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HIGH TEMPERATURE LUBRICATING OIL COMPOSITION CONTAINING A SILICON-TIN-CONTAINING COMPOUND

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This invention relates to high temperature lubricants. More particularly, it relates to liquid lubricants of the organopolysiloxane type which are characterized by desirable lubricity at high temperatures and to the preparation of such lubricants.

It is well known that while many naturally occurring mineral and vegetable oils have good lubricating qualities and stability at lower temperatures, at a critical higher temperature the coefficient of friction of these materials rises sharply denoting the loss of their lubricity. It has been suggested that oils of the organopolysiloxane type be substituted for the natural oils for higher temperature uses and this has been done with some success. These organopolysiloxane materials are characterized by their outstanding resistance to heat and oxidation at elevated temperature, have low viscosity-temperature coefficients and low pour points. Many of these organopolysiloxane materials are those which one obtains from the hydrolysis, or cohydrolysis and condensation of the various substituted silanes. Lubricants of this general type are set forth, for example, in Patents 2,469,888; 2,469,890 and 2,689,859, among others, assigned to the same assignee as the present invention and also in Patent 2,599,984, the teachings of which are included herein by reference.

While such liquid organopolysiloxanes have been found to be very useful as lubricants at temperatures up to about 400° F. or less under varying loads, with further rise in temperature the coefficient of friction of these materials rises sharply, rendering the material of limited, if any, usefulness at temperatures above the order of 400° F. The loss of lubricity is aggravated, of course, at higher loads. There is a load and temperature for each such lubricant at which its lubricity is lost. With the continued development of power plants such as internal combustion engines, gas turbine engines, aircraft power plants and other equipment which operate at temperatures of the order of 700° F. and higher, the need for lubricants and hydraulic fluids which will retain desirable qualities at such temperatures is quite apparent.

An object of this invention, therefore, is to provide a material of the liquid organopolysiloxane type which has desirable lubricating qualities at temperatures of the order of 700° F. and higher.

Briefly stated, our invention comprises the hydrolysis and condensation products of organopolysiloxanes in combination with tin-silicon compounds which latter may be characterized by the following formula:

$$\left[R_3SiO-\right]_{4-m}Sn-R'_m$$

wherein R and R' are organic groups as described in more detail hereinafter and m is a number from 0 to 2.

The features of the invention which are believed to be novel are set forth with particularity in the appended claims. The invention, however, both as to its organization and method of operation, together with further objects and advantages may best be understood by reference to the following description.

The liquid organo-substituted polysiloxanes with which this invention is concerned are compositions comprising essentially silicon atoms connected to one another by oxygen atoms or 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 can typically be prepared by hydrolysis of hydrolyzable aliphatic-substituted silanes, for example, dialiphatic dihalogenosilanes such as dimethyldichlorosilane followed by complete or partial condensation of the hydrolysis product. They can also be prepared by hydrolyzing mixtures of hydrolyzable diorgano-substituted silanes either with themselves or with hydrolyzable silanes containing, for example, three organic radicals substituted on the silicon atom, for instance, trimethylchlorosilane.

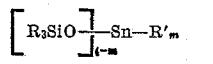
A further method for preparing the liquid organo-substituted polysiloxanes comprises hydrolyzing a diorgano-substituted dihalogenosilane, isolating the hydrolysis product and effecting reaction between the hydrolyzed product and, for example, hexamethyl disiloxane in the presence of sulfuric acid. More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

By the term "hydrolyzable organo-substituted silanes" is meant derivatives of SiH_4 which contain hydrolyable groups or radicals, for example, halogens, amino groups, alkoxy, aryloxy, and acryloxy 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 can also contain substituents substituted thereon, for instance, halogens, e.g., di-, tri-, tetra-chlorophenylchlorosilanes, 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 can 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.

In accordance with the invention, we have found that the frictional properties at elevated temperatures, that is, from about 200° F. to 400° F. and higher of liquid organo-substituted polysiloxanes, especially those containing aromatic nuclearly substituted halogen, such as chlorine and having an average of from about 1.98 to 2.25 organic groups per silicon atom may be substantially improved by incorporating in the liquid polysiloxanes small amounts of certain tin-silicon compounds.

As pointed out above, the tin-silicon compounds of the present invention may be expressed by the formula having the general structure



where R and R' are aliphatic radicals including lower alkyl radicals such as methyl, ethyl, propyl, isopropyl, butyl, etc.; alicyclic radicals such as cyclopentyl, cyclohexyl, etc.; aryl radicals such as phenyl, diphenyl, naphthyl, anthracyl, etc.; aralkyl radicals such as benzyl, phenylethyl, etc.; alkaryl radicals such as tolyl, xylyl, etc.; heterocyclic radicals and mixtures of the above in the case of R, the above-mentioned radicals containing, if desired, substituents such as halogens, e.g., chlorophenyl, etc.; and *m* is a number from 0 to 2.

The tin-silicon compounds can be conveniently prepared by a metathesis reaction between a sodium silanolate of the silicone and the tin or organo tin halide. The following examples illustrate the preparation of such materials.

EXAMPLE 1

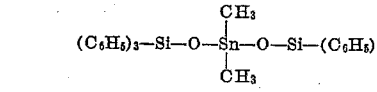
Trimethyl sodium silanolate was prepared by the method of Sommers and Whitmore. In a three-necked flask fitted with a stirrer and a thermometer and an addition funnel, 81 grams of hexamethyl disiloxane were combined with 196 grams of concentrated sulfuric acid. Ammonium fluoride was added slowly, maintaining the contents of the flask below 15° C. during the addition to reduce the reflux of the trimethyl fluorosilane formed. The trimethyl fluorosilane was distilled out of the mixture and 79 grams of product were obtained. This silane was hydrolyzed by combining it with ethyl ether in ice water and neutralizing with 0.1 normal sodium hydroxide until the solution was just faintly pink. The ether layer was then removed and dried over potassium carbonate. Next the silanol was reacted with 1 mol of sodium sand by adding the silanol-ether solution slowly to the sodium sand in ethyl ether in a three-necked flask fitted with a stirrer, thermometer and addition funnel. When the reaction had slowed down after the addition of all the silanol, the solution was refluxed for about 1 hour to complete the reaction. Excess sodium was filtered out and the ether evaporated to give a white powder of the trimethyl sodium silanolate.

Next, 20.8 grams of the trimethyl silanolate were dissolved in 100 cc. of warm toluene. In another flask, 21.9 grams of dimethyl tin dichloride were also dissolved in 100 cc. of warm toluene. The two solutions were combined and immediately a precipitate of sodium chloride formed. The sodium chloride was filtered off and the toluene evaporated until crystals started to form. The product was then allowed to crystallize, filtered and dried. This produced 14.5 grams of material which were shown by infrared analysis to be bis-(trimethyl siloxy dimethyl)-stannane.

EXAMPLE 2

Triphenylsilanol was converted to the sodium silanolate by reacting the silanol with sodium in toluene solution. The triphenyl sodium silanolate was crystallized and dried after the sodium had all reacted. This material was then reacted with dimethyl tin dichloride by a reaction similar to that of Example 1 and the compound

crystallized from the soluene solution. This compound had the formula



By similar reactions the following compounds were prepared:

$[(CH_3)_3SiO]_4Sn$
$[(CH_3)_3SiO]_2Sn(C_4H_9)_2$
$[(C_6H_5)_3SiO]_4Sn$
$[(C_6H_5)_3SiO]_2Sn,C_6H_5)_2$
$[(CH_3)_3SiO]_2Sn(C_6H_5)_2$

Generally, we have found that amounts of the tin-silicon compound, ranging from about 1.0 to about 10, by weight, of the additive based on the weight of the organopolysiloxane fluid are useful in improving the oxidation resistance, lubricity and load carrying ability of the organopolysiloxanes.

Preferably, from about 3% to 5% of the additive are used and about 3% has been found to be the specifically preferred amount. In general, amounts of additive over about 3% are tolerated but do not add anything in the way of proportionately improved characteristics. Of course, amounts less than 1% will also give some improvement as well.

The following examples will illustrate the practice of the present invention. The organopolysiloxane fluid used in the examples was a methylchlorophenylpolysiloxane chain-stopped with trimethylsilyl groups and having intercondensed dimethyl-siloxy groups and chlorinated phenyl-siloxy groups, there being present an average of about four 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. This 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.

EXAMPLE 3

A chlorophenylpolysiloxane as above was tested for stability to oxidation by heating to a temperature at which oxidation became apparent and further to a temperature at which gelation took place. When the organopolysiloxane as such was heated alone, the threshold temperature or the temperature at which oxidation began was 430° F. and the time to gelation at 600° F. was 10 hours. When there was added to the above organopolysiloxane 3%, by weight, of bis-(trimethylsiloxy dimethyl)-stannane, the threshold temperature rose from 80° F. to 510° F. and the time to gelation at 600° F. was 45 minutes.

The apparatus used for testing the lubricating qualities of the organopolysiloxanes described herein is the so-called Shell 4 ball wear tester. This testing device consists essentially of three steel balls, each about ½" in diameter, clamped securely in the non-rotating fashion in a cup with a fourth ball mounted in a rotatable chuck and adapted to spin on the cavity formed by the three adjacent balls. A loading arm is utilized to force the cup containing the balls against the chuck, the load being varied in any manner desired. Provision is made for holding the lubricant to be tested in the cup containing the balls so that the latter are continually immersed in the lubricant. In testing a lubricant, the apparatus is heated to a temperature desired and the chuck and top ball rotated for a given period of time at a particular number of revolutions per minute under a fixed load. After the test is completed, the lower or fixed balls are examined with a microscope and the size of the scar worn in them by the upper rotating ball noted and taken as a measure of the comparative lubricating quality under the particular set of conditions. The average diameter of the generally circular scar is used. In the tests

described below, the spindle speed of the apparatus was 600 revolutions per minute unless otherwise stated, and the time for each test run was 2 hours.

Shown in Table I is a comparison between the organopolysiloxane described in so far as its lubricating qualities are concerned as tested on the 4 ball tester, with the same material to which had been added 3%, by weight, of this trimethylsiloxy dimethyl stannane.

Table I

Load (kg.)	Temperature (° F.)	Scar (mm.) (Untreated Organopolysiloxane)	Scar (mm.) (Treated Organopolysiloxane)
4	212	.42	.35
40	212	1.10	.70
50	212	2.19	.77
4	400	.58	.53
40	400	1.70	.97
50	400	2.38	1.19
40	700	2.20	1.10

The load carrying capacity of the various lubricants, treated and untreated, were measured by stabilizing the sliding velocity, the temperature, test pieces and time intervals with the load gradually being increased until a sharp rise in the coefficient of friction was noted. This indicates that there has been a sudden change in the condition of the sliding surface and generally means that the lubricant has approached a point of failure or a so-called transition point. Shown in Table II below are the transition loads for various temperatures and spindle speeds for the above organosiloxane material untreated and containing 3%, by weight, of bis-(trimethylsiloxy dimethyl)-stannane.

Table II

Spindle Speed (r.p.m.)	Temperature (° F.)	Transition Load (kg) (Untreated Organopolysiloxane)	Transition Load (kg) (Treated Organopolysiloxane)
600	212	40	60–80
600	400	30	60
1,200	212	25–30	60
1,200	400	20–25	60

Keeping the load and speed constant and varying the temperature, the transition temperatures as shown in Table III were determined for a load of 40 kg.

Table III

Spindle Speed (r.p.m.)	Load (kg.)	Transition Temp. (° F.) (Untreated Organopolysiloxane)	Transition Temp. (° F.) (Treated Organopolysiloxane)
600	40	110	580
1,200	40	80	580

It will be seen from the above that by the addition of tin-silicon compounds of the type described the lubricating characteristics, as well as the oxidation resistance of organopolysiloxanes may be substantially improved. It will be understood, of course, that other concentrations of the additives described above may be employed without departing from the spirit and scope of our invention. It will also be apparent that other organopolysiloxane fluids, including those in the referenced patents, may be used with the additives to obtain improved high temperature lubricating characteristics.

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

1. A lubricating composition for use under heavy load at elevated temperatures consisting essentially of (1) a liquid polymeric organopolysiloxane having an average of from about 1.98 to 2.25 organic groups per silicon atom, and (2) from about 1 to 10% by weight, based on the weight of (1) of a silicon-tin-containing compound of the formula

$$\left[R_3SiO\right]_{4-m}Sn-R'_m$$

where R and R′ are selected from the class consisting of lower alkyl groups, aryl groups, aralkyl groups, alkaryl groups, alicyclic groups, chlorophenyl groups, and, in the case of R, mixtures of the above groups, and *m* is a number from 0 to 2.

2. A lubricating composition for use under heavy load at elevated temperatures consisting essentially of (1) a liquid methylchlorophenylpolysiloxane having an average from about 1.98 to 2.25 organic groups per silicon atom and (2) from about 1% to 10% by weight, based on the weight of (1) of a silicon-tin compound of the formula

$$\left[R_3SiO\right]_{4-m}Sn-R'_m$$

where R and R′ are selected from the class consisting of lower alkyl groups and phenyl groups, and *m* is a number from 0 to 2.

3. A lubricating composition for use under heavy load at elevated temperatures consisting essentially thereof (1) a liquid polymeric organopolysiloxane having an average of from about 1.98 to 2.25 organic groups per silicon atom and (2) from about 1% to 10% by weight, based on the weight of (1), of bis-(trimethylsiloxy dimethyl)-stannane.

4. A lubricating composition for use under heavy load at elevated temperatures consisting essentially of (1) a liquid polymeric organopolysiloxane having an average of from about 1.98 to 2.25 organic groups per silicon atom and (2) about 3% by weight, based on the weight of (1), of bis-(trimethylsiloxy dimethyl)-stannane.

References Cited in the file of this patent

"Organosilicon Compounds Containing Tin," Papetti et al., J. Org. Chem., vol. 22, pp. 526–8, May 1957.