Extending the Utility of Silicone Lubricants through Structural Modifications

H.M. SCHIEFER, R.W. AWE, and C.L. WHIPPLE
Dow Corning Corp., Midland, Mich.

SILICONE polymers are semiorganic compounds that can cover a wide range of polymer composition. The fluid polymers display excellent viscosity-temperature properties coupled with very good heat stability. These polymers have successfully fulfilled many lubrication requirements in the last decade. The excellent viscosity-temperature and stability properties of silicones are inherent in the inorganic siloxane backbone as shown in Figure 1. The properties of the siloxane polymer are varied largely through the use of a number of different types of organic substituents on the silicon atom.

Methyl substitution has been found to be the most stable alkyl group, and it best retains the viscosity-temperature relationship imparted by the siloxane backbone. This type of substitution also imparts low volatility characteristics to the oils. Longer alkyl groups can be substituted in place of methyl with a resultant sacrifice in stability. A methylethyl-substituted polysiloxane retains most of the desirable properties of the dimethyl substitution, but has better organic solubility.

A new series of oils is produced when phenylmethyl is substituted for dimethyl on the silicon atom (Figure 1). A polymer with low phenyl content has very good low temperature properties. Increased phenyl content adds to the heat stability of the siloxane polymer at the expense of low temperature and viscosity-temperature properties. The phenyl group adds to both thermal and oxidation stability (*14*), but has its largest effect on the latter.

The alkyl- and phenyl-substituted polysiloxanes have proved to be good lubricants in both rolling and sliding contact for many types of bearing metal combinations (*3*, *4*, *7*, *9*). The use of these lubricants has been restricted, to some extent, by their inherent lack of boundary lubricity for sliding ferrous metal bearings (*9*). A step towards overcoming this lubricity deficiency was made when halophenyl groups were substituted for methyl or phenyl (*10–12*). In general, incorporation of the halophenyl group has an effect similar to that of substituting phenyl, while additionally imparting better antiwear characteristics.

Introduction of a large number of halophenyl groups will enhance the extreme pressure properties of the oil at the expense of some low temperature and antiwear properties. The halogen on the phenyl can be chosen to have sufficient stability to withstand bulk oil temperatures, but have enough reactivity at boundary surface temperatures to form a lubricating film (*2*). Typical properties of a low chlorophenyl-substituted fluid (*60*) are compared to a low phenyl-substituted fluid in Table I.

The lubricants described above have been compounded into a variety of greases using suitable thickeners. Both oils and greases find use in applications requiring a wide temperature range or long life lubricant. With the proper choice of oil, the requirements for either a very low or a very high temperature lubricant can be met.

RADIATION AND HEAT-STABLE SILICONES

An area of recent advancement in polysiloxane chemistry has been in the development of materials which will withstand the combined effects of radiation and high temperature. Fischer, Zack, and Warrick (*8*) have shown that increasing the phenylmethyl substitution in a siloxane polymer increases its radiation stability. Their work proved that a correlation exists between G_{gas} values and aliphatic electron fraction for phenylmethylpolysiloxanes as shown in Figure 2. A G_{gas} value represents the moles of gas evolved per 100 e.v. radiation including both condensable and noncondensable gases. The aliphatic electron fraction represents the number of electrons associated with all of the atoms of the aliphatic groups divided by the total number of electrons associated with all of the atoms of the entire molecule. The electron fraction of a phenylmethylpolysiloxane calculated from molecular structure can be used to obtain the G_{gas} value (Figure 2) which in turn will predict the radiation stability of the material. Present silicone lubricants have G_{gas} values of 0.082 and higher.

New silicone polymers have been prepared with higher phenyl contents by incorporating the phenyl group into the chain stopping unit. The properties of two of these high phenyl-containing fluids are given in Table II. The maximum radiation stability and lowest G_{gas} value are exemplified by Silicone A, the lower molecular weight species. The approximate gelation radiation dosage is increased fivefold in Silicone B when compared to 710, a commercial, high phenylmethyl silicone fluid, of equal viscosity. The lower molecular weight polymer has a sevenfold advantage over 710 fluid. The G_{gas} values for 710 and Silicone A were obtained experimentally, whereas the 0.035 value for Silicone B was calculated from molecular structure. Radiation studies were conducted on these fluids to obtain viscosity and acid number changes by radiation as well as to allow prediction of approximate gelation dosages.

Various radiation dosages were given to the fluid by the use of a 2 m.e.v. van de Graaff generator. The sample was irradiated with a beam of electrons from the generator,

Table I. Typical Properties for Two Silicone Fluids

Property	Low Phenylmethyl Polysiloxane	60
Viscosity, cs.		
−65° F.	1000	3000
77° F.	50	60
400° F.	6.0	4.0
Freezing point, below, ° F.	− 94	− 94
Flash point, ° F.	550	550
Spontaneous ignition temp., ° F.	850	850
Shell 4-ball lubricity		
Wear scar diameter, mm., with 52–100 steel, 1200 r.p.m., 2 hours		
4 kg., 77° F.	0.39	0.30
10 kg., 77° F.	1.40	0.46
40 kg., 77° F.	2.00	1.80
4 kg., 400° F.	1.39	0.60
10 kg., 400° F.	>2.00	0.73
40 kg., 400° F.	. . .	>2.00
Thermal stability, 24 hours, 550° F.		
% viscosity change 210° F.	− 4	− 4
Acid number change	0.0	+ 0.2

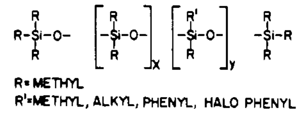

Figure 1. Chemical structure of silicone polymers

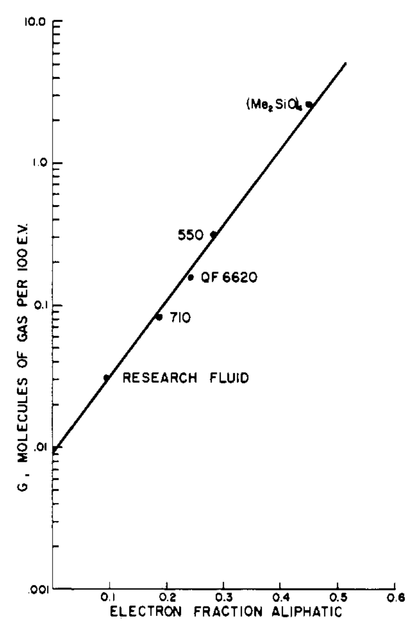

Figure 2. Radiation stability as a function of composition

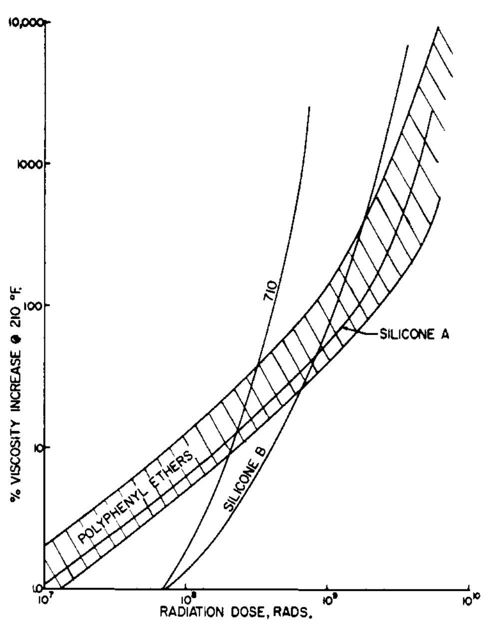

Figure 3. Effect of radiation on the viscosity of oils

while the oil was being stirred and purged with nitrogen. The samples were cooled with a water jacket during the radiation period to maintain fluid temperatures below 150° C. The changes in viscosity at 210° F. as a function of radiation dosages for the high phenyl silicone polymers are plotted in Figure 3. Only a slight increase in viscosity was noted for the fluids at radiation levels below 1 × 10^9 rads. The viscosity increases were more pronounced at dosages above 1 × 10^9 rads, with the lower molecular weight polymer showing the best stability. The radiation induced viscosity changes for the best available silicone (710) are shown for comparison in Figure 3. The resistance to viscosity change during radiation for the new fluids was considerably superior to that of 710. The radiation levels needed to give a 100% viscosity increase at 210° F. are as follows: 710, 4 × 10^8 rads; Silicone B, 1.2 × 10^9 rads; Silicone A, 1.6 × 10^9 rads. Acid numbers remained relatively constant over the entire radiation period.

Mahoney (*13*) and associates have described the excellent radiation and heat stability of polyphenyl ethers. Polyphenyl ethers are used for comparison in this paper because they appear to have good potential as high temperature radiation-resistant lubricants. Typical radiation-induced viscosity changes for unsubstituted polyphenyl ethers as a class are given as a band in Figure 3. Silicones A and B were equal to or better in radiation stability than the stable phenyl ether structure at dosages up to 1 × 10^9 rads. Above a radiation level of 1.5 × 10^9 rads, the viscosity change of the high molecular weight Silicone B was poorer than phenyl ethers or Silicone A.

A number of greases were compounded from Silicone B using various fillers that were known to be more stable toward radiation than the conventional organic soaps. The grease samples were irradiated using the same procedure as for the fluid, except that the samples were heated to maintain a temperature of 135° to 150° C., while being scanned with the electron beam. Figures 4 and 5 show the effect of radiation on the unworked and worked consistencies of the grease samples. For comparison, Figure 4 includes a curve for a grease compounded from 710 and copper phthalocyanine that was irradiated in a cobalt-60 source at an ambient temperature of 38° C. as reported by Fischer, Zack, and Warrick (*8*).

Table II. Properties of High Phenyl Polysiloxanes

Property	Silicone A	Silicone B	710
Viscosity, cs., 77° F.	167	600	500
Specific gravity, 25° C.	1.096	1.115	1.110
Flash point, ° F.	490	600	580
Freezing point, ° C.	−15	−5	−22
G^a_{gas}	0.031	0.035	0.082
Approximate gelation radiation dosage, rads.	6.5 × 10^9	4.5 × 10^9	9 × 10^8

[a] Moles of gas evolved per 100 e.v. radiation, including both condensable and noncondensable gases.

Figure 4 indicates that the greases, as shown by unworked penetration, undergo an initial hardening at low radiation dosages followed by a softening effect and finally by another hardening stage, leading to gelation at high radiation dosages. On the other hand, Figure 5, showing worked penetration, indicates an initial softening action followed by a period of relatively small consistency change until the gelation of the base fluid occurs with subsequent hardening of the grease.

These data point out that differences exist between the trends shown by measuring the unworked and worked ASTM penetration of an irradiated grease. The worked penetration may be a more realistic measure of radiation induced changes, since most applications place a grease under shearing stresses.

It can be seen from the curves that the greases compounded with Silicone B have an average life, before gelation, of approximately 2000 to 2500 megarads at 150° C., or about twice that of the grease based on 710. The curves also illustrate that the type of thickener used, and the amount of working a grease is subjected to, will have a bearing on the behavior of a grease under this type of exposure.

Increasing the phenyl content in a polysiloxane polymer also increases both oxidation and thermal stability. Theoretically, initial thermal decomposition points can be measured with an isoteniscope apparatus (*1*). A break in the straight line of log vapor pressure *vs.* reciprocal absolute temperature denotes the incipient decomposition point for a pure compound. It is more difficult to determine the break point with isoteniscope data for a polymer oil, since a curved line is usually obtained. The isoteniscope method was used to measure the thermal stability levels of phenyl

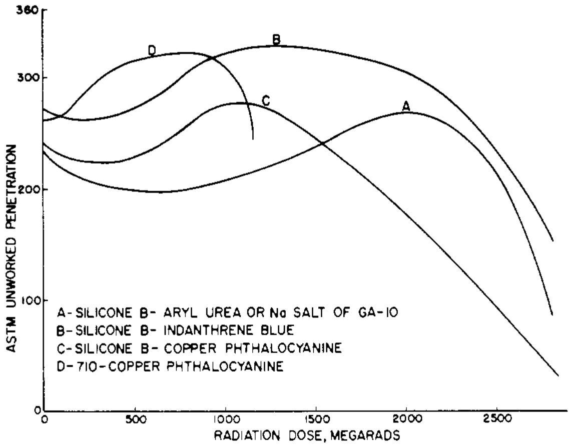

Figure 4. Radiation effect on grease consistency

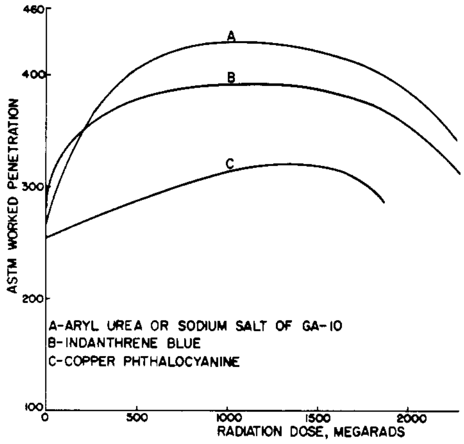

Figure 5. Radiation effect on silicone B grease consistency

end-blocked siloxane fluids, since a relatively narrow distribution of polymer sizes existed in the fluids. Plots of the vapor pressure-temperature curves for Silicones A and B are given in Figure 6. The initial thermal decomposition point for Silicone A is above 810° F. and for Silicone B is above 760° F. based on the isoteniscope data. These points are higher than for any other siloxane polymers and compare favorably with that of a typical polyphenyl ether (835° F.).

The changes in fluid properties due to thermal decomposition were studied at 800° F. The sample was sealed in a thick-walled glass tube, placed in a metal bomb, and heated in an oven for 8 hours. Physical property changes after this exposure period were small (Table III). These data indicate that the high phenyl silicone oils may be satisfactory lubricants at 800° F. in a closed inert atmosphere system. As expected, increased phenyl substitution also enhanced the oxidation stability (Table III). The stability in the presence of air was studied by placing a 40-gram sample of oil in a 150-ml. beaker and heating the sample in an air-circulating oven until the gelation point was reached. The introduction of phenyl end blocking improved gelation time by approximately 60%.

A study of the volatility properties of the radiation and thermally stable Silicone A indicated that this oil would be limited in high temperature open lubrication systems (Figure 7). The volatility test was conducted in a manner similar to the gel time test, except that a 10-gram sample of oil was heated in a 50-ml. beaker. Silicone B represents an oil which embodies a compromise of radiation stability and volatility properties. The volatility of the latter oil, as measured at 550° F., is similar to 710 and superior to bis(mixed phenoxy phenoxy)benzene.

The silicone polymers have always been recognized for their superior viscosity-temperature properties when compared to organic fluids. This advantage is due to the flexibility of the siloxane backbone. Although high phenyl

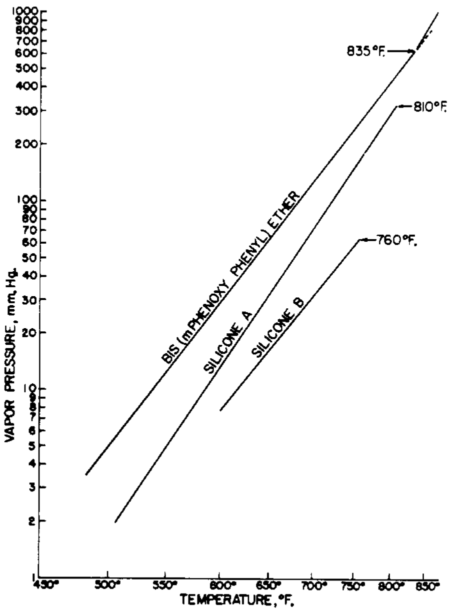

Figure 6. Vapor pressure vs. temperature (isoteniocope data)

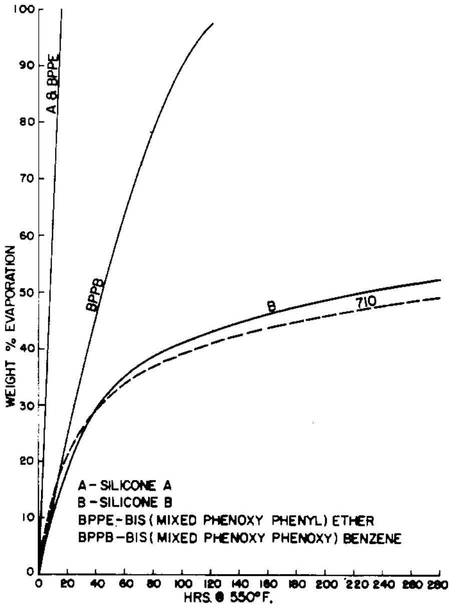

Figure 7. Volatility of oils at 550°F.

Table III. Stability of High Phenyl Polysiloxanes

Property	Silicone B	710
Thermal stability, 8 hours, 800° F.		
% viscosity change, 210° F.	+7	+15
Acid number change	0.0	0.0
Gel time[a] 550° F., hours	500-600	350-400

[a] As determined by heating a 40-gram sample in a 150-ml. breaker in an air-circulating oven.

substitution reduces some of the flexibility of the siloxane polymer, the viscosity-temperature properties remain superior to high phenyl organic fluids (Figure 8).

SOLVENT-RESISTANT LUBRICANTS

A recent departure from the conventional alkyl- and phenyl-substituted silicones has been the introduction of fluoroalkyl groups in the siloxane polymer, resulting in a lubricant with new and unusual properties. Other haloalkyl groups, such as chloroalkyl, had been incorporated previously and shown to improve boundary lubricity with a loss in stability. The trifluoropropyl group has proved to be stable, to improve sliding steel lubricity, and to provide solvent resistant properties.

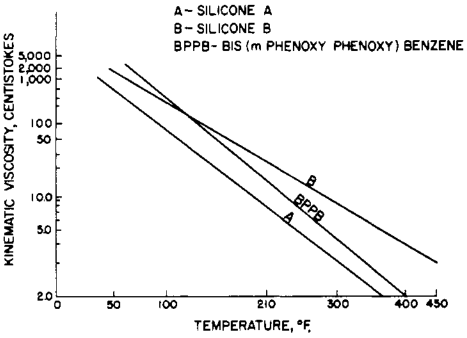

Figure 8. Viscosity-temperature relationships

Typical properties for a trifluoropropylmethylsiloxane fluid are listed in Table IV. This type of fluid has viscosity-temperature properties similar to those of a medium phenylmethyl-containing polysiloxane, but has superior low temperature properties. The lubricity, as measured by the Shell 4-ball wear tester, is much superior to that of non-halogen-containing silicones and also better than that of halophenyl-containing silicones. The thermal and oxidative stabilities of these fluids are similar to those of dimethylpolysiloxanes.

Fluoroalkyl-containing polysiloxanes provide equally interesting properties when compounded into greaselike materials. These greases exhibit excellent resistance to a variety of hydrocarbon solvents, chemicals, oxidizers, and fuels, among them the most modern high-energy liquid propellants. They also retain the good water and alcohol resistance and excellent consistency-temperature characteristics of the more standard silicone greases and compounds. Their lubricating characteristics are considerably better than those of standard silicone greases.

Table IV. Typical Properties of a Trifluoropropylmethylsiloxane Fluid

Property	Value
Viscosity, cs.	
0° F.	6800
77° F.	360
210° F.	34
Freezing point, ° F.	– 70
Flash point, ° F.	450
Shell 4-ball lubricity	
Wear scar diameter, mm., with 52-100 steel, 400° F., 1200 r.p.m., 2 hours	
4 kg.	0.45
10 kg.	0.54
40 kg.	1.55
Thermal stability, 24 hours, 550° F.	
% viscosity change, 210° F.	– 14.0
Acid number change	+ 0.02

Table V shows the solubility of two such greases in a content than grease B. This improves its low temperature consistency properties. Its resistance to this variety of materials, although lower than that of grease B, is good. Grease B, containing the larger amount of trifluoropropyl substitution, has lower solubility in the test materials. Its low temperature suitability, although good, is less than that of grease A. The solubility of these materials was determined by vigorous and lengthy agitation in the test fluid, followed by evaporation of the decanted test fluid. This solubility test is described in MIL-G-6032A. This specification requires less than 20% solubility in Reference Fluid II.

Table V. Solubility of Fluoroalkyl-Containing Siloxane Greases
(MIL-G-6032A test method)

Solubility, % by Weight, in	Grease A	Grease B
Reference Fluid II (MIL-H-3136)	18.0	4.0
JP-4	11.7	Nil
Gasoline	31.6	9.6
Benzene	24.2	4.3
Acetone	79.5	80.2
Perchloroethylene	24.3	6.4
Ethyl alcohol	5.8	5.7
Water	1.2	Nil

Table VI-A illustrates the resistance of greases A and B to materials not used in the solubility test. This resistance test, also described in MIL-G-6032A, consists of smearing a thick coat of grease on an aluminum strip, half immersing it in the test material, and observing it during an 8-hour exposure and after removal and drying. Greases A and B have very good resistance to all materials, except unsymmetrical dimethylhydrazine. Dimethylpolysiloxane fluids thickened with special inorganic fillers exhibit good resistance to this particular material.

The low temperature characteristics of these greases, as mentioned earlier, are good. Table VI-B gives the torque required to cause rotation in a bearing packed with these greases at below zero temperatures. These results were obtained on equipment described in MIL-I-8660. The operability or inoperability of a valve or other piece of equipment lubricated with one of these materials and operating at a given temperature is primarily a function of design. Therefore, one can only predict serviceable temperature ranges for the greases in most applications. These are

Table VI. Fluoroalkyl-Containing Greases

A. Resistance (MIL-G-6032 test method)

Resistance to	Grease A	Grease B
30% hydrogen peroxide	Excellent	Excellent
Unsymmetrical dimethylhydrazine	Poor	Poor
Diethylenetriamine	Very good	Very good
Fuming nitric acid	Very good	Very good

B. Torque Required to Rotate Packed Bearing
(MIL-I-8660 test method)

	Torque, G./Cm.	
Temperature, ° F.	Grease A	Grease B
–30	<1000	3,000
–65	1000	>10,000
–80	2000	. . .

−80° to 400° F. for grease A and −30° to 400° F. for grease B.

Just as the lubricity of the trifluoropropylmethylsiloxane fluids on which these greases are based is good, so also is the lubricity of the greases. Falex wear machine tests on these materials showed them to have load-carrying capacities in excess of the 1100-pound limit of the machine. The torque measurements at 1100 pounds were 54 and 45 pound-inches, respectively, for greases A and B. This compares to a load of 250 pounds and torque of 25 pound-inches at the point where excessive wear caused failure for a typical phenylmethylpolysiloxane-based grease tested in the same manner. A dimethylpolysiloxane-based grease, compounded similarly to A and B, allows wear at such a rapid rate that no values could be recorded. The Falex test method used for making the above load-carrying capacity measurements was making the above load-carrying capacity measurements was as follows.

The grease was buttered on the steel V-blocks and run in for a period of 1 minute at a 50-pound jaw load. The ratchet wheel was then engaged and the load increased steadily until failure occurred. Torque at the failure point was noted. Failure was denoted by excessive wear or breaking of the shear or test pin.

ADDITIVE IMPROVEMENT OF POLYSILOXANES

The most desirable method of achieving property improvement or variation for polysiloxanes is through polymer modification as described earlier. Certain additional improvements can be obtained by the use of selected additives.

The sliding steel lubricity of the halophenyl-containing fluids can be further improved by the addition of a small percentage of a copolymer fluid. The copolymer fluid consists of an organometallic compound copolymerized with dimethylsiloxane to achieve compatibility. The properties of a fluid containing the additive are very similar to those of the base fluid with the exception of lubricity and high temperature stability. Typical properties of Silicone D, consisting of a halophenyl-containing polysiloxane base fluid plus a lubricity additive, are shown in Table VII. Large improvements in lubricity were obtained at 400° F., as measured by the Shell 4-ball machine, at the expense of some high temperature thermal and oxidation resistance. Shell 4-ball wear scar values for Silicone D at 400° F. are similar to those of compounded mineral and diester oils at the same or lower temperatures.

The improvement in lubricity has been substantiated in terms of performance by conducting hydraulic pump tests with Silicone D. A Vickers (Model V105Y) vane pump test was run at 105° C. with 60 fluid and at 135° C. with Silicone D (Table VIII). Satisfactory performance was obtained with the latter fluid in a 12-hour test and it gave less vane wear than a shorter test with 60 fluid. Silicone D was also used successfully to lubricate a Vickers (Model PF3911) piston-type aircraft hydraulic pump for 300 hours at an average bulk oil temperature of 95° C. No significant wear occurred on the pump parts, as shown by only a 0.7-mil change on the pins of the universal link. A test with 60 fluid, in a similar pump test at 60° C., was at the point of failure after 35 hours.

Table VII. Typical Properties of Silicone D

Property	Value
Viscosity, cs.	
−65° F.	2800
77° F.	80
400° F.	7.4
Acid number	Trace
Freezing point, below	− 94° F.
Flash point, ° F.	530
Vapor pressure, mm. Hg	
300° F.	5
400° F.	12
500° F.	46
Shell 4-ball lubricity	
Wear scar diameter, mm., with 52-100 steel balls, 400° F., 1200 r.p.m., 2 hours	
4 kg.	0.39
10 kg.	0.52
40 kg.	0.95
Thermal stability, 24 hours, 550° F.	
% viscosity change 210° F.	− 30
Acid number change	+ 2.0

Table VIII. Hydraulic Pump Test Data for Two Fluids

Conditions	60	Silicone D
Vickers vane pump test		
Temperature, ° C.	105	135
Pressure, p.s.i.	600	600
Time, hours	8	12
Vane wear, mg. loss	11.9	0.7
Vickers piston aircraft hydraulic pump test		
Temperature, ° C.	60	95
Speed, r.p.m.	3650	3650
Pressure cycle	3 min. at 3000 p.s.i.g. 12 min. at 750 p.s.i.g.	
Time, hours	35	300
Av. wear on pins of universal link, mils	4.0	0.7

Although silicone lubricants are noted for their good oxidation stability, much work has been done to improve this property by the use of an antioxidant additive (*5*, *6*, *15*). Many different types of additives have been investigated, but most of them are limited because of their poor efficiency, solubility, and stability. Certain organoiron compounds have been found to be among the most efficient antioxidants investigated for silicone fluids. When normal blending techniques are used, the organoiron compounds have a tendency to form an objectionable sludge when the blended fluid is exposed to high temperatures. A special processing technique to incorporate the iron compounds into the fluid has been developed. This technique prevents sludge formation at high temperatures and increases the antioxidant efficiency of the additive. At 0.1% concentration in a medium phenyl content fluid, the processed antioxidant resulted in an 800% increase in gel time at 580° F. and produced no sludge. The unprocessed additive only doubled the gel life and caused sludging.

Although most types of silicones can be stabilized against oxidation by using the special processing technique, the silicone fluids with a medium phenyl content possess the best over-all properties and benefit most from improved oxidation stability. Silicone E is an example of a medium phenyl content fluid that has been stabilized with an organoiron compound. This silicone fluid combines good low temperature properties with good stability in the 550° to 730° F. temperature range. Figures 9 and 10 illustrate the gel life of Silicone E together with two other inhibited silicones at 550° and 730° F. The 550° F. gel time test was run in the same manner as explained earlier, whereas the 730° F. gel time test consisted of exposing 1 gram of fluid in a 6-cm. diameter aluminum foil dish in an air-circulating oven. Silicone E offers a compromise of the stabilities of the inhibited methyl and high phenylmethyl silicone fluids at both 550° and 730° F. At 550° F. the all-methyl silicone fluid showed the greatest additive susceptibility, while at 730° F. the high phenylmethyl fluid had the largest precentage improvement. Also, while no data are given,

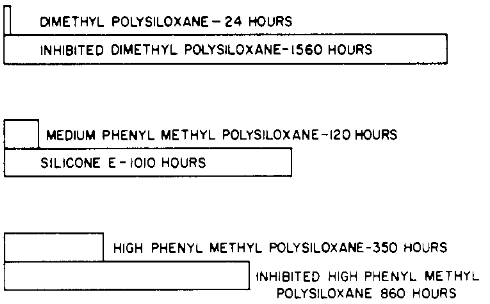

Figure 9. Gel life at 550° F. of inhibited and uninhibited polysiloxane fluids

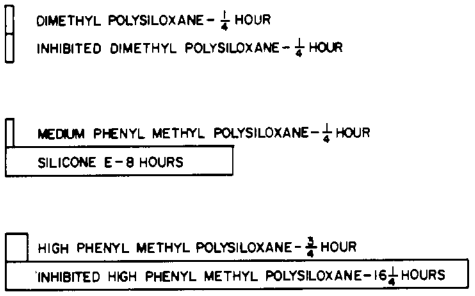

Figure 10. Gel life at 730°F. of inhibited and uninhibited polysiloxane fluids

the optimum additive concentration is also dependent on phenyl content and exposure temperature. Another noteworthy improvement of the inhibited fluids is that the rate of volatilization is reduced although the total amount of weight loss at the gel point is much greater (Figure 11). These results indicate that the maximum useful temperature limit of silicone fluids, in an oxygen-containing atmosphere, can be extended by the use of selected antioxidant additives.

SUGGESTED APPLICATIONS OF NEW LUBRICANTS

The modifications recently made in silicone polymer composition suggest that these oils may be useful in new or extension of old areas. The high phenyl-containing polymers may find use as extreme high temperature or radiation-resistant lubricants. Silicone B appears to be a good candidate for a high temperature and/or radiation-resistant grease base oil, since it has the desirable properties of low volatility and high degrees of thermal, oxidative, and radiation resistance.

The fluoroalkyl-containing polymers may possibly be used in lubricant applications requiring better antiwear properties and/or solvent resistance than dimethyl- or phenylmethylpolysiloxanes. The combination of properties of the greases compounded from these fluids makes them ideal valve lubricants for a variety of applications. These include lubrication of valves designed to handle strong oxidizers and fuels used in missiles and rockets, and valves for handling wet and corrosive gases, chemicals, and hydrocarbons.

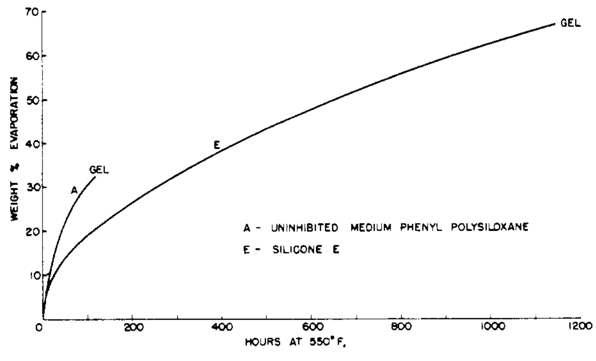

Figure 11. Volatility of silicone fluids during 550°F. gel time test

The additive-improved polysiloxanes should extend the application range of present silicone lubricants. The improved lubricity Silicone D may find use in applications requiring a high degree of boundary lubricity, such as hydraulic fluids. The oxidation-inhibited oils, such as Silicone E, should extend the useful life of present silicone lubricants at high temperatures in the presence of air.

SUMMARY

Silicone lubricants are semiorganic liquids that can be modified to have a wide range of physical and chemical properties. The most versatile and desirable method of modification is through organic group variation. Additive modification can enhance certain properties beyond the improvements obtainable through molecular changes.

The commercial silicone lubricants possess a wide range of viscosity, volatility, and stability properties. New polymer modifications have increased the oxidation, thermal, and radiation resistance by high phenyl substitution. Likewise, the boundary lubricity and solvent resistance have been increased by fluoroalkyl substitution.

The boundary lubricity and oxidation resistance of the currently available lubricants have been increased manyfold by a selected lubricity additive and an oxidation inhibitor. Both of these additives must be added to the base oil by special techniques to achieve maximum improvement in the respective property.

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