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2,937,994

LUBRICATING OIL COMPOSITION CONTAINING A SILICON-TIN-CONTAINING COMPOUND

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10 Claims. (Cl. 252—49.7)

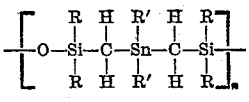
This invention relates to lubricants. More particularly it relates to liquid lubricants which are characterized by desirable lubricity at high temperatures and to the preparation of such lubricants.

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 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. 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 more 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 up to 700° F. and higher, the need for lubricants and hydraulic fluids which will retain desirable qualities at such temperatures is quite apparent.

A principal object of this invention, therefore, is to provide lubricating materials which have desirable lubricating qualities at temperatures of the order of 700° F. and higher.

Briefly stated the invention comprises the hydrolysis and condensation products of organopolysiloxanes or other natural or synthetic materials in combination with organopolysiloxanes containing tin, carbon and silicon units which later may be characterized by the following formula:



wherein R and R′ are various organic groups as described more fully hereinafter and n is a number from about 1 to 1000 and preferably from about 15 to 40.

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 better 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.

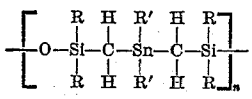
By the term "hydrolyzable organo-substituted silanes" are meant derivatives of SiH_4 which contain hydrolyzable groups or radicals, for example, halogens, amino groups, alkoxy, aryloxy, and acyloxy radicals, etc., in addition to the organic groups substituted directly on the silicon atom that are joined 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 can also contain substituents substituted thereon, for instance, halogens, e.g., di-, tri-, tetrachlorophenylchlorosilanes, 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 oxy-

gen 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 it has been 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 can be substantially improved by incorporating in the liquid polysiloxanes small amounts of certain tin-carbon-silicon compounds.

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

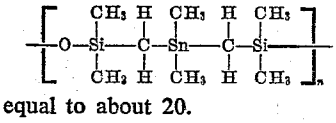


where R and R′ are aliphatic radicals including lower alkyl radicals such as methyl, ethyl, propyl, isopropyl, butyl, etc.; alicyclic radicals such as cyclopentyl, cyclohexyl, etc.; aryl radicals such as phenyl, diphenyl, naphthyl, anthracyl, etc.; aralkyl radicals such as benzyl, phenylethyl, etc.; alkaryl radicals such as tolyl, xylyl, etc.; heterocyclic radicals and mixtures of the above in the case of R, the above mentioned radicals also containing, if desired, substituents such as halogens, e.g., chlorophenyl, etc.; and *n* is a number from about 1 to 1000 and preferably from about 15 to 40.

The tin-silicon compounds may be conveniently prepared through the reaction of the Grignard of haloalkyl siloxanes and diorgano tin dihalides. The following examples illustrate the preparations of such materials, it being realized that other methods of such preparation will occur to those skilled in the art.

EXAMPLE 1

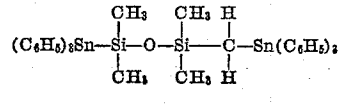
To 8 grams of magnesium and diethylether there was added 35 grams of bischloromethyltetramethyldisiloxane slowly after the reaction had been started with heating and a small amount (0.5 cc.) of ethyl bromide. When the reaction has ceased, practically all the magnesium had been used indicating that the di-Grignard had been formed. Then 30 grams of dimethyl tin dichloride and dry toluene was added slowly to the above, cooling the reaction as reflux became too vigorous. When all the tin dichloride was added, the flask was heated for about one hour to complete the reaction, the contents of the flask then being added to ice water and the solvent layer separated and dried. After removal of the toluene and ether a low viscosity liquid was obtained having the structure



where *n* is equal to about 20.

EXAMPLE 2

This example is the same as Example 1 except that the Grignard reagent was reacted with triphenyl tin chloride to give a compound having the following structure



In general it has been found that compounds of the described type of Example 1 above in which *n* is equal to from about 15 to 40 are most useful in connection with this invention, it being realized that compounds having a lower *n* value may be used, taking into consideration that their volatility will result in loss of material. Compounds having an *n* value up to about 1000 have also proved useful. Generally, it has been 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 base lubricating material are useful in improving the oxidation resistance, lubricity and load carrying ability of the lubricant. Preferably about 3 to 5% of the additive is used. In general, amounts over 3% while not deleterious do not improve the characteristics of the lubricant. Of course, amounts less than 1% will also give some improvement.

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. at 5 mm. of mercury 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 methyl 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 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 minutes. When there was added to the above organopolysiloxane 3%, by weight, of the tin-silicon-carbon organopolysiloxane of Example 1 above, the threshold temperature rose 80 deg. F. to 510 deg. F. and the time to gelation at 600 deg. 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 in 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 and 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 except as otherwise stated and the time for each test run was 2 hours.

Shown in Table I is a comparison between the exemplary organopolysiloxane described insofar as its lubricating qualities are concerned as tested on the 4 ball tester, with the same material to which has been added 3%, by weight of the material of Example 1 above.

Table I

Spindle Speed (r.p.m.)	Load (kg.)	Temp. (° F.)	Scar (mm.) Untreated Organopolysiloxane	Scar (mm.) Treated Organopolysiloxane
600	4	212	.42	.37
600	10	212	.47	.54
600	40	212	1.10	.80
600	50	212	2.19	1.00
600	4	400	.58	.52
600	10	400	.61	.54
600	40	400	1.70	.90
600	50	400	2.38	1.20
600	40	700	2.20	1.00
1200	40	212	2.40	.97
1200	40	400	2.70	1.10
1200	40	700	2.70	1.80

The superiority of the present materials at elevated temperatures is at once evident from the above.

The load carrying capacity of the various lubricants, treated and untreated, was 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 noticed. This indicates that there has been a sudden change in the condition of the sliding surface and generally means than 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 the tin-silicon material of Example 1.

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
1200	212	25-30	60
1200	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
1200	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 can 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 the invention. It will also be apparent that other organopolysiloxanes including those in the referenced patents may be used with the additives to obtain improved high temperature lubricating characteristics.

The additives of the present invention are desirable as additions not only to organopolysiloxane type materials but to other materials such as mineral oils, vegetable oils and synthetic lubricants. For example, when 3% by weight of the additive was added to the materials shown in Table IV below with the material being tested in a four-ball tester rotating at 1200 r.p.m. at 212 degrees, scars of the dimension shown in the table were obtained.

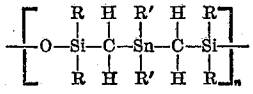
Table IV

Spindle Speed (r.p.m.)	Temperature (° F.)	Load (kg.)	Scar (mm.)	Material
1200	212	40	.97	Organopolysiloxane.
1200	212	40	.94	Diester blend [di-(2 ethylhexyl) sebacate].
1200	212	40	.90	Light Mineral oil.
1200	212	40	.98	Mineral oil.
1200	212	40	1.10	Dimethyl silicone oil.

The above data demonstrates that the present invention is useful not only in conjunction with organopolysiloxanes but, surprisingly, with other types of lubricants as well.

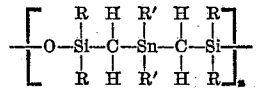
What I claim as new and desire to secure by Letters Patent of the United States is:

1. A lubricating composition having improved lubricating characteristics consisting essentially of (1) a lubricating material selected from the group consisting of mineral oils and organopolysiloxane oils and (2) from 1 to 10% by weight based on (1) of a tin-carbon-silicon-containing compound of the formula:



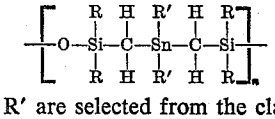
where R and R′ are selected from the class consisting of lower alkyl groups, aryl groups, aralkyl groups, alkaryl groups, alicyclic groups and chlorophenyl groups, and, in the case of R, mixtures of the above groups, and *n* is equal to a number up to about 1000.

2. A lubricating composition for use under heavy load at elevated temperatures consisting essentially of (1) a lubricating material selected from the group consisting of mineral oils and organopolysiloxane oils, and (2) from about 1 to 10 percent based on the weight of (1) of a tin-carbon-silicon-containing compound of the formula:



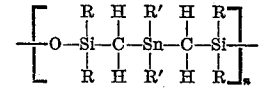
where R and R′ are selected from the class consisting of lower alkyl, aryl, aralkyl, alkaryl, alicyclic groups, and chlorophenyl groups, and, in the case of R, mixtures thereof, and *n* is a number from about 15 to 40.

3. A lubricating composition for use under heavy load at elevated temperatures consisting essentially of (1) a lubricating material selected from the group consisting of mineral oils and organopolysiloxane oils, and (2) from about 1 to 10 percent based on the weight of (1) of a tin-carbon-silicon-containing compound of the formula:



where R and R′ are selected from the class consisting of lower alkyl groups, aryl groups, aralkyl groups, alkaryl groups, alicyclic groups, and chlorophenyl groups, and, in the case of R, mixtures thereof, and *n* is equal to about 20.

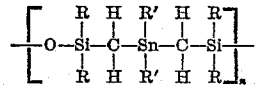
4. A lubricating composition for use under heavy load at elevated temperatures consisting essentially of (1) a liquid organopolysiloxane having an average of about 1.98 to 2.25 organic groups per silicon atom, and (2) from about 1 to 10 percent by weight based upon the weight of (1) of a tin-carbon-silicon-containing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



where R and R′ are selected from the class consisting of lower alkyl groups, aryl groups, aralkyl groups, alkaryl

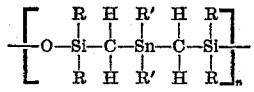
groups, alicyclic groups, and chlorophenyl groups, and, in the case of R, mixtures of the above groups, and *n* is a number up to about 1000.

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



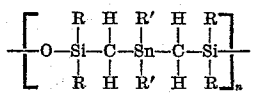
where R and R′ are selected from the class consisting of lower alkyl groups, aryl groups, aralkyl groups, alkaryl groups, alicyclic and chlorophenyl groups and, in the case of R, mixtures of the above groups and *n* is a number equal to from 15 to 40.

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



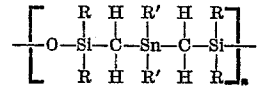
where R and R′ are selected from the class consisting of lower alkyl groups, aryl groups, aralkyl groups, alkaryl groups, alicyclic groups and chlorophenyl groups, and, in the case of R, mixtures of the above groups and *n* is equal to about 20.

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



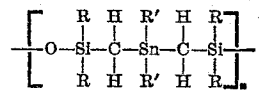
where R and R′ are selected from the class consisting of lower alkyl groups, aryl groups, aralkyl groups, alkaryl groups, alicyclic groups, and chlorophenyl groups, and, in the case of R, mixtures of the above groups, and *n* is a number up to about 1000.

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



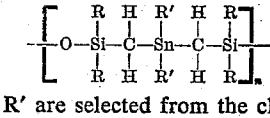
where R and R′ are selected from the class consisting of lower alkyl groups, aryl groups, aralkyl groups, alkaryl groups, alicyclic groups, and chlorophenyl groups, and, in the case of R, mixtures of the above groups, and *n* is a number equal to from about 15 to 40.

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



where R and R′ are selected from the class consisting of lower alkyl groups, aryl groups, aralkyl groups, alkaryl groups, alicyclic groups and chlorophenyl groups, and, in the case of R, mixtures of the above groups, and *n* is equal to about 20.

10. A lubricating composition having improved lubricating characteristics consisting essentially of (1) a lubricating material selected from the class consisting of mineral oils and organopolysiloxane oils and (2) about 3% by weight based on (1) of a tin-carbon-silicon-containing compound of the formula:



where R and R′ are selected from the class consisting of lower alkyl groups, aryl groups, aralkyl groups, alkaryl groups, alicyclic groups and chlorophenyl groups and, in the case of R, mixtures of the above groups, and *n* is equal to a number up to about 1000.

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