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2,716,129

HALOGENATED ORGANOPOLYSILOXANES

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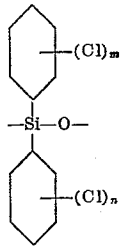
5 Claims. (Cl. 260—448.2)

This application is a continuation-in-part of our earlier filed application Serial No. 722,458, filed January 16, 1947, now U. S. Patent 2,623,019, and assigned to the same assignee as the present invention.

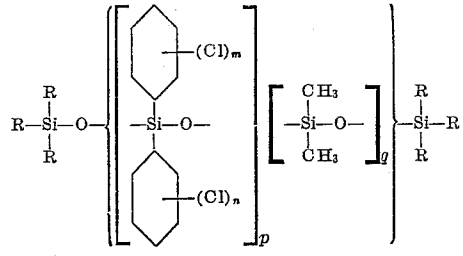
This invention relates to new and useful synthetic non-resinous liquid compositions and methods of making the same. More particularly the invention is concerned with fluid or oily (non-resinous) compositions some of which have improved lubricating qualities comprising a liquid polysiloxane containing the recurring structural units



and



where m and n are integers equal to at least 1, for instance, from 1 to 5. The invention also embraces linear polysiloxanes having the same recurring structural units but also having terminal silicon atoms to each of which are attached three hydrocarbon groups. The liquid linear polysiloxanes embraced by the claimed invention can also be defined as corresponding to the general formula



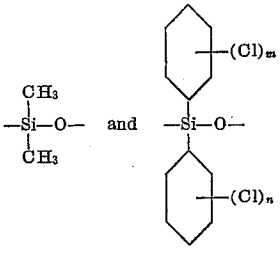
where R is a monovalent hydrocarbon radical which may be the same or different (for example, alkyl, for instance, methyl, ethyl, propyl, etc.; aryl, for instance, phenyl, naphthyl, etc.; aralkyl, for instance, benzyl, phenylethyl, etc.; alkaryl, for instance, tolyl, ethylphenyl, xylyl, etc.; and halogenated derivatives of the aforesaid monovalent hydrocarbon radicals), m and n have the meanings given above, and p and q are integers equal to at least 1, e. g., from 1 to 200 or more. Preferably, R is the methyl radical.

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, in many respects such materials show certain deficiencies when employed for lubricating purposes, especially under certain lubricating conditions where a fluid film cannot be formed or if formed has broken down. Because of the latter defect, such organopolysiloxanes do not afford the protection against bearing seizure or "freezing" of the revolving member or shaft supported by the bearing that has come to be expected for certain petroleum-base oils of like viscosity. This disparity in lubrication purposes is especially 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.

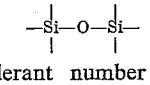
The primary object of this invention is to provide liquid compositions capable of adequately lubricating the bearing surfaces of metallic bodies moving in relation to each other, even under increased loads, said liquids being characterized by high resistance to oxidation, little change in viscosity with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

We have now discovered that liquid organopolysiloxanes containing the structural units



where m and n have the meanings given above, have improved properties as lubricants over other liquid polysiloxanes, e. g., liquid methylpolysiloxanes, or even liquid methyl and phenyl polysiloxanes employed in the same application. We have found that the presence of the chlorinated phenyl radical (in which the chlorine is stably attached to the phenyl radical) chemically attached to the silicon atom in the polysiloxane by a carbon-silicon linkage, improves the lubricating properties of the organopolysiloxane when it is employed as a lubricant in high pressure applications. Liquid lubricating oils of our invention show much less wear between steel-on-steel and steel-on-brass rubbing surfaces than do heretofore known organopolysiloxanes containing intercondensed diphenylsiloxy units in which the phenyl groups are not halogenated, e. g., chlorinated.

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 the siloxane structure:



wherein a preponderant number of the valences of the silicon atoms are satisfied by the substitution thereon of organic radicals, for example, methyl radicals. These compositions of matter may be prepared, e. g., by individual hydrolysis of di-(chlorinated phenyl)dichlorosilane and dimethyldichlorosilane, followed by complete or partial intercondensation of the hydrolysis products. They may also be prepared, for example, by cohydrolyz-

ing mixtures of the aforementioned hydrolyzable diorgano-substituted silanes, e. g., the di-(chlorinated phenyl)dichlorosilane and the dimethyldichlorosilane (other hydrolyzable groups such as alkoxy, amino, etc., may be present in place of the silcon-bonded chlorine atoms) alone or with other hydrolyzable silanes containing, for example, three organic radicals substituted onto the silicon atoms, for instance, trimethylchlorosilane.

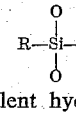
A further method for preparing the linear liquid organo-substituted polysiloxanes herein disclosed and claimed comprises hydrolyzing the di-(chlorinated phenyl) dichlorosilane with a dimethyldihalogenosilane, for example, dimethyldichlorosilane, isolating and washing the hydrolysis product and effecting reaction between the hydrolyzed product and a hexaorganodisiloxane, e. g., heaxemthyldisiloxane, in the presence of an acid such as hydrochloric, phosphoric, and sulfuric acids. More specific directions for the hydrolysis of hydrolyzable organo-substituted silanes to form liquid organo-substituted polysiloxanes, including the linear products therefrom, may be found, for example, in our earlier issued Patent 2,483,158, issued September 27, 1949, as well as in Patnode Patent 2,469,888, issued May 10, 1949, both patents being assigned to the same assignee as the present invention.

Where the dimethyldihydrolyzable silane is cohydrolyzed with the di-(chlorinated phenyl) dihydrolyzable silane, the product generally comprises cyclic derivatives consisting solely of dimethylsiloxy units and di-(chlorinated phenyl) siloxy units in cyclic arrangements. The number of the respective units in the molecule will depend on the ratio of the hydrolyzable organosilanes.

By the term "hydrolyzable organo-substituted silane" is intended to mean derivatives of silane 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 atoms, which organic groups are joined to the silicon through carbon-silicon linkages. As pointed out above, in the linear polysiloxane, the silicon atoms which lie between the terminal silicon atoms, have two chlorinated phenyl radicals attached thereto by carbon-silicon linkages. There may also be intercondensed terminal trimethylsiloxy units. In this respect compositions herein disclosed and claimed are similar to those described in our U. S. Patent 2,483,158 with the exception that the phenyl groups attached to the intermediate silicon atoms have chlorine attached thereto. The number of chlorines which may be on the phenyl groups may vary widely and may range from about 1 to 5 chlorine atoms for each phenyl group. We have found that from 1 to 4 chlorine atoms per phenyl group are sufficient and that 2 to 3 chlorine atoms on each phenyl group impart marked improvement to the liquid organopolysiloxane.

Hydrolysis of the aforementioned silanes and mixtures of silanes results in the formation of silanols, that is, organo-substituted silanes containing hydroxy groups substituted directly in 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 2.5 organic radicals substituted per silicon atom, usually from about 2.0 (for cyclic derivatives) 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 the organic radicals are attached to silicon atoms 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. Generally, if proper precaution is taken, there are little, if any, hydroxyl radicals or hydrolyzable radicals remaining in the final product.

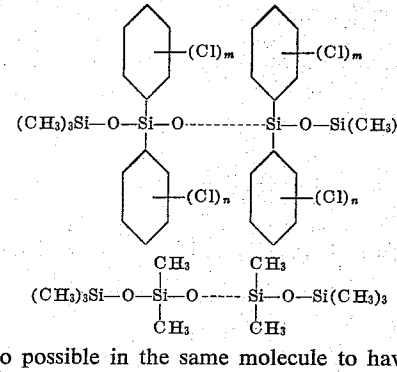
The presence of intercondensed monoorganosiloxy units is not precluded for the purpose of introducing branching. Such units, which may be described as having the formula



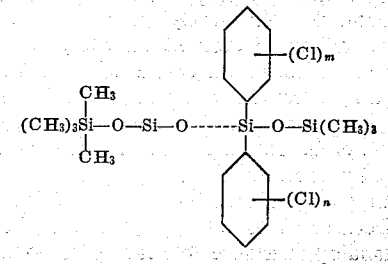
where R is a monovalent hydrocarbon radical, can be obtained by cohydrolyzing a monoorganotrihydrolyzable silane, e. g., trimethylchlorosilane, at the time that the diorganodichlorosilanes are hydrolyzed.

As pointed out above, the chlorinated phenyl radical in our claimed compositions of matter may contain from 1 to 5 chlorine atoms attached directly to the benzene nucleus and the chlorine atoms may be spaced in any manner around the benzene nucleus, for example, they may be ortho, meta, para, symmetrical, assymmetrical, or vicinal in relationship with the silicon atom to which the benzene nucleus is attached.

When both the di-(chlorinated phenyl)siloxy units and dimethylsiloxy units are present in a linear polysiloxane, the relationship of these units to the terminal silicon atoms may vary. It is possible that in one instance one or more of the same structural units, that is, the di-(chlorinated phenyl) siloxy or dimethylsiloxy units, may be adjacent each other or it is possible there may occur regular alternations of the two different siloxy units for certain lengths of the linear chain, etc. Whichever final structure may exist in the linear polysiloxane, under such circumstances both aforementioned units are present in the chain simultaneously. Also, it has not been determined clearly which of the two aforementioned structural units are closest the terminal silicon atom when both of the units are in the molecule. Thus, in one combination in connection with terminal trimethylsilyl groups, it is possible to have either a dimethylsiloxy or a di-(chlorinated phenyl)siloxy unit immediately adjacent each of the two terminal silicon atoms to give the following general formula:



It is also possible in the same molecule to have one dimethylsiloxy unit and one di-(chlorinated phenyl) siloxy unit adjacent each of the two terminal silicon atoms respectively as illustrated by the following general formula:



Regardless of the actual structure where these mixed siloxy units are present, the final product comprises a mixture of liquid linear polysiloxane wherein the distribution of the structural units is one of generally random distribution depending upon such factors as, for instance, proportions of ingredients employed in the preparation of liquid polysiloxanes, hydrolysis conditions, etc.

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.

Example 1

Di-(trichlorophenyl)dichlorosilane was prepared similarly as described in Rochow Patent 2,258,219 by chlorinating diphenyldichlorosilane until the composition indicated the presence of an average of three chlorine atoms substituted directly on each phenyl group. Analysis of the compound established that it contained 61.8 percent chlorine which indicates that there was present an average of three chlorine atoms on each benzene nucleus. 116 grams (0.9 mol) dimethyldichlorosilane was mixed with 46 grams (0.1 mol) di-trichlorophenyl)dichlorosilane and this mixture was then added slowly to a mixture of 475 grams water and two solvents comprising 100 grams t-amyl alcohol and 100 grams toluene over a period of about 40 minutes during which time the temperature rose from about 30° to 58° C. Thereafter, the entire reaction mass was stirred for an additional 10 minutes and then permitted to separate into two layers. The upper layer containing the hydrolyzed organopolysiloxane was removed and washed three times with 100 cc. portions of water, and filtered to give about 303 grams of a solvent layer. This mixture was distilled to remove the solvents and to give a product boiling above 150° C. and weighing about 92 grams. This material was a pale yellow oil which solidified partially on cooling. To effect complete intercondensation, this reaction product was then heated to about 150 to 175° C. for about 5 hours at the end of which time there was obtained an oily viscous product which remained liquid even after it cooled to room temperature. This composition was a mixture of cyclic intercondensation products containing dimethylsiloxy units and di-(trichlorophenyl) siloxy units, in which the latter diorganosiloxy units comprised approximately 10 mol percent. The aforementioned product was 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 Company, 1939). The bearing pressure at seizure was 1470 p. s. i. A straight linear methylpolysiloxane, when tested similarly, showed seizure at 300 p. s. i.

To 22.6 grams of the aforementioned intercondensed product was added 2.6 grams of hexamethyldisiloxane and 1.5 grams of concentrated sulfuric acid. This mixture was shaken for several hours and then washed free from acid to give a product comprising a chain-stopped polysiloxane. This composition comprised a mixture of linear polysiloxanes containing terminal trimethylsilyl groups and intercondensed dimethylsiloxy and di-(trichlorophenyl) siloxy units.

Example 2

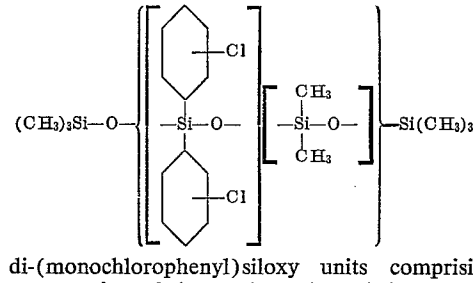
In this example 122.5 grams (0.95 mol) dimethyldichlorosilane and 23.0 grams (0.05 mol) di-(trichlorophenyl) dichlorosilane were mixed together and added to the water and solvent mixture described in Example 1, using the same procedure as described in the aforesaid Example 1. The hydrolysis was carried out in the same manner as was done in Example 1. The mixture was stirred for an additional short period of time and permitted to settle after which the upper layer was washed several times with water and filtered. There was thus obtained a filtrate weighing about 246 grams. The solvents were removed by fractional distillation, and the residue further fractionally distilled to give a product boiling above 150° C. in an amount equal to 77 grams. This material was then heated at about 160° to 180° C. for about 5 hours in order to insure the intercondensation of the dimethylsiloxy and the di-(trichlorophenyl)siloxy units. At the end of this time there was obtained a viscous oil which remained liquid at room temperature. This composition was also a mixture of cyclic derivatives containing dimethylsiloxy units and di-(trichlorophenyl)siloxy units. To 23.8 grams of this viscous oil were added 3.4 grams hexamethyldisiloxane and 1.4 grams concentrated sulfuric acid. This mixture was then shaken thoroughly at room temperature for about 44 hours. A small amount of additional water was added and the mixture again shaken. The mixture was then centrifuged, filtered, and the water removed to give a clear, slightly yellow oil. The viscosity of this linear organopolysiloxane was measured at 100° F. and at 210° F. From this was obtained a viscosity temperature coefficient of about 0.684. This viscosity temperature coefficient was found to be much better than the viscosity temperature coefficients of many hydrocarbon oils of which the best, measured similarly, ran about 0.776 to 0.883. Analysis of this composition showed that it contained a little less than 6 percent phenyl-bonded chlorine. A sample of this oil was tested for weight loss at 150° C. by placing a sample thereof in an open vessel. At the end of one day and at the end of seven days the weight loss was less than the weight losses of many hydrocarbon lubricating oils and even less than other non-halogenated organopolysiloxane oils, including oils containing intercondensed, non-halogenated diphenylsiloxy units. This oil can be used to advantage as a lubricant whereby it is possible to obtain improved lubrication over nonchlorinated silicone oils of similar construction.

Example 3

Improved liquid organo-substituted polysiloxanes are also obtainable where there is one chlorine atom substituted on each phenyl group. An example of such a polysiloxane is one prepared, for instance, by cohydrolyzing a mixture of chlorosilanes comprising dimethyldichlorosilane and a minor proportion, for example, approximately 5 mol percent of di-(monochlorophenyl) dichlorosilane, and thereafter effecting rearrangement of the siloxane units with hexamethyldisiloxane in the presence of sulfuric acid similarly as that described in Examples 1 and 2. Such a product comprises a linear polysiloxane containing terminal trimethylsilyl groups

$$[(CH_3)_3Si—]$$

and having intermediate recurring dimethylsiloxy units and di-(monochlorophenyl)siloxy units, the latter units comprising a minor proportion of the total number of diorganosiloxy units. The structural formula for such a composition may be considered to be as follows:



the di-(monochlorophenyl)siloxy units comprising a minor proportion of the total number of the latter units and the dimethylsiloxy units.

The improvements in the lubricity of the claimed compositions of matter appears to increase with the number of chlorine atoms attached to the benzene nucleus. We may employ advantageously from about 1 to 4 chlorine

atoms in each phenyl group and an average of about 3 to 6 total chlorine atoms on the two phenyl groups. The position of the chlorine atoms around the phenyl nucleus is not believed to be critical and may occupy any one of the positions substituted by the hydrogen.

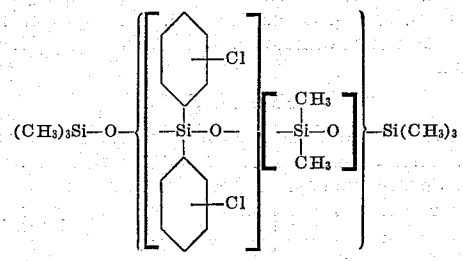
Generally, it is preferred that the number of dimethylsiloxy units be in a major proportion. Generally, we have found that of the total number of dimethylsiloxy and di-(chlorinated phenyl)siloxy units, the dimethylsiloxy units preferably comprise from about 80 to 99 mol percent, in order to have the most suitable lubricating compositions which will have the optimum extreme pressure lubrication properties.

It is desired to point out that the organopolysiloxanes described above may also be described as being composed of at least two silicon atoms per molecule connected to each other through an oxygen atom disposed between each two successive silicon atoms the remaining valences of silicon being satisfied by (*a*) a methyl radical and (*b*) chlorinated (e. g., from 1 to 5 chlorine atoms) phenyl radicals, an average of not less than two chlorinated phenyl radicals being present in each siloxane molecule, the ratio of chlorinated phenyl radicals to silicon atoms being not less than 0.02 and not exceeding 1.0.

Our claimed compositions of matter in addition to having application in the lubricating fields are also eminently suitable as electrical insulating fluids, hydraulic fluids, damping fluids, etc. They can be admixed with other materials, for example, metallic soaps, inhibitors, antioxidants, etc., to form useful fire-resistant greases.

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

1. A liquid composition of matter comprising a linear organopolysiloxane corresponding to the general formula



the di-(monochlorophenyl)siloxy units comprising a minor molar proportion up to 5 mol percent of the total number of the latter units and the dimethylsiloxy units.

2. A liquid composition of matter comprising the cohydrolysis product of dimethyldichlorosilane and di-(chlorinated phenyl) dichlorosilane, the di-(chlorinated phenyl) dichlorosilane being present in a minor molar proportion up to 5 mol per cent of the di-(chlorinated phenyl) dichlorosilane and the dimethyldichlorosilane.

3. A linear organopolysiloxane consisting essentially of terminal trimethylsilyl groups and intermediate dimethylsiloxy units and di-(chlorinated phenyl) siloxy units, the aforesaid di-(chlorinated phenyl) siloxy units comprising a minor molar proportion up to 5 mol per cent of the total number of the latter units and the dimethylsiloxy units.

4. A linear organopolysiloxane consisting essentially of terminal trimethylsilyl groups and intermediate dimethylsiloxy units and di-(monochlorophenyl) siloxy units, the di-(monochlorophenyl) siloxy units comprising a minor molar proportion up to 5 mol per cent of the total number of the latter units and the dimethylsiloxy units.

5. A linear organopolysiloxane consisting essentially of terminal trimethylsilyl groups and intermediate dimethylsiloxy and di-(monochlorophenyl) siloxy units, the di-(monochlorophenyl) siloxy units comprising 5 mol per cent of the total number of the above-mentioned two types of diorganosiloxy units in the linear organopolysiloxane.

References Cited in the file of this patent

UNITED STATES PATENTS

2,258,219	Rochow	Oct. 7, 1941
2,258,222	Rochow	Oct. 7, 1941
2,410,346	Hyde	Oct. 29, 1946
2,483,158	Sprung	Sept. 27, 1949
2,599,984	Fletcher	June 10, 1952
2,623,019	Wilcox et al.	Dec. 23, 1952