

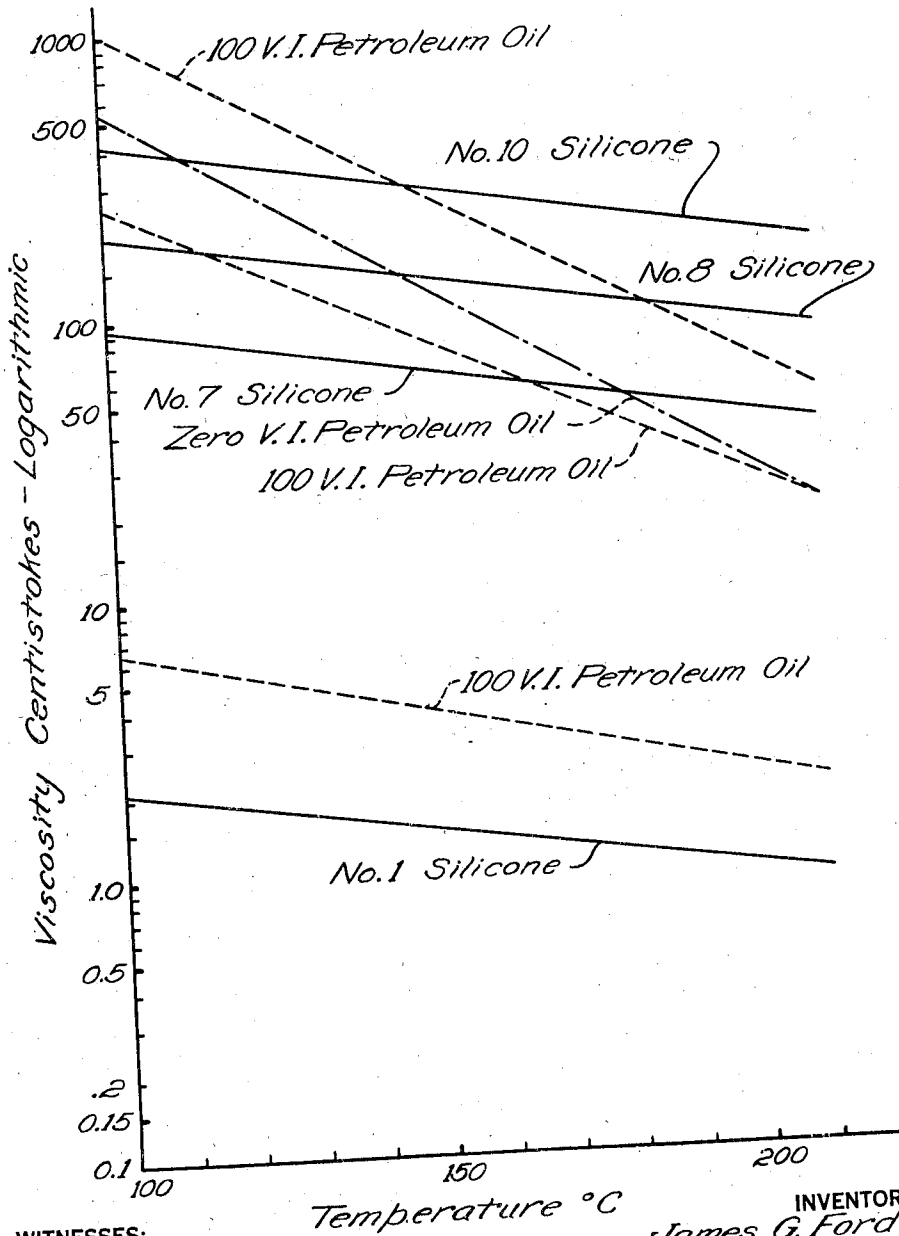
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LUBRICANTS

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WITNESSES:

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# UNITED STATES PATENT OFFICE

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## LUBRICANTS

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This invention relates to lubricants, and more particularly to synthetic compositions characterized by a relatively flat viscosity-temperature curve.

The object of this invention is to provide a lubricant composed essentially of liquid polymers of dimethyl silicone.

A further object of this invention is to provide for polymerizing essentially dimethyl silicols in producing lubricants characterized by an extremely flat temperature viscosity curve.

Other objects of the invention will, in part, be obvious, and will, in part, appear hereinafter.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description in which the single figure of the drawing is a graph of the temperature viscosity curves of the lubricants prepared according to this invention and prior art type of lubricants.

In the application of lubricating substances to bearings or surfaces to be separated during relative movement, it is desirable that the lubricating substance remain present at the applied surfaces without evaporating or creeping away therefrom. Changes in the lubricating substance due to the presence of atmospheric gases in combination with the temperatures to which it is subjected should not cause sludging or gumming of the lubricant. In addition, a satisfactory lubricant is characterized by relative non-reactivity with the surfaces to which it is applied. Usually lubrication fails when any one of these three changes takes place in an applied lubricant.

Heretofore petroleum oils, vegetable oils and animal oils have been employed as lubricants for bearing surfaces. However, owing to the nature of these materials they have been subject to reaction with moisture and atmospheric oxygen. The reaction products are sludges, gums and emulsions which are unsatisfactory lubricating media. In some cases additions have been made to lubricating materials in the form of stabilizers or inhibitors which have decreased the rate of sludge and gum formation. Lubricants so treated have exhibited some increase in efficiency and a greater effective life.

Under certain severe conditions which occur in practice, even lubricants containing inhibitors and other additives have not been satisfactory as lubricants over a prolonged period of time. For example, electrical meters attached to the exterior of buildings and exposed to the hot sun in tropical climates often reach temperatures of 85° C. The lubricants of the most highly developed type have

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been able to last for only a month before requiring cleaning of the meters and application of new lubricant.

A further unsatisfactory characteristic of prior art lubricants is the rapid change in viscosity with temperature change.

A lubricant which has been selected because it is satisfactory in viscosity at a mean temperature in a given mechanism may become thin and considerably less effective as a lubricant at high temperature conditions. On the other hand, when the mechanism is at its lowest temperature, the lubricant may become extremely thick and viscous. In this state the lubricant not only causes an increased power loss, but frequently surfaces may run bare for a period of time before the lubricant penetrates to all parts of the bearing surfaces and is effective. The problem of a satisfactory lubricant for many types of apparatus, therefore, is not successfully met by employing the usual types of materials, with or without the addition of inhibitors and other additives.

It may be stated that for most purposes the requirements for a satisfactory liquid lubricant are:

1. Low vapor pressure
2. High resistance to oxidation or reaction with moisture at all operating temperatures
3. No corrosive action upon bearing members
4. Flat viscosity curve within operating range temperature -30° F. to +185° F.
5. Noncreeping
6. Nonpolymerizing or condensing
7. Nontoxicity

It has been discovered that a lubricant meeting all of the above seven requirements as well as or better than any known lubricant may be prepared from silicones. In particular, it has been found that dimethyl silicone polymers which have been treated to remove low boiling constituents meet the above requirements for a lubricant more successfully than any material heretofore known.

Several general processes for preparing silicone polymers are known to the art. The following illustrative examples are given:

### Example 1

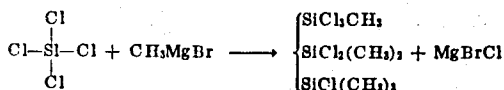
As disclosed by Kipping and his colleagues, silicon tetrachloride in cold ether solution may be treated with an aliphatic magnesium halide to replace chlorine atoms of silicon tetrachloride with alkyl groups. A mixture of mono-di- and tri-alkyl silicon chlorides is thus formed.

Hydrolysis is then employed to replace the residual chlorine atoms with hydroxyl groups, by

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means of which the molecules condense, with the loss of water, to form silicone polymers.

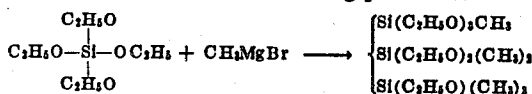
In employing this process for the production of dimethyl silicones, methyl magnesium bromide is reacted with silicon tetrachloride to produce a mixture of methyl silicon chlorides:



The individual components of this mixture have different boiling points and can be separated by fractional distillation. Dimethyl silicon dichloride may thus be isolated. Its subsequent reaction with water yields dimethyl silicic acid and the silicic acid then polymerizes, spontaneously or through the agency of applied heat or catalysts which may be employed to control, within limits, the degree of polymerization and the physical properties of the resulting polymeric product.

#### Example 2

K. A. Andrianov, J. General Chemistry U. S. S. R. 8, 1255, 1263 (1938) and other workers have disclosed the preparation of silicols and silicones from ethyl silicate. Ethyl silicate may be treated with methyl magnesium bromide in a Grignard reaction to produce the following products:

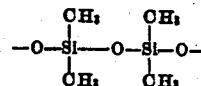


The methyl ethoxysilanes are readily separable by distillation into monomethyl, dimethyl and trimethyl ethoxysilanes. As mentioned previously, it is desirable to work with only the dimethyl compound. The isolated dimethyl di-

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product is unsatisfactory as a lubricant, since the monomethyl silicones present permit the formation of solids and thermosetting types of compounds due to cross linkages between chains of polymer. If liquid polymers from such mixtures are subjected to heat when exposed to oxygen and moisture, they are not stable and will polymerize further to form more viscous liquids and plastic or rigid solid bodies.

If on the other hand the dimethyl derivative which is substantially free of the mono- and trimethyl silicon compounds, is hydrolyzed and polymerized, the product is a liquid characterized by extreme stability. It is believed that chains or closed rings having the following general form occur:



There is always obtained a mixture of polymers, their average molecular size, size distribution, complexity of structure and resulting properties depending upon the conditions, including temperature, agitation and catalysts, under which the reaction with water is carried out.

Polymeric dimethyl silicones which may be produced by practicing any of the processes above disclosed, or other possible methods, so as to isolate essentially the dimethyl fraction consist of a mixture of polymers of different molecular weight. The viscosity depends to a great extent upon the nature of the polymers present. The following table is indicative of the range of physical properties obtainable when mixtures prepared under different conditions were fractionated.

Sample No.	Polymerization Catalyst	Fraction	Approx. Average Mol. Wt.	Viscosity 37.8° C. (c. s.)	Density 37.8° C.	Surface Tension (dynes/cm.)
1	HCl	Volatile	540	2.1	0.9370	21.5
2	do	do	500	2.0	0.9364	21.0
3	do	do		2.3	0.9384	21.0
4	do	Non-vol.	1,500	33.5	0.9538	22.8
5	do	do	1,560	28.4	0.9610	23.2
6	do	do	2,500	49.4	0.9595	23.3
7	do	do	3,500	97.5	0.9605	23.2
8	do	do	5,000	200.7	0.9583	23.7
9	H <sub>2</sub> SO <sub>4</sub>	do	900	107	0.9519	22.4
10	do	do	1,500	413	0.9537	22.0

ethoxysilane may be hydrolyzed to produce dimethyl silicic acid. This product may be condensed and polymerized, as indicated in the first example, to produce the polymers of predetermined characteristics.

#### Example 3

Stock and Somieski, Ber. Deuts. Chem. Ges. 52, 695 (1919), disclose that silane may be reacted with hydrogen chloride to produce monochlorosilane and dichlorosilane. Exhaustive methylation of the dichlorosilane with zinc methyl vapor produced dimethylsilane.

The dialkylsilane produced is hydrolyzed with sodium hydroxide to produce a solution which when acidified precipitates silicones. Stock and Somieski have shown that dimethyl silicone is conveniently prepared by this method. They further disclose that polymers obtained by this process are of a nature similar to those secured by the practice of the Kipping process.

Silicone polymers are built up through chains of alternating silicon and oxygen atoms. If an unseparated mixture of mono-, di-, and trimethyl silicon derivatives is hydrolyzed, the polymerized

The column headed "fraction" refers to the volatile and non-volatile fractions which separate on distilling at 200° C. at an absolute pressure of 5 millimeters of mercury. The "volatile" fraction in the table in each instance is liquid at room temperature.

It will be noted from the above table that the viscosity of a silicone polymer fraction having an approximate average molecular weight of 1500 and produced with a HCl catalyst is considerably less than the viscosity of a polymer of approximately the same average molecular weight when produced with the relatively more active H<sub>2</sub>SO<sub>4</sub> catalyst. A relatively unexpected characteristic is the substantially uniform surface tension for the liquid polymers of all molecular weights.

According to this invention a satisfactory lubricant can be secured only if essentially dimethyl silicic acid molecules are condensed and polymerized. The product produced by condensing essentially dimethyl silicic acid will be radically different from the polymerized product resulting when a mixture of mono-, di- and trimethyl silicic acids having an average of 2 methyl groups

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per silicon atom is used. For example, in the art there is described the product consisting of substantially two methyl groups per silicon atom but containing mono- and trimethyl silicols in addition to dimethyl silicols. This product is stated to be essentially an oily liquid which, when heated for four hours at 120° C., sets to a soft, somewhat rubbery gel. Obviously a gel is an unsatisfactory lubricant. Other properties of these mixtures have been described by those working in the art as forming solids upon being polymerized by exposure to temperatures of 200° C. These solids are not stable at elevated temperatures, since heating for several days at 200° C. causes an increasing embrittlement. They have been described further as oxidizing in air at 300° C. with disintegration taking place when this heating is prolonged for 24 hours.

On the contrary, the product produced from essentially dimethyl silicol polymerized at any temperature with or without a catalyst is a liquid. No solid products have been encountered when this material has been polymerized in numerous ways. When heated at 200° C. for prolonged periods of time, there is no observable chemical change. By heating at this temperature in vacuo light fractions may be removed as a vapor, but the major portion of the liquid does not distill even at 5 mm. of Hg and 200° C.

Among the exceptional properties of polymeric dimethyl silicone is its resistance to oxidation at elevated temperatures. In one test dimethyl silicone polymer has been heated at 200° C. while agitated by a stream of pure oxygen for 17 hours and longer without any observable change in physical or chemical characteristics. The liquid was as mobile and as clear after the test as before. No sludging or gumming occurred.

Various atmospheric gases have been applied to the dimethyl silicone at elevated temperatures without causing any change in the properties of the liquid polymer.

These fractions feel oily. The fractions may be produced from a reaction mixture in grades ranging from water thin liquids to liquids that are relatively thick and syrupy in consistency.

Exceptionally good viscosity-temperature characteristics have been discovered on testing the various dimethyl silicone polymer fractions over a wide range of temperatures. The following is a table of viscosities for various fractions:

Sample No.	Temp., °F.	Viscosity, centistokes	$m = \text{Slope of Curve } \log \nu = f(t)$
1.....	100	2.10	-0.00321
	150	1.300	
	210	0.933	
7.....	100	97.46	-0.00364
	150	61.34	
	210	38.73	
8.....	100	200.7	-0.00357
	150	127.8	
	210	81.26	
10.....	100	413.5	-0.00352
	150	271.7	
	210	169.1	

The data in the above table have been plotted and shown as a graph in Fig. 1. Referring to the figure, the four relatively straight lines drawn for each of the silicones are substantially parallel to one another. Furthermore, the relative slope of the lines is believed to be the nearest to a zero slope that is obtainable for any known types of material.

For comparison there have been plotted the values of three petroleum oils of 100 V. I. (vis-

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cosity index) and one oil of a zero V. I. It will be noted that the petroleum oils have much steeper viscosity-temperature curves than the synthetic dimethyl silicone lubricants. Considering that the viscosity is plotted on a logarithmic scale, the relative change of viscosity with temperature for the silicones is exceptional.

The slope  $m$  in the table is calculated from the viscosities at 210° F. and 100° F. according to the following formula:

$$m = \frac{\log \nu_{210} - \log \nu_{100}}{210 - 100}$$

where  $\nu$  = viscosity at the indicated temperature.

The following table indicates the slopes of the viscosities of a number of oils which are in commercial use today. The viscosity data were secured from the "A. S. T. M. Standards for Petroleum Products and Lubricants," September 1940.

$\nu_{100}$	$\nu_{210}$		$m$	
	100 V. I. Oil	Zero V. I. Oil	100 V. I. Oil	Zero V. I. Oil
2.00	6.620	8.360	-0.00472	-0.00565
10.00	89.178	162.49	-0.00865	-0.0110
20.00	249.31	551.07	-0.0105	-0.0131
30.00	480.9	1156.0	-0.0108	-0.0144
40.00	714.6	1967.4	-0.0114	-0.0154
50.00	1010.4	2990.8	-0.0119	-0.0161
60.00	1345.8	4220.7	-0.0123	-0.0168
70.00	1719.9	5854.4	-0.0126	-0.0173
75.00	1921.3	6446.7	-0.0128	-0.0176

It will be noted on comparing the viscosity slope columns of the tables for the dimethyl silicone polymers and the petroleum oils that the slope of the former is relatively constant from the thinnest liquid to the most viscous liquid. On the contrary, the table for petroleum oils shows that the slope changes rapidly from the thinner oils to the heavier oils. The change for petroleum is approximately three times from the thinnest to the heaviest oil in the table.

The silicone polymers have been subjected to extensive tests on various types of apparatus. In one test electrical watt-hour meters have been lubricated with suitable dimethyl silicone polymer and operated in ovens maintained at 85° C. These watt-hour meters have been subjected to atmospheric gases such as oxygen, water vapor and the normal constituents of air. The best obtainable petroleum lubricants prepared from high grade petroleum products and containing anti-oxidants and inhibitors failed under these conditions in one month. Ordinary untreated petroleum oils would fail in a day or two. An original supply of dimethyl silicone lubricant has been operating satisfactorily under these conditions for over a year without any observable failure or change in properties. On examination of a meter all the metal parts of the bearings were found to be clean and bright with no signs of gumming. The lubricant appeared to be as good as when it was originally introduced into the apparatus with no apparent discoloration.

The dimethyl silicone polymer lubricant appears to meet all of the seven requirements herein set forth for an exceptionally satisfactory lubricant. Every test to which the material has been subjected has been successfully met.

It will be appreciated that a lubricant having the extremely flat viscosity temperature curve exhibited by the dimethyl silicone polymers is highly advantageous for use in apparatus subjected to a wide range of temperatures. Precision instruments such as watches, clocks me-

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ters, scientific apparatus and the like will operate with less power being required at temperatures below 0° F. with the silicone lubricant retaining sufficient body and film forming characteristics to lubricate the bearings adequately at temperatures as high as the boiling point of water and even higher. The lubricant has been found not to freeze or harden until considerably below -70° F.

Dimethyl silicones have been found to be satisfactory lubricants since they are stable at high temperatures even when exposed to oxygen. However, other dialkyl silicones, such, for example, as diethyl silicone, may be utilized as lubricants depending on the conditions met.

Since certain obvious changes may be made in the above procedures and different embodiments of the invention could be made without distinguishing from the scope thereof, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

We claim as our invention:

1. A lubricant composed of a mixture of liquid polymers of dialkyl silicones in which the alkyl groups each have at least two carbon atoms substantially free of the monoalkyl and trialkyl silicone derivatives, the lubricant being characterized by resistance to deterioration at high temperatures.

2. In a method of lubricating the bearing surfaces of moving parts, the step of applying to said surfaces a fluid composition composed of a mixture of liquid polymeric dimethyl silicones having an average molecular weight greater than 740.

3. In the method of lubricating the bearing

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surfaces of moving parts, the steps of applying to said surfaces a fluid composition composed of a mixture of liquid polymeric dialkyl silicones substantially free of the monoalkyl silicone derivatives and substantially free of components which distill at 200° C. and at a pressure of 5 mm. of mercury.

4. In the method of lubricating the bearing surfaces of moving parts, the steps of applying to said surfaces a fluid composition composed of a mixture of a liquid polymeric dimethyl silicone fraction substantially free of components which distill at 200° C. and at a pressure of 5 mm. of mercury.

5. A lubricant composed of a mixture of liquid polymers of dialkyl silicones, the dialkyl silicones each having a substantial number of alkyl groups with at least two carbon atoms to provide an average of more than two carbon atoms per silicon atom, the silicones being substantially free of the monoalkyl and trialkyl silicone derivatives, the lubricant being characterized by resistance to deterioration at high temperatures.

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