unreacted isocyanate, log $(a - x)$, is linear. The slope of the resultant straight line is equal to $-2.303/k$.

The plot of the reaction rate of phenyl isocyanate with 2-ethylhexanol is shown in Figure 3.

The first-order reaction rate constants of the isocyanates described herein were determined in this manner (Table I).

When the substituent group was a meta- or para-isocyanato group—e.g., *m*- or *p*-phenylene diisocyanates—the specific reaction rate, *k*, was determined from the data shown in Figure 2.

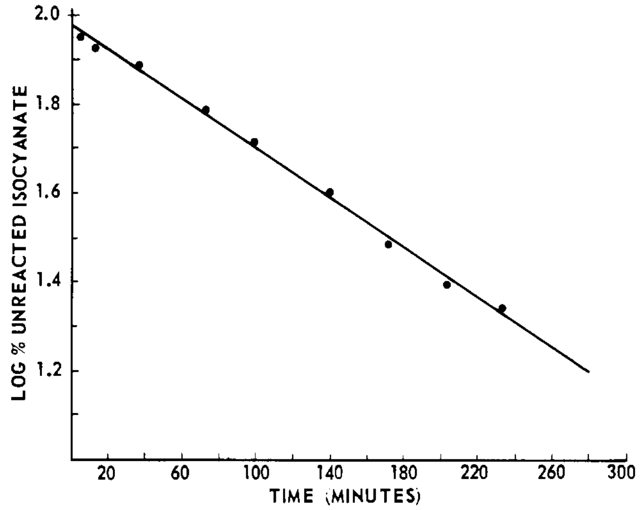

Figure 3. First-order plot of phenyl isocyanate and 2-ethylhexanol at 28° C.

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Flow Characteristics of Linear, End-Blocked Dimethylpolysiloxane Fluids

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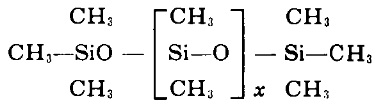
HIGH VISCOSITY silicone fluids offer important advantages over organic fluids for many mechanical applications. The shear stability, inertness, and flow characteristics of dimethyl silicone fluids make them ideally suited for use in fluid couplings, torsional vibrational dampers, dash pot dampers, shock absorbers, and power boosters. Proper design of these devices requires knowledge of the flow characteristics of the silicone fluids under the varying conditions of shear and temperature. The flow properties of silicone fluids from room temperature to 200° C. and at shear rates to 750,000 reciprocal seconds are presented in this article. Currie and Smith (*4*) studied the apparent viscosity-shear relationship of dimethyl silicone fluids at shear rates to 10,000 reciprocal seconds.

The structural formula and general physical properties of dimethylpolysiloxanes have been discussed (*7, 11*). To review, an end-blocked dimethylpolysiloxane has the following formula:



$$\mathrm{CH_3{-}\overset{CH_3}{\underset{CH_3}{Si}}O-\left[\begin{array}{c}\mathrm{CH_3}\\ \mathrm{Si{-}O}\\ \mathrm{CH_3}\end{array}\right]_x-\overset{CH_3}{\underset{CH_3}{Si}}{-}CH_3}$$

where the average value of x can vary from 0 to over 2000. The viscosity of the dimethylpolysiloxanes used in this investigation ranged from 1000 to 100,000 centistokes (x varying from 250 to 2000) as determined using Ostwald and Ubbelohde viscometers. The viscosities were measured at shear rates of less than 1 reciprocal second, which is in the range of Newtonian behavior for these fluids. The viscosities so measured are referred to as the Newtonian viscosity. Typical properties are given in Table I.

EXPERIMENTAL

The experimental work was conducted using a capillary rheometer developed by the Research Department, Union Carbide Chemicals Co., for accurate examination of the melt flow behavior of high polymers. This equipment provides for measuring pressure and temperature immediately ahead of the orifice with accuracies within ± 0.5%, preselecting any piston speed, and maintaining the speed constant within ± 0.25% irrespective of load.

The fluids were first extruded through the small-diameter capillaries, then reloaded into the chamber and extruded through the larger capillaries. New samples were used at each temperature. This procedure of using the small capillary first, with the resulting higher shear rates, was used to detect possible polymer degradation which would cause a decrease in viscosity. As a further check on possible degradation of the polymer, the Newtonian viscosities of the 60,000- and 100,000-cs. fluids were measured after the fluids were sheared at 400° F. using the smaller capillaries. A comparison of the original Newtonian viscosity and the Newtonian viscosity after the fluids had been sheared at 400° F. showed no significant change in viscosity.

CALCULATIONS

The average flow rate was calculated based on the speed and cross-sectional area of the piston. The speed of the piston had been previously calibrated.

The apparent viscosity was calculated using the Poiseuille equation, where

$$\eta = \frac{P^* R/2L}{4Q/\pi R^3} \text{ and } S_R = 4Q/\pi R^3$$

η = viscosity, poise
P^* = corrected pressure, dynes/sq. cm.
R = radius of capillary, cm.
L = length of capillary, cm.
Q = flow rate, cc./second
S_R = shear rate, second^{-1}

The pressure term in the Poiseuille equation was corrected for the entrance and exit effects of the capillary, using the procedure suggested by Cosner (*3*). The pressure resulting from entrance and exit effects was determined by measuring the pressure at a given shear rate using capillaries of the same diameter but varying lengths. The pressure was plotted against the length-diameter (L/D) ratio at constant shear rates and extrapolated to the zero L/D ratio. This pressure was considered the result of entrance and exit effects and was subtracted from the pressure obtained with the long capillary (large L/D ratio, point B). Greatest accuracy is obtained when the small L/D ratio, A, is as near zero as practical. Figure 1 illustrates the procedure.

No pressure correction was possible at low shear rates with fluids of low Newtonian viscosity, because the pressure under these conditions was less than the sensitivity of the instrument. However, omission of the pressure correction step in the calculations, under these conditions of low Newtonian viscosity and low shear rates, does not introduce a major error, as the pressure drop due to the entrance effects is small.

The apparent viscosity at different temperatures, as a function of the shear rate, is presented graphically in Figures 2 to 4. Average temperatures are used in designation of the curves. A small portion of the data, given in Table II by way of example, shows the relationships between the measured temperature, pressure, capillary size, and nominal shear rate, and the calculated shear stress and apparent viscosities of the 60,000-cs. silicone fluids.

DISCUSSION

Determination of the viscosity of a non-Newtonian fluid at the shear rates obtained in this study presents many problems, both theoretical and practical. The pressure

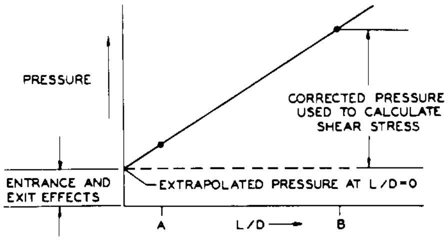
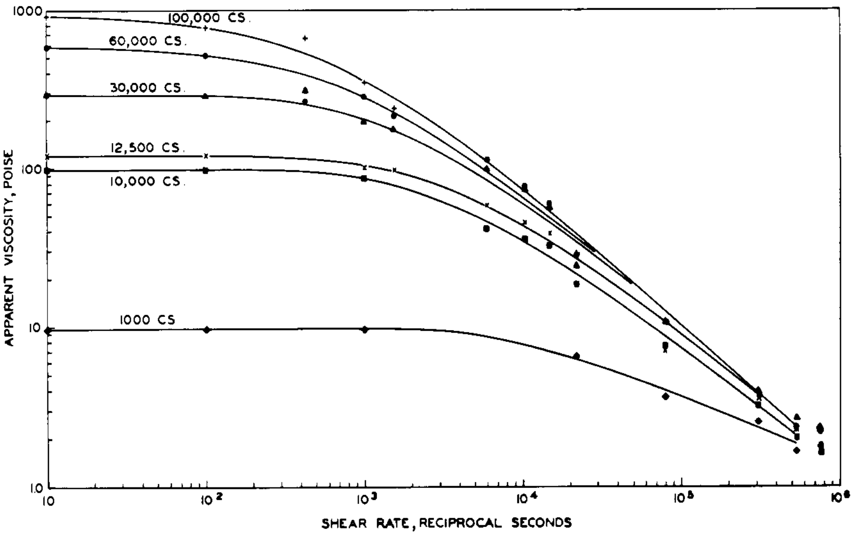


Figure 1. Procedure for graphically extrapolating to determine pressure drop in a capillary of zero length

Figure 2. Shear viscosity relationship of linear, end-blocked dimethylpolysiloxane fluids at 21° C. ⟶



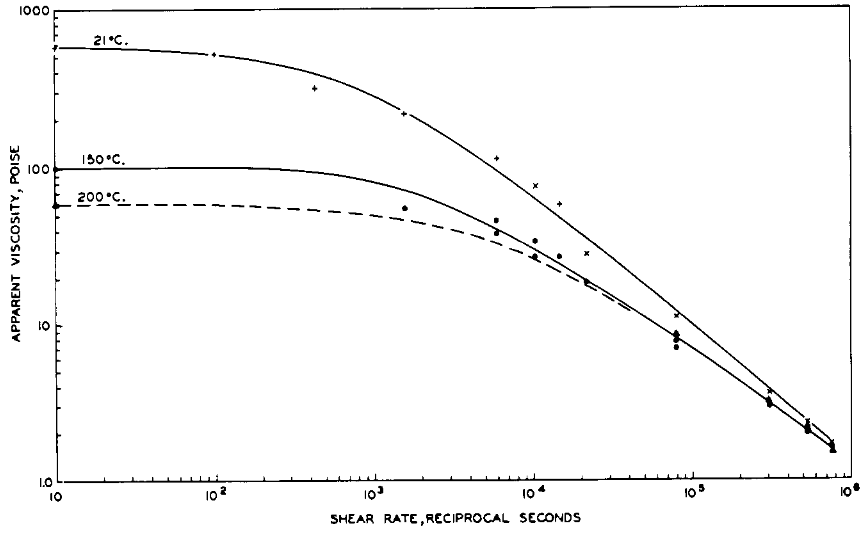


Figure 3. Effect of shear rate and temperature on apparent viscosity of 60,000-cs. dimethylpolysiloxane fluid

Table 1. Physical Properties of Dimethylpolysiloxane Used for Shear Studies

(Union Carbide L-45 silicone oil)

Viscosity, Cs. at 77° F. Nominal	Viscosity, Cs. at 77° F. Measured, Newtonian	Viscosity-Temp. Coefficient $\left[1 - \frac{\text{Visc. at 210° F.}}{\text{Visc. at 100° F.}}\right]$
1,000 ± 5%	1,023	0.62
10,000 ± 5%	9.375	0.62
12,500 [illegible] 5%	12,400	0.62
30,000 ± 5%	30,000	0.61
60,000 ± 5%	60,925	0.61
100,000 ± 10%	95,258	0.61

Specific gravity (77° F./77° F.)	0.970–0.973
Refractive index (77° F.)	1.4035
Flash point	Above 600° F.
Pour point	Below −40° F.

Table II. Measured and Calculated Shear Viscosity Relationship for 60,000-Cs. End-Blocked Dimethylpolysiloxane

(Union Carbide L-45 silicone oil)

Temp., ° C.	Capillary		L/D	Pressure, P.S.I.		Shear Rate, Sec.$^{-1}$ $4Q/\pi R^3$	Shear Stress × 10^4, Dynes/Sq. Cm., $PR/2L$	Viscosity, Poises
	Diam., mm.	Length, mm.		Measured	Corrected			
21	1.40	25.40	18.20	120	120	426	11.4	268.0
				350	350	1,555	33.2	213.0
				710	710	5,950	67.4	113.2
				890	870	10,380	82.5	79.4
				1000	930	14,710	88.3	60.0
21	1.40	1.12	0.80	70		10,380		
				110		14,710		
21	0.38	8.76	23.00	1000	870	21,800	65.3	30.0
				1500	1190	79,800	89.3	11.2
				2300	1570	305,000	117.8	3.86
				2750	1770	531,000	132.8	2.5
				3130	1830	754,000	137.3	1.82
21	0.38	0.94	2.47	220		21,800		
				480		79,800		
				900		305,000		
				1180		531,000		
				1500		754,000		
152	1.40	25.40	18.20	90	90	1,555	8.54	54.8
150				240	240	5,950	22.8	38.3
150				300	300	10,380	28.4	27.3
153				410	410	14,710	39.9	27.1
126	0.38	8.76	23.00	560	530	21,800	39.8	18.25
145				900	740	79,800	55.5	6.96
143				1580	1230	305,000	92.3	3.03
				1850	1400	531,000	105.1	1.98
				2100	1580	754,000	118.6	1.57
132	0.38	0.94	2.47	80		21,800		1.57
130				240		79,800		
140				460		305,000		
147				590		531,000		
152				690		754,000		
180	0.38	8.76	23.00	900	900	79,800	67.5	8.45
224				1500	1300	305,000	97.6	3.2
204				1700	1450	531,000	108.8	2.05
215				1850	1500	754,000	112.5	1.5
199	0.38	0.94	2.47	350		305,000		
205				400		531,000		
213				500		754,000		

capillary viscometer was used, because this type of device would give the desired high rate of shear at various temperatures. Asbeck's theoretical comparison of rotational and capillary viscometers (*1*) has shown that there will be a numerical difference between the apparent viscosity as measured by these two different types of instruments, although the general effect of shear on viscosity will be evident in either type. Currie and Smith (*4*) have shown that there is a numerical difference between the results obtained with a rotational or capillary viscometer for dimethyl silicone polymers.

The Poiseuille equation used to calculate the apparent viscosity is based on laminar flow of a Newtonian liquid through a capillary. In such a Newtonian system, a simple relationship exists between the shear velocity and the shear stress. In the non-Newtonian system, such as silicone fluids at high shear rates, the flow relationship becomes undefinable. However, the "apparent viscosity" can be calculated using the Poiseuille equation, once the shear rate and shear stress have been measured. This treatment of data, obtained from the use of a capillary pressure viscometer, has practical applications. Bestul (*2*) used pressure capillary measurements to study the degradation effect of shear on concentrated polymer solutions. McKee and White (*8, 9*) used a similar system to study the flow properties of greases. The validity of the concept of apparent viscosity, as applied to silicone oils, is strengthened by the continuity of the calculated viscosities obtained at varying shear rates with different diameter capillaries. If the apparent viscosity applied only to the one capillary being used, the relationship between apparent viscosity and shear rate would have been discontinuous on changing from one capillary diameter to another.

The possibility of a change from laminar to turbulent flow at the higher shear rates, which would prohibit the use of the Poiseuille equation, was also considered. The Reynolds number was calculated, based on both Newtonian viscosity and apparent viscosity, and found to be less than 75, well below the value of 2000 normally considered to be the Reynolds number where transition from laminar to turbulent flow occurs.

A comparison of Newtonian viscosities before and after shear showed no permanent degradation of the polymer chains. The use of first the small capillary and high shear further demonstrated lack of degradation. Had degradation occurred, the apparent viscosity calculated from the data obtained from the large capillary would be equal to or less than that calculated for the small capillary. Lower apparent viscosities were not obtained with the large capillary, but rather the data obtained gave a smooth continuation between the Newtonian viscosity and the apparent viscosity at the higher shear rates. It is concluded that no degradation

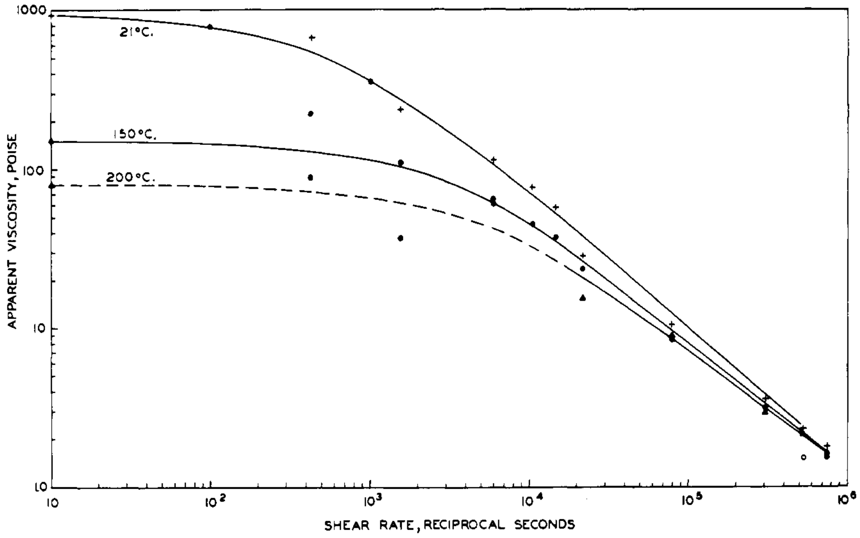


Figure 4. Effect of shear rate and temperature on apparent viscostiy of 100,000-cs. dimethylpolysiloxane fluid

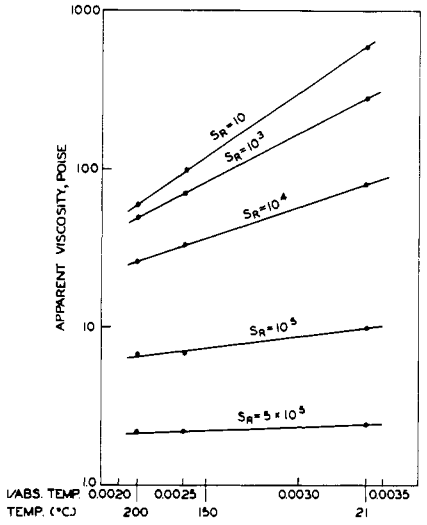


Figure 5. Effect of temperature on apparent viscosity at constant shear rate of 60,000-cs. dimethylpolysiloxane fluid

occurred. The excellent shear stability of dimethylpolysiloxane has been reported (*5, 10*).

Figure 2 shows that the apparent viscosities of the dimethylpolysiloxane fluid decreased with increased shear. Kauzmann and Eyring (*6*) proposed a qualitative explanation for the decreasing apparent viscosity with increasing shear rates, based on a theory of chain entanglement. This theory proposes that at low shear or rest a viscous fluid will have a high degree of chain entanglement or interaction. With increased laminar flow, the polymer chains will become more aligned. This increased alignment will be accompanied by decrease in the resistance to flow; hence, lower viscosities. Examination of Figure 2 reveals that the apparent viscosities of all the fluids with nominal viscosities of 1000 to 100,000 cs. converge toward a common value of 1.5 to 2.0 poises at 750,000 reciprocal seconds. The converging of the apparent viscosities for all the fluids is considered an indication that the polymer molecules are becoming aligned or structurally oriented to the same degree.

The apparent viscosity of the 60,000- and 100,000-cs. fluids was determined at temperatures to 400° F. The shear-viscosity relationship of these oils at elevated temperatures was indistinguishable from the room temperature shear-viscosity relationship of an oil whose Newtonian viscosity, at room temperature, was the same as the viscosity of the oil at the elevated temperature. As an example, the Newtonian viscosity of the dimethyl oil decreased from 60,000 to 10,000 cs. when heated from room temperature to 300° F. At 300° F., the shear-viscosity curve for this oil was indistinguishable from the room temperature shear-viscosity curve of a dimethyl oil having a room temperature viscosity of 10,000 cs. This was the only direct comparison obtained; however, when the other apparent viscosity-shear rate data obtained at elevated temperatures are compared with the family of curves determined at room temperature, the similarity in the curves is again apparent. It is concluded that temperature and shear have a similar effect on the degree of molecular entanglement. Because the shear viscosity curves at elevated temperatures can be matched to a room temperature curve of corresponding Newtonian viscosity, the apparent viscosity of a dimethyl silicone oil at any temperature and shear rate can be predicted. Only the Newtonian viscosity at the temperature of interest need be known.

Even though the viscosity of dimethylpolysiloxanes changes less with temperature than petroleum oils, the change of viscosity at low shear rates is noticeable. At high shear rates, the change of apparent viscosity with temperature becomes essentially nonexistent. This is illustrated in Figure 5, where the logarithm of the apparent viscosity at constant shear rates of the 60,000 cs. fluid is plotted against the reciprocal of the absolute temperature. The decreasing effect of temperature on the apparent viscosity with increasing shear rates was found to be true for the 100,000- and 30,000-cs. oils also. No data were obtained on the apparent viscosity of the less viscous oils at high temperatures.

CONCLUSION

The apparent viscosities of 10,000- to 100,000-cs. dimethyl silicone polymers converge to a common value of 1.5 to 2.0 poises at shear rates of 750,000 reciprocal seconds. This convergency is temperature-independent, in that temperature has a noticeable effect only on the Newtonian viscosity. The decrease in apparent viscosity is transient and is probably caused by orientation or alignment of the otherwise entangled silicone molecules and not by polymer degradation.

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