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2,830,953

SILICONE LUBRICATING OILS

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No Drawing. Application May 28, 1956
Serial No. 587,490

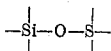
4 Claims. (Cl. 252-49.6)

The present invention relates to improvements in liquid organo-substituted polysiloxanes employed for lubricating purposes. More particularly, the invention is concerned with a lubricating composition exhibiting improved load bearing properties, especially at elevated temperatures, which composition comprises (1) a liquid polymeric organo-polysiloxane lubricant, and (2) a boron compound selected from the class consisting of the trimer of phenyl boron oxide, tris-(diisobutylcarbonyl) borate and tris-(cyclohexylcyclohexyl) borate and mixtures thereof, the boron compound being employed, by weight, in an amount equal to from 0.01% up to the solubility limit of the boron compound in the organopolysiloxane, e. g., at a temperature of from 25° C. to the operating temperature of the lubricant.

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 excessive wear and 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. The 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 and at elevated temperatures, 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 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 of hydrolyzable aliphatic-substituted silanes, for

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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 in the literature now available in the art.

By the term "hydrolyzable organo-substituted silanes" is intended to mean derivatives of SiH₄ 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, e. g., di-, tri-, tetra-chlorophenyl-chlorosilanes, for example, trichlorophenyltrichlorosilane, tetrachlorophenyltrichlorosilane, etc.

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, but preferably from 1.98 to 2.25 organic groups 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.

Other directions for preparing the liquid organo-polysiloxane lubricating compositions employed in the practice of the present invention may be found disclosed and claimed in Patnode Patents 2,469,888 and 2,469,890, issued May 10, 1949; Burkhard Patent 2,689,859, issued September 21, 1954, the latter three patents being assigned to the same assignee of the present invention, as well as in Fletcher et al. Patent 2,599,844, issued June 10, 1952.

In accordance with my invention, I have found that the

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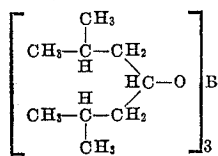
frictional properties at elevated temperatures (e. g., 100 to 200° C.) of liquid organo-substituted polysiloxanes, especially those containing aromatic nuclearly substituted halogen, for instance, chlorine, and having an average of from about 1.98 to 2.25 organic groups per silicon atom may be greatly improved by incorporating in the said liquid polysiloxane small amounts of certain organo-boron compounds more specifically mentioned above.

This result was quite surprising and unexpected since the use of other boron compounds, for instance, boric acid and elemental boron, gave only slight improvement in wear characteristics over the same lubricating oils free of any additive. The organo-boron compounds employed in the practice of the present invention have the following formulae:

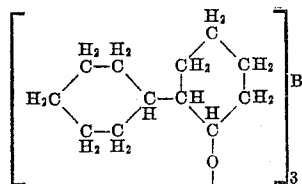
(1) Trimer of phenyl boron oxide



(2) Tris(diisobutyl carbonyl) borate



(3) Tris(cyclohexylcyclohexyl) borate



The amount of additive which may be employed to effectively increase the load bearing properties of the organopolysiloxane lubricant at elevated temperatures should not be more than is necessary for the required purposes and is generally used up to the solubility of the organo-boron additive in the lubricating fluid at room temperature of about 20° to 35° C. Generally, I have found that amounts ranging from about 0.01 to 6%, by weight of the additive, based on the weight of the organopolysiloxane fluid, are soluble within the operating temperature range of the fluid, for instance, from about 100 to 125° C. Within this temperature range, the fluid is able to effect lubrication between the metal surfaces even though high loads are exerted on the bearing surfaces and such lubrication is still satisfactory at the upper temperature range of about 150 to 175° C. for long periods of time.

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

The organopolysiloxane fluid used in the example as originally prepared was a methyl chlorophenylpolysiloxane, chain-stopped with trimethylsilyl groups and having intercondensed dimethyl-siloxy groups and chlorinated phenyl-siloxy groups, there being present an average of about 4 chlorine atoms on each phenyl nucleus and the molar concentration of silicon-bonded chlorinated phenyl groups being of the order of about 4.4 mol percent. The fluid was heated to 300° C. with a nitrogen sparge and all volatiles boiling up to that temperature were removed. The viscosity of the devolatilized oily liquid was approximately 60 centistokes at about 50° C.

The load bearing properties of this oily methyl phenylpolysiloxane were tested in a Shell four ball wear tester which consists essentially of three steel balls clamped in a cup. A fourth ball mounted in a chuck spins in the cavity formed by the three touching balls. A loading arm forces the cup containing the balls against the chuck.

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Loads on the arm can be varied at will. A heater is provided to allow the organopolysiloxane fluid temperature to be adjusted from room temperature to over 300° C. To evaluate the fluid, a temperature is selected at which a run is to be carried out. The cup is heated to this temperature and the spinning ball allowed to revolve for about two hours at a given rate of revolutions per minute. This was repeated for loads of 10 kg. and 40 kg., at 100° C. and 200° C. The contact points on the three stationary balls grow to circulate scars as wear progresses. The average diameter of these scars in millimeters (mm.) after an hour's run at 600 revolutions per minute was taken as the measurement of wear. The balls used were all steel.

EXAMPLE 1

To the above-mentioned methyl chlorophenylpolysiloxane described above were added varying amounts of organo-boron compounds previously described. Each of these lubricating fluids containing the additives as well as a control free of any additive, was tested in the above-described Shell four ball tester at 100° C. and 200° C. under the two loads. The following Table I shows the ingredients used including the additives employed and the concentration of additives. Table II shows the wear scar in millimeters induced by each of the fluids tested at the two temperatures under varying load:

Table I

Sample No.	Additive	Parts Additive/100 Parts Methyl Chlorophenylpolysiloxane
1.....	Trimer of Phenyl Boron Oxide.....	0.5
2.....	do.....	1.0
3.....	Tris(diisobutyl carbonyl) borate.....	0.5
4.....	do.....	1.0
5.....	do.....	5
6.....	Tris(cyclohexylcyclohexyl) borate.....	5
7.....	Boron.....	0.5

Sample No.	Temperature			
	100° C.		200° C.	
	Load		Load	
	10 Kg.	40 Kg.	10 Kg.	40 Kg.
1.....mm.....	0.43	1.5	0.60	1.95
2.....mm.....	0.38	0.79	0.59	1.09
3.....mm.....	0.37	0.87	0.61	1.6
4.....mm.....	0.44	0.56	0.63	1.7
5.....mm.....	0.43	0.91	0.50	1.46
6.....mm.....	0.43	0.58	0.50	1.68
7.....mm.....	0.47	2.2	---	---

The coefficient of friction of the methyl chlorophenyl polysiloxane oil was determined with and without 0.5 percent, by weight, of the trimer of phenyl boron oxide as an additive. It was found that the coefficient of friction of the lubricating oil containing the additive (at 100° C. and under a load of either 40 or 50 kilograms) was from about 60 to 90 percent lower than the coefficient of friction of the same lubricating material free of the additive.

It will, of course, be apparent to those skilled in the art that other concentrations of the above-described additives may be employed in combination with both the organopolysiloxane fluid employed in Example 1 and that other organopolysiloxane fluids, many examples of which have been given previously and in the aforementioned Patnode patents, may be used with these additives in place of the methyl chlorophenylpolysiloxane, to improve the lubricating characteristics of the latter at elevated temperatures over similar fluids free of additives.

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Other examples of organopolysiloxane fluids which may be employed are, for instance, 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 Sprung et al. U. S. Patent 2,483,158 issued September 27, 1949, and assigned to the same assignee as the present invention.

My claimed compositions can be used to make various lubricating greases using many of the thickening agents, such as soaps, ordinarily used for that purpose as thickening agents. These include, for instance, lithium stearate, lithium hydroxy stearate, lithium octoate, etc. Other additives may be incorporated in order to improve certain properties thereof as, for example, organic diesters for improving low temperature properties [e. g., di-(2-ethylhexyl) sebacate], etc.

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

1. A composition of matter capable of lubricating under heavy load at elevated temperatures consisting essentially of (1) a liquid polymeric organopolysiloxane containing an average of from about 1.98 to 2.25 organic groups per silicon atom and (2) from 0.01 to 6 percent, by weight, based on the weight of (1) of a boron compound selected from the class consisting of the trimer of phenyl boron oxide, tris(cyclohexylcyclohexyl) borate, and tris-(diisobutylcarbinyl) borate and mixtures thereof.

2. A composition of matter having good lubricating characteristics under heavy load at elevated temperatures consisting essentially of (1) a liquid methyl chlorophenyl

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polysiloxane containing an average of from about 1.98 to 2.25 total methyl and chlorophenyl groups per silicon atom and (2) from 0.01 to 6 percent, by weight, based on the weight of (1) of the trimer of phenyl boron oxide.

3. A composition of matter having good lubricating characteristics under heavy load at elevated temperatures consisting essentially of (1) a liquid methyl chlorophenyl polysiloxane containing an average of from about 1.98 to 2.25 total methyl and chlorophenyl groups per silicon atom and (2) from 0.01 to 6 percent, by weight, based on the weight of (1) of tris-(diisobutylcarbinyl) borate.

4. A composition of matter having good lubricating characteristics under heavy load at elevated temperatures consisting essentially of (1) a liquid methyl chlorophenyl polysiloxane containing an average of from about 1.98 to 2.25 total methyl and chlorophenyl groups per silicon atom and (2) from 0.01 to 6 percent, by weight, based on the weight of (1) of tris-(cyclohexylcyclohexyl) borate.

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