexane and (*b*) ethyl thioglycollate, the compound (*b*) comprising from 30 to 70 per cent, by weight, of the total weight of (*a*) and (*b*).

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