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LUBRICANT

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8 Claims. (Cl. 252-49.6)

1 This invention relates to liquid phenyl alkyl
siloxanes and more particularly to their use as
lubricants for metallic bearing surfaces.

This application is a continuation-in-part of
my co-pending application Serial Number 432,528,
filed February 26, 1942, and assigned to the as-
signee of the present invention.

The lubricants in common use are for the most
part petroleum oils. While they have a wide
range of use, they have certain inherent defects
which make them inapplicable under certain con-
ditions. The most evident of these defects are
their ease of oxidation, their inflammability, in-
stability at high temperature as evidenced by
acid formation and viscosity increase, inability
to lubricate at low temperatures, and their great
change of viscosity with change of temperature.

It is known that certain of the liquid organo-
siloxanes are useful as lubricants for metallic
bearing surfaces where the load imposed thereon
is light. However, their inability to withstand
even moderate loads renders them unsuitable for
many applications. It would be highly desirable
if liquid organo-siloxanes could be found which
possess improved lubricity with respect to the
lubrication of relatively moving metallic bearing
surfaces under moderate or heavy loads.

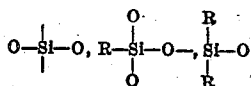
The primary object of this invention is to pro-
vide such a liquid for lubricating the bearing
surfaces of relatively moving metallic bodies, said
liquid being characterized by high resistance to
oxidation, little change of viscosity with tem-
perature and low pour point. Other objects and
advantages of the present invention will be read-
ily apparent from the following description and
claims.

I have discovered that liquid polymeric organo-
siloxanes comprising at least 40 mol. per cent of
the recurring unit

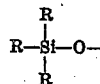


within their structure are greatly superior in their
lubricity under heavy loads to the organo-silox-
anes hitherto employed as lubricants. R is a
lower alkyl radical having from one to five car-
bon atoms. The remainder, if any, of the organo-

2 siloxane may consist of one or more different
units selected from the class consisting of



and

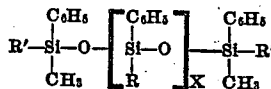


where the R's are the same or different organic
radicals selected from the class consisting of
phenyl and lower alkyl radicals. The incorpora-
tion of these units into the siloxane polymer may
be effected by hydrolyzing suitable mixtures of
the corresponding silanes, i. e., SiX_4 , RSiX_3 ,
 R_2SiX_2 and R_3SiX , where X is a hydrolyzable
radical, for example, an ethoxy or a chlorine radi-
cal and dehydrating the hydrolysis products.
The only requirement of such a mixture is the
presence of at least 40 mol. per cent of a silane
of the formula $(\text{C}_6\text{H}_5)_3\text{RSiX}_2$.

I prefer to use those liquid organo-siloxanes
within the class specified above which are sub-
stantially or completely dehydrated and wherein
an appreciable amount of the unit



30 is present where R' is either a methyl or a phenyl
radical. Such an organo-siloxane would include
the following structure:



It is understood, of course, that the $(\text{C}_6\text{H}_5)_3\text{RSiO}$
unit is present to the extent of at least 40 mol.
per cent and also that still other structural units
may be present such as $(\text{CH}_3)_2\text{SiO—}$, etc. By
substantially complete dehydration is meant the
presence of less than 1 per cent by weight of hy-
droxyl groups attached to silicon. More than this
amount results in a tendency of the siloxane to
change in viscosity due to condensation or elimi-
nation of water.

The phenyl alkyl siloxane liquids of this inven-
tion are characterized by relatively slight changes
in viscosity over a wide range of temperature:

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low pour points; high flash points; low volatility; low hygroscopicity; little or no corrosion or decomposing effect upon metal or rubber; and little or no gasification or solidification tendencies under the higher or lower temperature conditions encountered in various types of applications.

For a better understanding of my invention, reference should be made to the following examples wherein are disclosed compositions falling within the purview of the invention and methods of making them.

Example 1

Polymeric phenyl ethyl silicone having a viscosity of 60 centistokes was prepared by dropping phenylethylsilicon dichloride into aqueous ethyl alcohol and recovering the organo-silicon liquid. The latter exhibited marked ability to lubricate metallic surfaces. Since many lubricating applications require a more viscous liquid, the above polymeric silicone was treated with solid sodium hydroxide in such amount that the atomic ratio of Si/Na was equal to 25/1. The temperature of the mixture was held at 130–140° C. for several hours. After washing out the alkali and drying by subjecting to vacuum, the viscosity of the product was 5023 centistokes.

Example 2

Polymeric phenyl methyl silicone liquids of two different viscosities were prepared as follows: Phenylmethylsilicon dichloride was hydrolyzed to yield a fluid having a viscosity of 332 centistokes. This fluid was then treated with solid sodium hydroxide in an amount corresponding to a ratio of 50 silicon atoms to one sodium atom. The temperature of the mixture was held at about 150° C. for several hours until the viscosity appeared to attain a constant value. The alkali was removed by neutralization and washing, leaving a fluid of 1100 centistokes viscosity.

Example 3

A copolymer was prepared from SiCl_4 and $(\text{C}_6\text{H}_5)(\text{CH}_3)\text{Si}(\text{OC}_2\text{H}_5)_2$ in the molar ratio of 1/3 by adding aqueous ethyl alcohol to the mixture dropwise. The product was a clear viscous liquid which withstood having air blown through it for 20 hours at 250–270° C. without gelation.

Example 4

A copolymer from $\text{Si}(\text{OC}_2\text{H}_5)_4$ and $(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)\text{SiCl}_2$

in the molar ratio of one to three was prepared by slowly adding dropwise to the stirred mixture approximately the required amount of water diluted with an equal volume of ethyl alcohol. The product was a liquid which did not gel even when air was blown through it at 200–250° C. for 18 hours.

Example 5

A mixture of equi-molecular parts of $\text{C}_2\text{H}_5\text{SiCl}_3$ and $(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)\text{SiCl}_2$ was diluted with an equal volume of dioxane. Aqueous dioxane was added dropwise with vigorous shaking until a permanent turbidity developed. After removing the solvent and any excess water by vacuum treatment at room temperature an oil of medium viscosity remained. It was quite fluid at 200° C. and its viscosity was little affected in one to two hours of heating at that temperature.

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Example 6

Two equivalents of $(\text{C}_6\text{H}_5)(\text{CH}_3)\text{SiCl}_2$ and one of $(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{SiCl}$ were mixed and diluted with dioxane. An amount of water slightly in excess of the calculated quantity was slowly added. On dilution with water after completion of the intercondensation the product was precipitated as an oil.

Example 7

To a solution of $(\text{C}_6\text{H}_5)(\text{CH}_3)\text{Si}(\text{OC}_2\text{H}_5)_2$ and $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$ in equimolar proportions 95% ethyl alcohol containing a few drops of concentrated hydrochloric acid was added slowly with warming to effect hydrolysis and copolymerization. Water was then added in excess. After evaporating the solvents, a rather viscous liquid was obtained which withstood being heated at 190° C. for 72 hours without gelling.

Example 8

A mixture of 31.3 grams $(\text{C}_2\text{H}_5)_2\text{SiCl}_2$ and 41 grams of $(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)\text{SiCl}_2$ was hydrolyzed by dropping in 7.5 ccs. of water slowly with stirring at room temperature over a period of about two hours. There was considerable cooling due to evaporation of HCl. The product which was a low viscosity liquid was washed with water to remove all traces of acid. Heating at elevated temperatures for several hours failed to increase the viscosity.

Example 9

A mixture of 29.7 grams of $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$ and 41.0 grams of $(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)\text{SiCl}_2$ was added dropwise over a period of 8 hours to excess water. Another 200 ml. of water was then added and the mixture was stirred about 12 hours. The copolymer and aqueous layer were separated. The copolymer was then washed once with water and was then refluxed for an hour with an equal volume of water. After another washing at room temperature no test for acid was obtained with the wash water. The sample was dried and solvents removed by bubbling air through the sample at room temperature. It was then heated to 150° C. for about an hour under a pressure of 15 to 18 mm. The viscosity of the product at 250° C. was 23.0 centistokes.

Example 10

A mixture of 14.8 grams of $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$ and 41.0 grams of $(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)\text{SiCl}_2$ was added dropwise over a period of six hours to 50 ml. of 95% $\text{C}_2\text{H}_5\text{OH}$ and 50 ml. of water. The mixture was stirred for an hour after the chloride had all been added with 200 ml. of water. An oily liquid and an aqueous layer formed which were separated. The latter was extracted with diethyl ether and the ether extract was then added to the copolymer oil. The ether solution was then washed repeatedly with water until no test was obtained for acid in the wash water. The copolymer was then dried under 15 mm. pressure by heating to 150° C. Viscosity at 25.0° C. was 29.6 centistokes.

The superiority of the liquids of the present invention as extreme pressure lubricants over other organo-siloxanes hitherto used or considered as lubricants, was demonstrated by subjecting several liquids to the following test. A ball bearing was arranged to slide back and forth on a metal test strip while being completely immersed in the oil being tested. The ball bearing was also arranged in such a manner that varia-

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ble loads could be applied thereto in order to determine the effect of increasing load. The lubricating property of the oil was based upon the wear or weight loss of the test strip after having been subjected to the sliding action of the ball bearing for a period of two hours. The following table tabulates the results obtained in the case of certain liquids of the present invention as contrasted with other organo-siloxanes as well as a conventional hydrocarbon petroleum oil. In this table the wear is expressed in 0.0001 gram.

Fluid	25° C. viscosity	Metals in contact wear of test strip					
		Bearing	Test strip	Load in grams			
				500	1,500	3,000	4,000
Univis No. 48.....	Centistokes 61	Hardened steel..	Soft steel....	5	8	11	9
Dimethyl silicone.....	100	do	do	340	740		
Diethyl silicone.....	50	do	do	330	440		
Cyclic trimer of phenylethyl silicone.....	63	do	do		4	5	4
Cyclic trimer of diethyl silicone.....	3.6	do	do	668	872		
A ¹	160—	do	do				2

¹ A liquid organosilicon oxide polymer consisting essentially of 40 mol. per cent of $(C_6H_5)_2SiO_{1.5}$ units, and 11 mol. per cent of $(CH_3)_2SiO_{0.5}$ units.

It will be observed that the liquids falling within the purview of the present invention exhibited wearing properties corresponding to that of the standard hydrocarbon petroleum oils, while the organo-siloxanes, dimethyl silicone, diethyl silicone, and diethyl silicone trimer were definitely inferior to both the hydrocarbon oil and the phenyl alkyl siloxanes.

I claim:

1. The method of lubricating relatively moving metallic bodies which comprises maintaining between their bearing surfaces a lubricant film comprising a liquid polymeric organo-siloxane whose organic substituents consist essentially of lower alkyl and phenyl radicals attached to silicon through carbon-silicon linkages, said siloxane containing at least 40 mol. per cent of the recurring structural unit corresponding to the formula $(C_6H_5)_2RSiO$ where R is a lower alkyl radical.

2. The method of lubricating relatively moving metallic bodies which comprises maintaining between their bearing surfaces a lubricant film comprising a substantially completely dehydrated liquid polymeric organo-siloxane whose organic substituents consist essentially of lower alkyl and phenyl radicals attached to silicon

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through carbon-silicon linkages, said siloxane containing at least 40 mol. per cent of the recurring structural unit corresponding to the formula $(C_6H_5)_2RSiO$ where R is a lower alkyl radical.

3. The method according to claim 2 wherein R is a methyl radical.

4. The method according to claim 2 wherein R is an ethyl radical.

5. The method of lubricating relatively moving metallic bodies which comprises maintaining between their bearing surfaces a lubricant film

comprising a polymeric liquid phenyl methyl silicone.

6. The method of lubricating relatively moving metallic bodies which comprises maintaining between their bearing surfaces a lubricant film comprising a polymeric liquid phenyl ethyl silicone.

7. The method of lubricating relatively moving metallic bodies which comprises maintaining between their bearing surfaces a lubricant film comprising a substantially completely dehydrated liquid polymeric organo-siloxane whose organic substituents consist essentially of lower alkyl and phenyl radicals attached to silicon through carbon-silicon linkages, said siloxane containing at least 40 mol. per cent of the recurring structural unit corresponding to the formula $(C_6H_5)_2RSiO$ where R is a lower alkyl radical and said siloxane also containing structural units corresponding to the formula



where R' is selected from the class consisting of phenyl and methyl radicals.

8. The method according to claim 7 wherein R and R' are methyl radicals.

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