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INVESTIGATION OF SILICONE POLYMER FLUIDS PART VII, THERMAL AND OXIDATION STABILITIES OF THE POLYMETHYLSILOXANES

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ABSTRACT

Exploratory studies have been made on the oxidation and thermal stabilities of the polymethylsiloxanes at temperatures up to 250° C. Both static and dynamic oxidation methods were employed. The influence of metals on the oxidation stability was also investigated by both methods. The viscosity changes, evaporation losses and the amounts and nature of the volatile products evolved were used as criteria of oxidation stability. The thermal stability was evaluated by the viscosity changes after heating the silicone in a closed system.

Dynamic oxidation studies with air at 175° C (347° F) reveal that the polymethylsiloxanes are quite resistant to oxidation at this temperature. At 200° C (392° F) oxidation takes place as revealed by viscosity increases and the evolution of formaldehyde, paraformaldehyde and formic acid. The viscosity increases are attributed to the condensation of two or more siloxane fragments from which methyl groups have been ruptured or oxidized. The oxidation rate varies with the oxygen concentration of the oxidizing atmosphere. Most of the common metals had only a negligible influence on the oxidation reaction at 200° C. The exceptions were copper, lead and selenium which inhibited oxidation. The silicone fluid gelled within 24 hours when oxidized at 225° C (437° F). At this temperature tellurium as well as copper, lead and selenium inhibited the oxidation and increased the gellation time. However, their presence caused the cracking of the siloxane chain with the formation of low-molecular-weight products which were volatile at the test temperature.

The static type experiments though less accelerated were in substantial agreement with those by the dynamic method. Viscometric evidence of the thermal instability of the polymethylsiloxanes at 250° C (482° F) was obtained. Thus at this and higher temperatures in an oxidizing atmosphere both "cracking" and oxidation takes place.

PROBLEM STATUS

This is an interim report on this problem; work is continuing.

AUTHORIZATION

This investigation was initiated as a result of Bureau of Ships Project Order 414/46 dated 1 July 1945 for the study of petroleum and synthetic lubricating oils and greases and Project Order 897/46 dated 28 June 1946 on high-temperature lubricants for electric-motor ball bearings. Corresponding NRL Problem Numbers are: 32C02-01 and 32C02-09.

INVESTIGATION OF SILICONE POLYMER FLUIDS PART VII, THERMAL AND OXIDATION STABILITIES OF THE POLYMETHYLSILOXANES

INTRODUCTION

Statement of the Problem

The wartime demands of lubricants and hydraulic fluids revealed the need for fluids having extremely small coefficients of viscosity with temperature, a wide liquidus range, low evaporation losses, reduced inflammabilities and excellent thermal and oxidation stabilities. The liquid polyorganosiloxanes developed during the war are reputed to have many of the properties desired for such lubricant and hydraulic applications. As the polymethylsiloxanes (5, 14, 21, 23, 26)* have the lowest coefficients of viscosity with temperature (highest V.I.) of this class of compounds, and as their freezing points and vapor pressures are adequately low and as they were immediately available, they were considered of immediate interest to the Navy.

The more efficient operation of some types of naval equipment, e.g., gas turbines and silicone-clad electric motors and generators, may be obtained by going to higher operating temperatures. Conventional petroleum oils have proven unsatisfactory as lubricants for these and other high-temperature applications because of their thermal and oxidation instabilities. As the silicones have many of the properties desired in lubricants for such applications, it is necessary that information as to their thermal and oxidation stabilities be obtained in order to determine their temperature range of usefulness. In service applications the lubricant is in contact with metals. Some metals are known to exert a catalytic action on the oxidation rate and rate of thermal decomposition of hydrocarbon and fatty oils. The possibility of a similar action of metals on the stability of the polymethylsiloxanes must be included in investigations on their thermal and oxidation stabilities before their usefulness can be determined.

Known Facts Bearing on the Problem

The synthesis, structures, and many of the physical and chemical properties of the methyl-substituted polyorganosiloxanes have been described (2, 3, 5, 8, 9, 14, 19, 21, 22, 23, 26, 30). The commercial polymethylsiloxanes (3, 19, 21, 22, 26) are mixtures of essentially linear homologues, having a more or less wide range of molecular weights depending upon the viscosity. Extensive research on various types of hydrocarbons (e.g. paraffin, isoparaffin, cycloparaffin, aromatic, etc.) reveals that their oxidation and thermal stabilities vary considerably depending upon their molecular configuration and the presence of impurities. It seems reasonable to expect that the various silicone types may also exhibit a similar variation in stability.

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* References are located on pages 15 and 16 of this Report.

It is well known that the thermal and oxidation stabilities of organic compounds decrease with increasing temperature. The empirical generalization that the reaction rate doubles for each 10° C rise in temperature, though not strictly true, illustrates the effect of temperature on non-ionic chemical reactions and shows that there is an upper temperature limit beyond which an oil cannot be used satisfactorily. This temperature limit for an oil is governed in practice not only by the amount of thermal decomposition and oxidation products formed but also by their objectionability such as corrosive or sludge-forming products.

Though the silicones are not considered good lubricants, investigations in this laboratory (4, 16, 18) revealed that they may be used advantageously as lubricants for journal bearings with certain metal combinations if the bearings were properly "broken-in" or pretreated. Their application as hydraulic fluids in systems employing gear and piston type pumps have also been investigated here (7, 15, 17) and they were shown to be superior in many respects to the polymer thickened oils now in common use. Other applications to lubrication have been discussed by others (5, 11, 12, 21, 22, 26, 27). The silicones in the lubricant and hydraulic range, when stripped of low-molecular-weight products, were found to be much less flammable than conventional oils (25). The polymethylsiloxanes are reputed to be very resistant to heat and thermal oxidation; but no information is available concerning the safe temperature range of operation, the nature and objectionability of the decomposition products, and the possible catalytic effects of metals.

EXPERIMENTAL

Silicone Fluids Investigated

The polymethylsiloxanes discussed here with some of their viscometric properties are listed in Table I. Other properties of these fluids of interest in lubrication and hydraulics have been reported to the Navy Department (14). The Viscosity-Temperature Coefficient (VTC) (28, 29) is defined by the relation

$$\mathrm{VTC} = \frac{\eta 100^\circ\ \mathrm{F} - \eta 210^\circ\ \mathrm{F}}{\eta 100^\circ\ \mathrm{F}}$$

where $\eta 100^\circ$ F and $\eta 210^\circ$ F are the kinematic viscosities at the temperatures indicated.

The fluids were made available by the following organizations: the Corning Glass Company Fellowship at the Mellon Institute of Industrial Research; The Dow Corning Corporation; the Research Laboratories of the General Electric Company; and the Westinghouse Electric Corporation. The fluids designated as "W" were obtained from the Westinghouse Electric Corporation and those designated as "A" and "B" were obtained from the Mellon Institute and were prepared early in the war and are not typical of present commercial production. These fluids are believed to contain some unreacted OH groups and were observed to increase in viscosity with time when stored in the dark at room temperature. The "C", "D" and "E" fluids showed insignificant viscosity changes after one year under these conditions. Fluid E-3 was especially prepared for its low temperature characteristics and contains branched structures. The other silicones are essentially open-chain polymers of polymethylsiloxane with trimethyl terminal groups and probably differ only in the method of synthesis. The infrared adsorption spectra of many of the silicones were examined and no branched or cyclic structures could be detected.

TABLE I

Some Viscometric Properties of the Polymethylsiloxanes Investigated

Identification	Viscosity (cs. at 100° F)	ASTM Slope	KVI*	VTC† 100° F
Westinghouse Electric Corp.				
W-2	138.	0.238	144	0.584
W-3	232.	0.219	-	0.585
Mellon Institute 190 Series				
A-1	22.9	0.410	191	0.641
A-2	65.6	0.323	161	0.649
Mellon Institute 190-200 Series				
B-1	210.	0.249	139	0.651
B-2	247.	0.240	-	0.642
B-3	276.	0.242	-	0.641
B-4	359.	0.216	-	0.653
Dow Corning Corp. 500 Series				
C-1	19.7	0.341	197	0.581
C-2	45.4	0.288	169	0.591
C-3	44.9	0.288	169	0.591
C-4	73.8	0.219	156	0.594
Dow Corning Corp. 200 Series				
D-1	82.5	0.253	153	0.594
D-2	162.	0.221	140	0.595
D-3	271.	0.203	-	0.595
D-4	640.	0.183	-	0.601
General Electric Co.				
E-1	24.7	0.328	188	0.585
E-2	104.	0.244	148	0.594
E-3	312.	0.212	-	0.622
E-4	466.	0.188	-	0.597

* KVI - Kinematic Viscosity Index
† VTC - Viscosity-Temperature Coefficient

Experimental Methods

Several different procedures were used in the investigation of the thermal and oxidation stabilities of the silicones. The dynamic type aeration apparatus previously described (1) was used extensively. A 25-gram sample was used with a gas flow of 20 ml per min. Runs were made at 175°, 200° and 225° C (±1.5° C) and were of 168-hours duration. The effluent gases from the oxidation cell were bubbled through 10 ml of 0.1 N potassium hydroxide solution which was back titrated at intervals with 0.1 N hydrochloric acid to determine the amount of volatile acidic products (calculated as moles of formic acid per gram of sample). The neutral solutions from the determination of volatile acids were tested for aldehydes using the hydroxylamine hydrochloride method (10) with bromophenol blue as the indicator. It was difficult to obtain reproducible results with this method and, as formic acid also reacts with hydroxylamine hydrochloride, the bisulfite method (13) was adopted. The viscosities of the fluids before and after each test, and in some instances at intervals during the 168-hour run, were determined in Cannon-Fenske modified Ostwald viscometers according to A.S.T.M. Method D:445-42T.

The effect of metals on the thermal and oxidation stabilities of a typical commercial silicone (C-4) was studied by aerating it at the test temperatures in the presence of clean polished metal strips having dimensions of 1 1/4 x 1/4 x 1/32 inches. The metals investigated include, antimony, cadmium, copper, lead, nickel, platinum, selenium, silver, tellurium, tin and zinc; each was of at least 99.8 percent purity. The alloys were duralumin 24 ST, SAE 1020 cold rolled steel and SAE 30915 stainless steel. Experiments were made with silicone C-4 in the absence of and in the presence of metals using purified air (1), oxygen, nitrogen and helium gases. Oxygen and nitrogen gases with a minimum purity of 99.5 percent were used. Nitrogen comprised the bulk of the impurities in the oxygen; and oxygen was the principal impurity in the nitrogen. The helium gas was the Navy balloon grade and was of 98.2 percent purity. Nitrogen was the principal impurity

and the oxygen content was less than 0.1 percent. Traces of the lower hydrocarbons and carbon dioxide may also have been present. All gases were dried by passing through anhydrous calcium chloride.

Static-type oxidation experiments were also made on the same silicone fluid at 225° and 250° C. This consisted of heating 25 grams of fluid in a 100 ml beaker in a forced-draft oven from 24 to 168 hours. The oven temperature was controlled to ± 1 1/2° C. Metal specimens of the same size were used in this procedure as in the dynamic method. The change in viscosity and the evaporation loss were found to be valuable criteria of stability.

The stability of this silicone in a closed system was also investigated. A 25-gram sample in the absence of and in the presence of various metals was sealed in a 50-ml Pyrex glass vial under atmospheres of air, nitrogen and helium gases and maintained at 250° C for 24, 72 and 168 hour intervals. The dissolved air was replaced by bubbling the desired gas through the sample for .30 minutes before sealing the glass vial. The change in viscosity was used as a criterion of the thermal stability.

DISCUSSION OF RESULTS

Dynamic Oxidation Experiments

The silicones listed in Table I were oxidized with air at 200° C in an all-glass system, as described under Experimental Methods. The viscosity of the oxidized sample was determined at 24-hour intervals as were the moles of formaldehyde and formic acid produced. The presence of formaldehyde in the volatile oxidation products was shown by the reaction with chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid) (6). This was confirmed by the melting point of the dimedone (5,5-dimethylcyclohexane - 1,3-dione) derivative (24). In some runs the odor of formaldehyde was readily detectable. A white deposit was also observed after some tests in the condensers above the oxidation cells. Upon heating this deposit, formaldehyde was identified as a decomposition product. It also reduced Fehling's solution; therefore, it was concluded to be paraformaldehyde, a polyoxymethylene. Even where no deposit of paraformaldehyde was observed, it is possible that lower-molecular-weight polymers were formed. As formaldehyde is readily oxidized it is likely that formic acid was present. The presence of formic acid was confirmed by the increase in aldehyde content after reduction of the solution containing the volatile products.

The silicones designated as "A" "B" and "W" increased in viscosity very rapidly with time. All of them gelled within 72 hours of oxidation with the exception of A-1, which required 125 hours for gelation. Silicone B-3 required only 25 hours for gelation. These silicones are believed to contain some unracted OH groups, since they reacted with lead oxide (PbO) at room temperature to form a semi-solid mass. Patnode and Schmidt (20) have discussed this reaction and showed that trimethylsilanol reacts with lead oxide to form an insoluable product. No definite evidence of a reaction with lead oxide was observed with any of the other silicones listed in Table I. The viscosity changes observed for these silicones on oxidation is, in part, due to the condensation of the silanols to form larger molecules thus increasing the viscosity.

The viscosity changes with time, of the completely methyl substituted siloxanes, are shown in Figure 1A. None of the "C" or "E" series silicones oxidized to a gel within the 168-hour period. Fluid E-3 showed the greatest viscosity increase of any of this series.

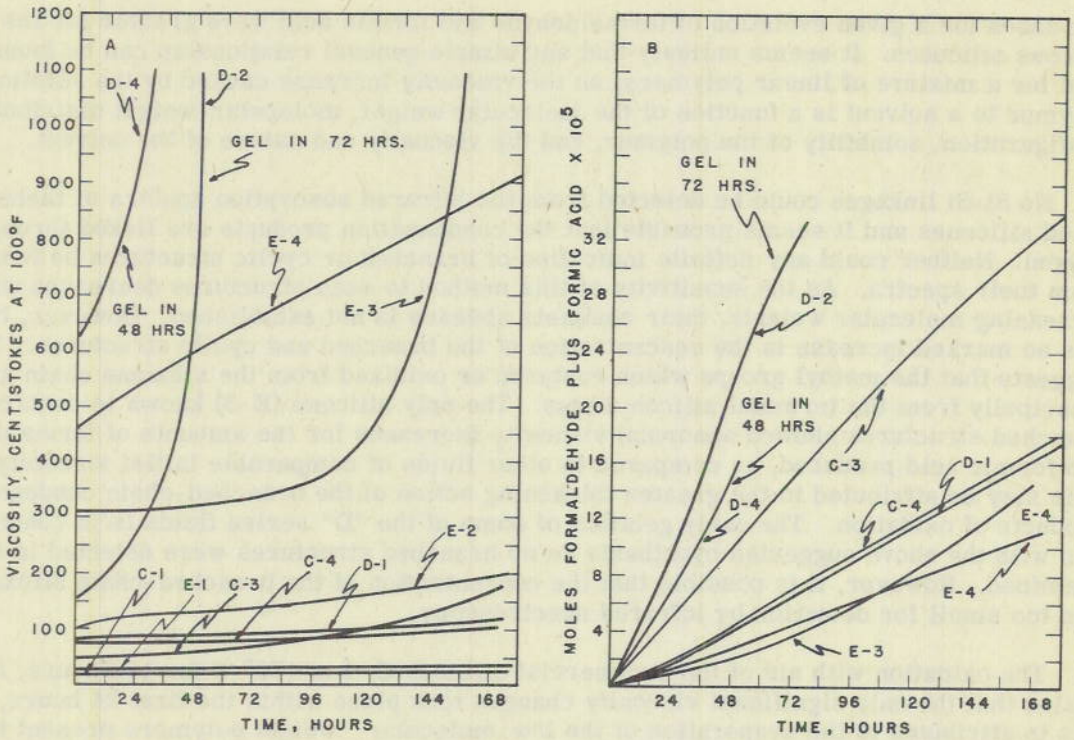

Figure 1

Comparison of Dynamic Oxidation Stabilities of Silicones at 200° C

Only the least viscous of the "D" series fluids remained liquid during the oxidation test. The gelation time of the other silicones in this series varied inversely with the initial viscosity. The number of moles of formaldehyde and formic acid produced is plotted against time in Figure 1B. This quantity is only approximately equivalent to the number of moles of methyl groups cracked off or oxidized from the siloxane chain, since paraformaldehyde is known to be formed in some runs and it is also likely that some formaldehyde is oxidized to carbon dioxide.

It is evident from the graphs of Figure 1 that the lower the viscosity of the silicone, the smaller the changes in viscosity with times of oxidation. The viscosity changes in the methyl substituted siloxanes may be accounted for by the condensation of two or more of the siloxane residues from which the methyl groups were ruptured. The apparent stability of the less viscous silicones as revealed by viscosity changes is misleading, for as much formaldehyde plus formic acid was evolved by them as by the more viscous silicones. No correlation between viscosity increases and the amount of methyl oxidation products formed by the various silicones was obtained, except the generalization that the viscosity

increases for a given evolution of formaldehyde and formic acid were greater for the more viscous silicones. It seems unlikely that any simple general relationship can be found to hold for a mixture of linear polymers, as the viscosity increase caused by the addition of a polymer to a solvent is a function of the molecular weight, molecular-weight distribution, configuration, solubility of the polymer, and the viscosity and nature of the solvent.

No Si-Si linkages could be detected from the infrared absorption spectra of these oxidized silicones and it seems probable that the condensation products are linked through oxygen. Neither could any definite indication of branched or cyclic structures be found from their spectra. As the sensitivity of this method to such structures decreases with increasing molecular weights, their complete absence is not extablished. However, there was no marked increase in the concentration of the branched and cyclic structures. This suggests that the methyl groups which ruptured or oxidized from the siloxane chain are principally from the terminal silicon atoms. The only silicone (E-3) known to contain branched structures showed abnormal viscosity increases for the amounts of formaldehyde and formic acid produced, as compared to other fluids of comparable initial viscosity. This may be attributed to the greater thickening action of the branched-chain condensation products of oxidation. The early gelation of some of the "D" series fluids is in contradiction with the above suggested hypothesis as no branched structures were detected in those examined. However, it is possible that the concentration of the branched-chain siloxanes was too small for detection by infrared spectroscopy.

The oxidation with air of the commercial silicone C-4 at 175° C for 168 hours, revealed that the only significant viscosity changes took place within the first 24 hours, and this is attributed to the evaporation of the low molecular weight polymers present in the original fluid. There was no appreciable evolution of acids or formaldehyde.

The results of the dynamic tests at 200° C for 168 hours on silicone C-4 using air, oxygen, nitrogen and helium gases are given in Table II. The effect of temperature variations due to the control of the thermostat are reflected in the results shown, as the check runs were not made simultaneously. Repeat runs showed that the viscosities of the silicone fluid, after the 168-hour test with a given gas, agree reasonably well and compare favorably with the reproducibility obtained by similar oxidation methods on hydrocarbons. As would be expected, oxygen accelerated the viscosity changes more than air. The increase amounted to approximately 50 percent. With nitrogen and helium gases the viscosity changes were, respectively, approximately one-third and one-tenth that obtained with air. A small amount of a white deposit was again observed in the condenser after several of the oxygen runs and it was identified as paraformaldehyde. For the reasons previously discussed, the moles of formaldehyde and formic acid produced is only approximately equal to the number of moles of methyl groups cracked or oxidized from the siloxane chain. Small amounts of formaldehyde were produced when nitrogen and helium gases were used. The acidity observed was presumably due to formic acid. With the gas flow used, a 0.1 percent oxygen concentration in the helium is more than sufficient to account for the formaldehyde and formic acid found. The viscosity increases observed with the different gases are roughly proportional to the number of moles of these products produced.

The detailed results of the effect of metals on the thermal and oxidation stabilities of silicone C-4 are also given in Table II. Table III was prepared from Table II in order to compare the effects of the various metals as reflected by the difference in viscosity changes, volatile oxidation products evolved, and evaporation losses. Duralumin, cadmium, silver, cold rolled steel, tin and zinc had no appreciable action on the stability of the silicone. The presence of tellurium caused increases in viscosities with corresponding increases in the evolution of volatile oxidation products when oxidized with air or oxygen.

TABLE II

Results of Dynamic Oxidation Tests on Polymethylsiloxane C-4 at 200° C for 168 hours. Initial Viscosity - 72.4 Centistokes at 100° F

Metals Present	Viscosity (Centistokes at 100° F)				Moles x 10^4 of Formaldehyde Plus Formic Acid Per Gram				Weight Loss (%)			
	Air	Oxygen	Nitrogen	Helium	Air	Oxygen	Nitrogen	Helium	Air	Oxygen	Nitrogen	Helium
None - Control Runs	100. 105. 102. 122. 94.1 118.	108. 137. 116. 119. 130. 112.	81.4 92.7 86.2 81.2 79.2 80.5	78.6 76.0 74.1	15 17 18 20 16	25 21 26 26 30 28	-- -- 9 8 8 12	2 1 trace	3 2 2 2 2 1 2	2 - 2 2 2 3 1	1 1 2 2 2 1	1 1 1
Average of Control Runs	107.	120.	83.6	76.2	17	26	9	1	2	2	1.5	1
Duralumin*	114.	119. 140.	85.2	78.8	25	23	9	2	2	2	--	1
Cadmium	101.	113.	80.6	78.9	16	22	7	3	2	2	--	1
Copper	82.6 79.6	79.6 81.1	88.3	78.0	6 2	4 3	2	3	- 1	1 3	2	1
Lead	146. 115. 90.2 112.	149. 119. 108.	91.5 104.	153.	2 2 2 6	2 2 2	trace 1	1	4 - 3 6	6 9 4	4 6	2
Selenium	78.1 77.5	76.4 76.9	78.2 78.1	78.4 74.4	2 2	2 trace	1 1	2 trace	2 2	2 1	2 1	1 2
Silver	114. 86.	125. 128.	76.1	79.2	21 16	21 28	10	-	3 -	2 1	2	1
Steel†	112.	127.	105.	78.6	15	28	-	1	3	2	2	2
Tellurium	114. 133.	145. 146.	78.2	77.6 79.0	16 34	32 26	-	trace 1	1 2	1 1	-	1 1
Tin	112.	127.	80.4	76.8	14	21	11	2	2	2	1	1
Zinc	107.	116. 148.	77.5	76.8	19	22 20	9	1	2	2 2	2	1

* Duralumin 24 ST
† SAE 1020 cold rolled

TABLE III

Analysis of Effect of Metals on the Thermal and Oxidation Stability of Polymethylsiloxane C-4 at 200° C for 168 hours.

Metal	Viscosity Increase				Moles of Formaldehyde plus Formic Acid				Weight Loss			
	Air	Oxygen	Nitrogen	Helium	Air	Oxygen	Nitrogen	Helium	Air	Oxygen	Nitrogen	Helium
Duralumin*	N	N	N	N	N	N	N	N	N	N	N	N
Cadmium	N	N	N	N	+?	N	N	N	N	N	N	N
Copper	-	-	N	N	-	-	-	N	N	N	N	N
Lead	+	+?	+	+	--	--	-	N	+	+	+	N
Selenium	-	--	N	N	--	--	-	N	N	N	N	N
Silver	N	N	N	N	N	N	N	N	N	N	N	N
Steel†	N	N	N	N	N	N	N	N	N	N	N	N
Tellurium	+	+	N	N	+	+		N	N	N	N	N
Tin	N	N	N	N	N	N	N	N	N	N	N	N
Zinc	N	N	N	N	N	N	N	N	N	N	N	N

N Normal as compared to control
+ Increase as compared to control
- Decrease as compared to control
* Duralumin 24ST
† SAE 1020 cold rolled

The runs with nitrogen and helium were normal as compared to the control. Copper and selenium acted as inhibitors, reducing the evolution of volatile products and viscosity changes to that obtained in the control runs with helium. In the runs with nitrogen the volatile oxidation products evolved were also low when copper and selenium were present. During the course of these runs some of the selenium was sublimed and deposited as an amorphous red powder in the cool condenser tube. The fluid had a pink tinge, probably due to the selenium being colloidally dispersed. The color of the fluid was more pronounced when hot but this may be partially explained by the settling of the larger particles after the bubbling had ceased.

The presence of lead in the silicone fluid caused larger viscosity increases than in the control runs. The total amount of formaldehyde and formic acid was low when air, oxygen and nitrogen were used, but the evaporation losses were high in all these cases. The silicone fluid was turbid after all the runs except where helium was used. The turbidity was observed to increase with time of oxidation.

Dynamic type tests were also made on silicone C-4 at 225° C. In the absence of metal the fluid gelled within 24 hours when air or oxygen was used. The amount of formaldehyde plus formic acid formed in 24 hours was twice as great as the amount formed in 168 hours at 200° C. In all these runs there was a heavy deposit of paraformaldehyde in the condenser tube after both air and oxygen runs. The evaporation losses at gelation were approximately 2 percent. In the 168-hour runs with nitrogen and helium gases at 225° C, the viscosity changes and the evaporation losses were approximately twice as great as after the tests at 200° C. Runs with air in the presence of various metals were also made, and (as in the control) the silicone fluid turned to a gel within 24 hours except when copper, lead, selenium or tellurium were present. The fluids gelled between 72 and 96 and between 96 and 120 hours, respectively, in the presence of copper and lead. The fluid remaining after 168 hours in runs when selenium and tellurium were present was less viscous than the original fluid, having a viscosity of 60 centistokes at 100° F. The weight loss amounted to approximately 70 percent, and only small amounts of formaldehyde and formic acid were produced. A considerable volume of a volatile water-insoluble liquid was collected in the aqueous solution through which the effluent gases were bubbled. A crystalline deposit also collected in the condenser tube after each run with air in the presence of lead, selenium and tellurium. The liquid was identified spectroscopically as being predominantly octamethylcyclotetrasiloxane and the crystalline deposit as hexamethylcyclotrisiloxane.

From these experiments it is apparent that the polymethylsiloxane fluid is much less stable to oxidation at 225° C than at 200° C. No accelerative action of metals on the viscosity changes could be detected at 225° C because of the rapid gelation encountered in the control runs. The presence of copper, lead, selenium and tellurium at 225° C inhibited the rate of change of viscosity and the evolution of formaldehyde and formic acid. At 200° C, lead though reducing the evolution of formaldehyde and formic acid did not materially affect the changes in viscosity. Tellurium at the lower temperature accelerated the oxidation rate as reflected by these criteria. All of these metals accelerated the the evaporation of the silicone, as compared to the control runs with helium. This suggests that they react in some manner to break the siloxane chain with the formation of lower molecular weight and more volatile products.

In the runs with lead, the silicone became turbid within the first 24 hours of oxidation, and the turbidity increased with time. At the end of the run a white deposit had settled in the bottom of the oxidation cell. Patnode and Schmidt (20) have shown that a reaction takes place between trimethylsilanol and lead oxide, which they consider to be

as follows:

$$2\,(CH_3)_3\,SiOH + PbO \rightarrow [(CH_3)_3\,SiO]_2\,Pb + H_2O$$

It is possible that under the influence of heat, lead oxide reacts with a siloxane breaking the chain to form a compound with lead similar to the above. The reaction may be represented as below:

$$(CH_3)_3\,Si\,[O\text{-}Si(CH_3)_2]_n\,O\text{-}Si(CH_3)_3 + PbO \rightarrow \begin{matrix}(CH_3)_3\,Si\,[O\text{-}Si(CH_3)_2]_x\,O \\ (CH_3)_3\,Si\,[O\text{-}Si(CH_3)_2]_y\,O\end{matrix}\!\!\diagdown\!\!\diagup\,Pb$$

The turbidity may be due to the presence of such a compound. If this product is thermally unstable, the lower-molecular-weight silicones formed would evaporate, thus accounting for the observed losses in weight. The increase in evaporation losses with increasing temperature could be accounted for by the greater speed of the reaction or the thermal instability of the intermediate. Though no insoluble products were observed with the other metals causing large evaporation rates, it is possible that they or their oxides may react as postulated above.

Dynamic-type oxidation experiments at 250° C were started, but no further work was done following several explosions which were attributed to the spontaneous ignition of some of the silicone decomposition products.

Static Oxidation Experiments

Static tests were used at the higher temperatures as they were simpler and less accelerative than the dynamic tests. The same silicone fluid, C-4, was used for these tests. The fluid was maintained at 225° C in the absence of and in the presence of various metals. The metals used were antimony, copper, lead, nickel, platinum, selenium, silver, tellurium, tin and zinc; each of at least 99.8 percent purity. Alloys used were duralumin 24 ST, SAE 1020 cold-rolled steel and SAE 30915 stainless steel. The viscosity at 100° F and the evaporation loss were determined after exposures of 24, 48, 72, 96, 120 and 168 hours. The fluid gelled in all cases between the 120 and 168-hour interval except in the runs made in the presence of antimony, lead and selenium. Antimony caused the gelation of the fluid between the 96 and 120-hour interval. But when lead or selenium was present the fluid did not gel after 168 hours of exposure.

The variations in viscosity of the fluid with time are shown graphically in Figure 2A. The presence of most of the metals caused no abnormal viscosity changes as compared to the control runs. This is shown by the narrow cross-hatched band in which these curves all lie. The samples containing lead and particularly those containing selenium caused much smaller viscosity changes than those found in the control runs. Tellurium and antimony caused somewhat larger viscosity increases than the control. From the shape of the viscosity-time curve it is seen that the effect was greatly accelerated somewhere between 72 and 96 hours, the curve rising more rapidly than an exponential.

The evaporation-time graphs are shown in Figure 2B. No great variations in evaporation rates were observed between the control runs and those in the presence of metals as shown by the narrow cross-hatched band in Figure 2B. Only lead greatly accelerated the evaporation rate. Antimony and tellurium caused much smaller increases in the

evaporation rate. As with the viscosity changes, the evaporation rate increased rapidly between 72 and 96 hours. The gradual decrease in the evaporation rate after 120 hours is attributed to gelation.

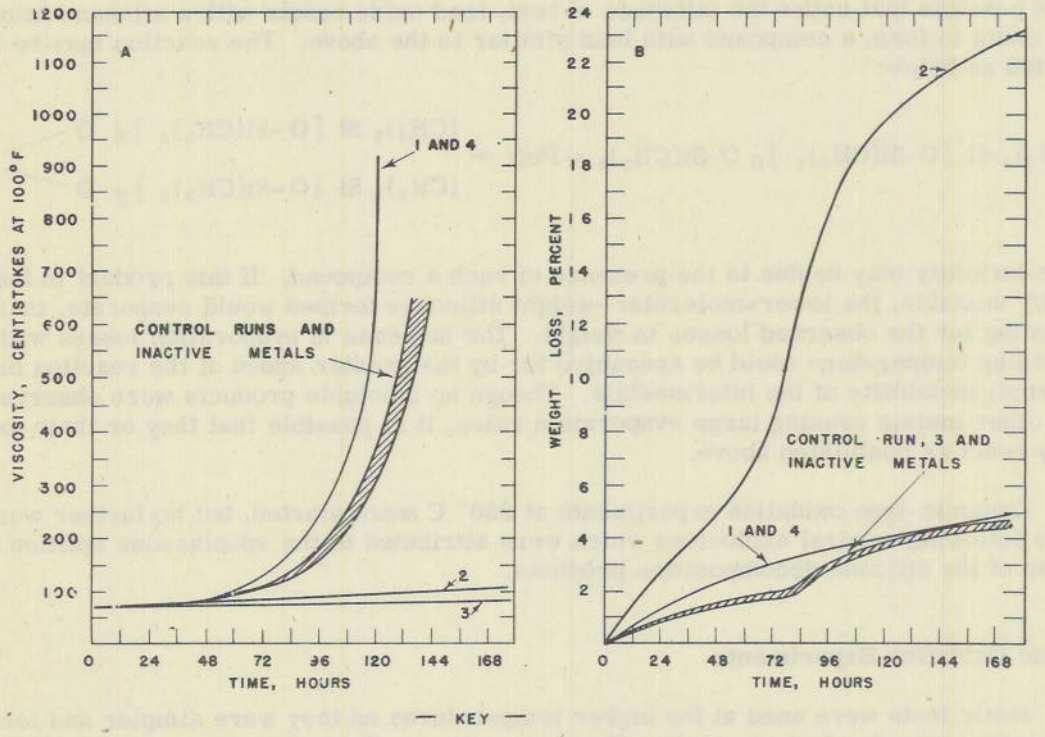

Figure 2

Influence of Metals on the Static Oxidation Stability of Polymethylsiloxane, C-4, at 225° C

Metal specimens of lead, zinc and tin having 10 times the surface area of the standard specimens and 20 grams of the granular metals having even larger surface areas were run in the silicone. Increasing the surface area of tin and zinc had no appreciable effect on the viscosity changes and the evaporation rates were increased only slightly. Increasing the surface area of the lead specimen by a factor of 10 increased the evaporation rate by a factor of 2. The granular lead of much larger surface area caused only a slight additional increase in the evaporation rate. These results indicate that the reaction is not surface catalytic. The reaction previously postulated to explain the action of lead on the silicone, necessitates its oxidation to the oxide (PbO). As the only source of oxygen is that in solution, the rate of the oxidation of lead would be expected to be slow

and this would govern the evaporation rate and not the area of the lead surface exposed. Varying the surface area of the lead specimens caused only negligible changes in viscosity. This was expected, as it was shown in dynamic type experiments that the presence of lead materially inhibited oxidation as shown by the decreases in the amounts of formaldehyde and formic acid evolved. Therefore the predominant reaction at 225° C in the static test is the cracking of the siloxane chain caused by lead oxide. Due to the evaporation of the low-viscosity siloxanes produced, only small changes in viscosity are to be expected.

The dynamic test was more accelerative than the static test as there is a more intimate contact between the fluid and air or oxygen. Whereas an exposure of over 120 hours was required to gel the silicone fluid at 225° C by the static method, less than 24 hours were required in the dynamic test. In the dynamic method at 225° C the presence of copper, lead, and especially selenium and tellurium greatly accelerated the evaporation effect and retarded the viscosity rise. In the static test only lead caused abnormally high weight losses. Tellurium accelerated the viscosity increases in the static test while it caused a decrease in viscosity by the dynamic method at 225° C. If the oxide of these metals accelerates the rupture of the siloxane chain, then it is apparent that the air in solution is the only source of oxygen for this reaction. In the dynamic test, fresh air continually sweeps over the metal surface, agitates the liquid and hastens the evaporation of the volatile reaction products. As in the dynamic test, the fluid containing lead was cloudy even after 24 hours of exposure to the static test and the turbidity increased with time. Similarly, selenium caused a slight pink color to develop in the fluid which faded as the fluid cooled.

The results of the static oxidation of silicone C-4 at 250° C are given in Table IV. At this temperature the silicone gelled somewhere between 24 and 48 hours of exposure. As the silicone fluid gelled so rapidly at this temperature it was difficult to ascertain the effect of metals. Copper was the only metal that inhibited the gelation. After 24 hours of exposure only selenium, lead, tellurium, nickel, and zinc inhibited the viscosity increase, the effect being very marked for the first two. No such effect was observed with nickel and zinc at the lower temperatures. As the oxidation stability of the silicone is very sensitive to temperature in this range, it is possible that the apparent inhibitive action observed is due to variations in the temperature control. The evaporation rate in the presence of lead was four times as great as in the control after 24 hours and was three times as great after 48 hours. The decrease in the evaporation rate after 24 hours is probably due to the gelation of the sample. The presence of selenium also caused an increase in the evaporation rate but is was only 50 percent greater than the control. After each of the runs of 48-hours duration a small amount of white powder was observed on the walls of the beakers and on the top of the gel. This was believed to be silica or a highly crossed linked siloxane network.†

The results of the static oxidation experiments, though less accelerated, are in substantial agreement with those of the dynamic experiments. They both show that the oxidation stability of the polymethylsiloxane fluid decreases rapidly as the temperature is raised above 200° C.

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† The formation of such a product due to the thermal or oxidative decomposition of the resin used in the "silicone clad" electric motors may account for the high brush and commutator wear observed.

TABLE IV

Results of Static Oxidation Tests on Polymethylsiloxane C-4 at 250° C.
Initial Viscosity - 72.4 Centistokes at 100° F.

Metals Present	Viscosity (cs. at 100° F)		Weight Loss (%)	
	After 24 hrs.	After 48 hrs.	After 24 hrs.	After 48 hrs.
No Metals	104.	gel	2.5	5.6
" "	101.	gel	2.5	5.4
Average	102.	gel	2.5	5.5
Duralumin*	104.	gel	2.7	5.5
Antimony	103.	gel	2.7	5.2
Copper	107.	1226.§	2.4	4.9
Lead	83.8	gel	10.3	16.9
Nickel	90.0	gel	2.6	5.7
Platinum	102.	gel	2.5	5.5
Selenium	75.8	gel	3.6	6.3
Silver	101.	gel	2.4	5.4
Steel†	110.	gel	2.6	5.3
Steel‡	105.	gel	2.4	5.1
Tellurium	88.4	gel	2.4	4.7
Tin	116.	gel	2.8	5.3
Zinc	91.0	gel	2.4	5.0

* Duralumin 24ST
† SAE 1020 cold rolled
‡ SAE 30915 stainless
§ Gelled within 72 hours

Thermal Stability Experiments

It has been shown (8, 19) that the polymethylsiloxanes undergo thermal rearrangements at temperatures of 350 to 400° C with the rupture of the siloxane chain to form products which are predominately low molecular weight cyclic siloxanes. The dynamic experiments at 225° C revealed that the presence of some metals, notably lead, selenium and tellurium, in an oxidizing atmosphere, greatly accelerated the rupture of the siloxane chain with the formation of cyclic products. As the low molecular weight cyclic products are volatile at temperatures of 200° C and above, viscometric evidence of the thermal instability of the silicone would likely be masked by the viscosity increases due to oxidation and the evaporation of the low molecular weight siloxanes originally present in the fluid.

To obtain some indication of the thermal stability of the polymethylsiloxanes, silicone C-4 was sealed in a pyrex vial with the various gases as described under the section "Experimental," and maintained at 250° C. The viscosities of the fluids were determined after 24, 72 and 168 hours of exposure and are given in Table V. These data reveal that cracking does occur and that equilibrium has not been reached at 168 hours. The viscosity decreases were greatest for the samples under an atmosphere of air. Atmospheres of helium and nitrogen resulted in smaller rates of viscosity changes. Probably the control runs under the inert gases would approach the same limiting value at

TABLE V

Effect of Metals on the Thermal Stability of Polymethylsiloxane C-4 in a Sealed Glass System at 250° C.
Initial Viscosity - 72.4 Centistokes at 100° F.

Metal Present	Viscosity, centistokes at 100° F		
	After 24 hrs.	After 72 hrs.	After 168 hrs.
Atmosphere of Air			
None - Control	67.3	64.8	62.4
Copper	67.4	64.8	63.8
Lead	66.5	64.2	59.5
Nickel	-	64.9	-
Selenium	55.9	57.3	57.9
Steel*	67.6	64.3	62.4
Tellurium	65.9	64.9	52.1
Atmosphere of Helium			
None - Control	71.4	70.6	67.4
Copper	71.0	70.4	65.4
Lead	71.9	70.1	67.3
Nickel	70.8	68.2	-
Selenium	71.7	69.9	69.7
Steel*	71.7	70.5	66.0
Tellurium	71.9	67.4	63.6
Atmosphere of Nitrogen			
None - Control	72.3	70.9	69.2
Copper	72.2	70.2	69.2
Lead	64.1	62.7	62.9
Nickel	72.4	70.9	-
Selenium	56.9	65.5	56.8
Steel*	72.4	71.4	69.1
Tellurium	71.9	69.1	48.8

* SAE 1020 cold rolled

equilibrium. Under an atmosphere of helium none of the investigated metals significantly affected the rate of the viscosity changes as compared to the control run. Copper, nickel and cold-rolled steel were also inactive under atmospheres of air and nitrogen. The metals (lead, selenium and tellurium) which accelerated the evaporation of the silicones and inhibited the viscosity increases in the dynamic experiments were also found to affect the thermal stability of the silicones as reflected by the decreases in viscosity. Lead caused only a slight acceleration in the viscosity decreases as compared to the control run under these atmospheres. In the presence of selenium, the viscosity of the silicone decreased greatly during the first 24 hours of exposure, and thereafter there was little change in the viscosity. With tellurium the great viscosity change generally occurred between 72 and 168 hours of exposure. However, variable results were obtained with tellurium under an atmosphere of nitrogen. In some experiments the equilibrium viscosity was obtained after 24 hours.

CONCLUSIONS AND RECOMMENDATIONS

The polymethylsiloxanes are remarkably stable to oxidation by the dynamic method as compared to conventional lubricants. No significant changes in the silicone fluid attributable to oxidation were observed at temperatures of 175° C (347° F). At 200° C (392° F) oxidation takes place as revealed by viscosity changes and the evolution of formaldehyde, paraformaldehyde and formic acid. The viscosity increases are attributed to the condensation of two or more siloxane fragments from which the methyl groups have been ruptured or oxidized off. The apparent stability of the less viscous silicones, as revealed by viscosity changes, is misleading as the amounts of volatile oxidation products evolved by them is of the same magnitude as that of the more viscous silicones which showed much greater viscosity increases. The rate of oxidation of the silicones at 200° C varies with the oxygen concentration of the oxidizing atmosphere. With an inert atmosphere (helium) the changes in viscosity observed were caused by the evaporation of the low-molecular-weight siloxanes originally present in the fluid.

Most of the common metals investigated had no significant influence on the oxidation reaction at 200° C. The exceptions were tellurium, whose presence caused an acceleration in the rate of oxidation; and copper, lead and selenium which retarded the oxidation reaction. Selenium was the most effective in inhibiting oxidation. At 225° C (437° F) the silicone fluid oxidized to a gel within 24 hours with air or oxygen. At this temperature tellurium acted as an inhibitor as did copper, lead and selenium. The evaporation losses with these metals were abnormally high and is due to the cracking of the siloxane chain with the formation of low-molecular-weight cyclic products. Hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane were identified among the products evolved. Though these metals inhibited the oxidation of the silicone fluid at 225° C they accelerate cracking and, therefore, cannot be used successfully to stabilize the polymethylsiloxanes for applications at such temperatures. A reaction of lead oxide with the silicone is postulated to explain the high evaporation losses observed with lead.

The results of the static-type oxidation experiments, though less accelerated, are in substantial agreement with those obtained by the dynamic experiments. Viscometric evidence of the thermal instability of the polymethylsiloxanes at 250° C (482° F) was obtained. Thus, at this and higher temperatures in an oxidizing atmosphere both cracking and oxidation will occur.

It is recommended that the polymethylsiloxanes be given consideration as lubricants and hydraulic fluids for unusual applications where their superior properties can be used advantageously and where the operating temperatures do not exceed 200° C (392° F). The possibility of obtaining a silicone-soluble compound of copper, lead, selenium or tellurium which will inhibit oxidation and not accelerate cracking is being investigated. The oxidation and thermal stabilities of other organo-substituted siloxanes are also under investigation.

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