Table III. Vapor Pressure of Tetrameric Phosphonitrilic Fluoride

Temp., °C.	Pressure, Mm.		ΔP,
	Obsd.	Calcd.	Calcd. − Obsd.
Solid Phase, Empirical Equation $\log P = \frac{-3046}{T} + 11.85$			
0.1	4.0	5.0	+1.0
6.3	9.1	8.9	−0.2
11.5	13.9	14.1	+0.2
15.6	18.0	20.0	+2.0
19.6	28.0	28.2	+0.2
23.0	34.3	37.2	−0.1
29.6	62.3	61.7	−0.6
Liquid Phase, Empirical Equation $\log P = \frac{-1947}{T} + 8.247$			
32.2	73.3	74.6	+1.3
36.0	89.0	89.1	+0.1
39.1	103.0	102.2	−0.8
43.7	125.7	126.4	+0.7
47.6	150.5	150.5	0.0
49.9	165.4	166.2	+0.8
53.5	197.0	193.5	−3.5
56.6	224.0	221.0	−3.0
59.2	250.0	245.5	−4.5
62.3	282.0	277.2	−4.8
65.2	317.0	312.0	−5.0
69.0	364.7	361.0	−3.7
72.2	411.0	407.0	−4.0
75.2	459.4	456.0	−3.4
77.8	501.5	501.0	−0.5
80.5	551.7	553.0	+1.3
83.5	610.5	616.0	+5.5
86.5	673.4	682.0	+8.6
89.0	732.3	743.3	+11.0

Physical Properties. Melting Points. The melting points of the first two homologs were determined using the magnetic plunger method described by Stock (*4, 6*). The melting point for the trimer determined by this method was found to be slightly lower than the value first reported by Seel and Langer (*5*); however, the capillary tube method gave a slightly higher value than that reported by the same investigators. A Harshaw 0.2° graduated thermometer, checked at the freezing point and boiling point of distilled water, was used for melting point determinations (Table I).

Vapor Pressures of Trimer and Tetramer. A water bath equipped with an efficient stirrer and two heaters, one having a thermoregulator, was used for all the measurements. The temperatures were read from Harshaw 50°, 0.2° graduated, thermometers, and the pressures were read from a mercury manometer with a cathetometer. All the vapor pressures were determined using a tensimeter similar to that described by Burg and Schlesinger (*2*). The results are summarized in Tables II and III. The constants to the empirical equations were determined by plotting log P vs. $1/T$ and drawing the best straight line. The heats of vaporization and sublimation were calculated from the corresponding empirical equations, and the heat of fusion was calculated from the differences of heats of vaporization and sublimation. Comparative physical data for the trimer and tetramer are summarized in Table I.

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Preparation and Comparison of the Physical Properties of Alkyl and Alkforyl Silicates

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Normal alkyl and alkforyl alcohols reacted with silicon tetrachloride to produce tetraalkyl and tetraalkforyl silicates (*8*) as well as hexaalkoxy and hexaalkforyloxy disiloxanes. Differences were noted in their mode of reaction and physical properties.

A comparison of the physical properties of the three series of organosilicates exhibited some unusual variations. Unfortunately, a more complete comparison was not possible because of the unavailability or the high cost of the alkforyl alcohols in this homologous series. Nonetheless, generalizations may be made concerning the three series from the available data.

Although the alkyl silicates are stable thermally (*1,2*), the object of this study was to compare the thermal stability, physical properties, and hydrolytic stability of these with the 1,1,(*n* + 2)-trihydroalkforyl silicates and the 1,1-dihydroalkforyl silicates. These silicates may be represented by the following general formulas:

Tetra-*n*-alkyl silicate

$$[H_3C(CH_2)_N-CH_2-O]_4\,Si$$

Tetra-1,1(*n* + 2)-trihydroalkforyl silicate

$$[HF_2C(CF_2)_N-CH_2-O]_4\,Si$$

Tetra-1,1-dihydroalkforyl silicate

$$[F_3C(CF_2)_N-CH_2-O]_4\,Si$$

Hexa-*n*-alkoxy disiloxane

$$[H_3C(CH_2)_N-CH_2-O]_3\,Si-O-Si\,[O-CH_2(CH_2)_N-CH_3]_3.$$

Table I. Thermal Stability of Silicates

600° F. (315° C.)	*n*-Octyl silicate	10.3^0	10.8^3	13.1^{10}	18.1^{27}	...	29.2^{46}	45.0^{65}	261^{92}
	n-Amyl triphenyl silicate	9.6^0	11.8^3	15.9^{10}	33.6^{24}	43.9^{35}	58.3^{46}	74.5^{65}	160^{92}
	Diphenyl dicresyl silicate	23.0^0	32.5^3	33.2^{10}	...	39.9^{35}	45.0^{46}	56.0^{65}	109^{92}
	1,1,7-Tri-*H*-heptforyl silicate	43.8^0	39.5^4	40.2^{10}	42.0^{21}	42.5^{32}	43.4^{46}	61.9^{62}	91.0^{84}
500° F. (260° C.)	*n*-Octyl silicate	10.3^0	10.9^3	12.1^{13}	16.6^{31}	18.5^{34}	26.7^{63}	36.3^{79}	...
	1,1,-5-Tri-*H*-pentforyl silicate	21.0^0	21.8^8	21.9^{14}	24.5^{42}	29.7^{84}	51.0^{126}	...	...
400° F. (205° C.)	Diisopropyl diisobutyl silicate	1.90^0	1.94^5	2.68^{28}	4.85^{53}	11.0^{75}	21.7^{90}	...	...
	1,1,3-Tri-*H*-propforyl silicate	9.22^0	9.22^1	9.83^7	11.9^{19}	12.3^{33}	14.4^{50}	15.9^{66}	...

Table II. Physical Properties of Tetraorthosilicates

Tetraorganosilicates	B.P.[a], °C./Mm.		Refractive Index, n_D^t	Specific Gravity, d^t/t'	Viscosity, Centistokes		
					n^{-35} °C.	n^{25} °C.	n^{85} °C.
n-Propyl-	228/760	70/2.0	1.4016^{20}	$0.9158^{22.6/4}$	5.3	1.43	0.72
n-1,1,3-Trihydropropforyl-	247/762	92/2.0	1.3353^{25}	$1.5837^{25/25}$	315	9.22	2.60
n-1,1-Dihydropropforyl-	183/762	41/1.0	1.27^{25}	$1.5858^{25/25}$	12.4	2.26	1.06
n-Butyl-	275/760	108/2.0	1.4128^{20}	$0.9130^{25/4}$	9.5	2.20	1.16
n-1,1-Dihydrobutforyl-	230/763	88/1.0	...	...	...	...	...
n-Amyl-	340/761	162/4.0	1.4180^{21}	$0.8933^{25/4}$	23.0	3.30	1.38
n-1,1,5-Trihydropentforyl-	355/763	152/0.5	1.3285^{25}	$1.7281^{25/25}$	1300	21.0	3.94
n-Hexyl-	355/760	175/3.0	1.4337^{25}	0.8321^{21}	40.0	5.00	1.83
n-Heptyl-	398/760	200/3.0	1.4388^{25}	$0.8958^{25/4}$	105	7.10	2.20
n-1,1,7-Trihydroheptforyl-	405/764	180/0.1	1.3219^{25}	$1.7986^{25/25}$	4900	43.8	6.05
n-Octyl-	415/760	204/3.0	1.4430^{25}	...	115	9.70	3.05
n-Nonyl-	465/761	240/3.0	...	...	...	16.0	...
n-1,1,9-Trihydrononaforyl-	470/764	226/0.1	Solid[b]	Solid[b]	...	Solid[b]	...

[a] All boiling points corrected.
[b] Melting point 47–9 uncorrected.

Hexa-*n*-1,1(*n* + 2)-trihydroalkforyloxy disiloxane

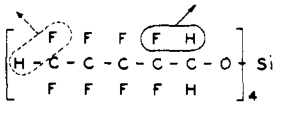
$$\left[HF_2C(CF_2)_N-CH_2-O\right]_3 Si-O-Si\left[O-CH_2(CF_2)_N-CF_2H\right]_3$$

Hexa-*n*-1,1-dihydroalkforyloxy disiloxane

$$\left[F_3C(CF_2)_N-CH_2-O\right]_3 Si-O-Si\left[O-CH_2(CF_2)_N-CF_3\right]$$

THERMAL STABILITY

As both the fluorocarbons and organosilicates have been shown to exhibit excellent thermal stability (*6,10,11*), it was felt that combining these into the same molecule would result in superior thermally stable liquids. These assumptions have proved correct. However, these new compounds are badly corrosive to iron. This is an unexpected development, as neither the organic silicates nor the fluorocarbons in themselves are corrosive. This untoward behavior may be due in part to the liberation of hydrogen fluoride due to thermal breakdown between the adjacent —CH_2—and—CF_2—groups (α and β in the chain). For example:



Another possible explanation may be the liberation of hydrogen fluoride from the terminal carbon atom—see dotted line in example. This would lead to chain lengthening or cross linking with a subsequent increase in viscosity. Because viscosity increase is the device used for determining thermal stability, it would be difficult to establish which is the cause of viscosity increase. Nevertheless, the thermal stability compares more than favorably with the straight alkyl silicates.

Because of the different order of magnitude of the boiling points of alkyl and alkforyl silicates, compounds of the same chain length could not be heat tested at the same temperature.

Tetra-1,1,7-trihydroheptforyl silicate was tested for thermal stability at 600°F. (315°C.) in apparatus especially designed for this use at the Pierce Foundation Laboratory. It was compared with a straight alkyl silicate, mixed tetraalkyl aryl silicates, and mixed tetraaryl silicates. Neglecting the corrosion factor, its thermal stability was greater.

The apparatus consists of a cylindrical tube of borosilicate glass, half filled with liquid and a strip of iron (mild carbon steel) (to simulate actual operating conditions) immersed in a molten salt bath (HT salts Du Pont) maintained at 600° ± 3°F. with a Fenwal thermoregulator and circumferential heating. The samples are removed periodically and their viscosities are determined at 77°F. (25°C.). A general rule of thumb for heat transfer fluids determines the "life" of a liquid as the time elapsed for the viscosity (in centistokes) to increase tenfold. Table I indicates the thermal stability of the various silicates—measured by their rate of increase in viscosity. In Table I the figure denotes viscosity, the superscript, the number of days.

The preceding test is an accelerated one, in which the values are comparative rather than absolute. Actual life of these liquids can be measured in years rather than months but for the purpose of quick comparisons this test was developed. "Useful life" is that period in which the pumping power required is low and efficiency is high. Beyond this it is economically not feasible and sometimes physically impossible to pump a viscous liquid.

The preceding tests at various temperatures for the several 1,1(*n* + 2)-trihydroalkforyl silicates demonstrate their superiority over the straight alkyl silicates of approximately the same chain length at comparable temperatures.

PHYSICAL PROPERTIES OF SILICATES

Differences in the physical properties of the three classes of silicates were marked and interesting (see tables).

Boiling Point. Taking the monomers first, a decided drop in boiling point was noted for the dihydroalkforyl silicates over the alkyl silicates. On the other hand, the replacement of the terminal fluorine in the chain by hydrogen completely changed this property by increasing the boiling point to a shade higher than the straight alkyl silicate. As the α-carbon atom in all three classes con-

Table III. Physical Properties of Hexaorgano Condensed Silicates

Hexaorgano-Disiloxanes	B.P., °C./Mm.[a]		Refractive Index, n_D^t	Specific Gravity, d^t/t'	Viscosity, Centistokes		
					n^{-35} °C.	n^{25} °C.	n^{85} °C.
n-Propyl-	320/760	140/3.0	1.4102^{25}	$0.977^{20/4}$	...	2.51	...
n-1,1,3-Trihydropropforyl-	305/764	112/1.0	1.3342^{25}	$1.5993^{25/25}$	355	18.0	5.05
n-1,1-Dihydropropforyl-	290/761	116/0.5	1.3104^{25}	$1.6276^{25/25}$	200	9.46	3.05
n-Butyl-	355/760	164/2.0	1.4150^{25}	...	23.8	3.90	1.63
n-1,1-Dihydrobutforyl-	320/761	138/1.0	...	...	...		...
n-Amyl-	435/760	220/2.0	1.4234^{25}	...	55.0	6.00	2.27
n-1,1,5-Trihydropentforyl-	425/764	175/0.1	1.3270^{25}	$1.7429^{25/25}$	3500	44.8	8.55
n-Heptyl-	...	...	...	...	130	11.0	3.41
n-1,1,7-Trihydroheptforyl-	470/764	222/0.1	1.3245^{25}	$1.8084^{25/25}$	7500	81.0	13.3
n-1,1,9-Trihydrononaforyl-	515/764	260/0.1	Solid[b]	Solid[b]	...	Solid[b]	...

[a] All boiling points corrected.
[b] Melting point 55–7 uncorrected.

tains two hydrogen atoms, the remaining, and especially the terminal carbon atom, must influence the boiling point. That the 1,1-dihydroalkforyl silicate boiling point is lower than its corresponding alkyl silicate follows from the corresponding lower boiling points of the fluorocarbons to those of the hydrocarbons (*9*). Thus the effect of a single hydrogen atom on the terminal carbon almost equates the 1,1 ($n + 2$)-trihydroalkforyl silicate with the straight alkyl silicate.

Refractive Index. The refractive index on the other hand produced more expected results. It increased steadily in the straight alkyl series, while that of the 1,1($n + 2$)-trihydroalkforyl series of a lower order of magnitude decreased with increasing fluorine content. The refractive index of the 1,1-dihydroalkforyl silicate is very low—e.g., the fluorocarbons (*4,7*).

Specific Gravity. The specific gravities of the straight alkyl silicates decrease to a low point at C_6 and then begin to increase like the hydrocarbons. Those of the 1,1 (n + 2)-trihydroalkforyl silicates increase steadily at the much higher level, reflecting the presence of the heavy halogen. Again the 1,1-dihydroalkforyl silicate has a high specific gravity due to the greater fluorine content. Here, the terminal carbon atom effects little difference on specific gravity.

Viscosity. Turning to viscosity, an anomalous situation was found. At 77°F., corresponding chain lengths showed viscosities of the 1,1-dihydroalkforyl silicates about two to four times those of the alkyl silicates while the 1,1 ($n + 2$)trihydroalkforyl silicates had viscosities six to ten times those of the alkyl silicates (*3*). Thus the former two of uniform structure were fairly close and similar, while the latter was greatly influenced by the hydrogen on the terminal carbon atom. This may be pictured as a "foreign" atom providing friction to flow versus free flow of like atoms.

PHYSICAL PROPERTIES OF DISILOXANES

The physical properties of the three classes of disiloxanes follow fairly closely the pattern of the silicates.

Boiling Point. Contrary to those of the monomers, the three boiling points for a given chain length were fairly uniform. The boiling point of the 1,1-dihydroalkforyl compound was still the lowest, while the boiling point of the alkyl compound was slightly higher than the boiling points of the 1,1 (n + 2)-trihydroalkforyl compounds.

Refractive Index. The refractive indices of the alkyl series increased with chain length. Those of the 1,1-dihydroalkforyl series were of a lower order of magnitude due to the fluorine stimulus and decreased with increasing chain (and thereby fluorine) chain length. Those of the 1,1 (n + 2)-trihydroalkforyl series were slightly higher in magnitude than the completely fluorinated series and also decreased with increasing chain length.

Specific Gravity. The greatest difference in density lies between the alkyl series and both of the fluorinated series.

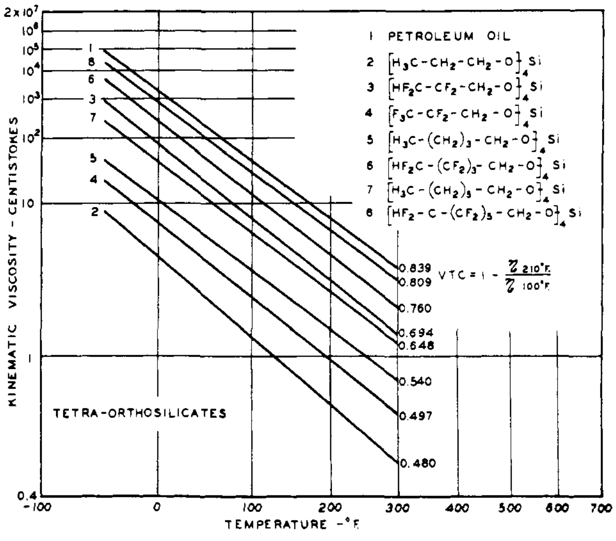


Figure 1. Viscosity-temperature chart for tetraorthosilicates

While the density of the alkyl series is less than unity, the densities of both of the fluorinated series are twice that, reflecting the strong halogen influence. For comparable chain length, the densities of the 1,1-dihydroalkforyl series are greater than of the 1,1 (n + 2)-trihydroalkforyl series.

Viscosity. For similar chain lengths, the viscosities of the 1,1 (n + 2)-trihydroalkforyl series ran approximately seven times that of the alkyl series while the viscosity of the 1,1-dihydroalkforyl series was about four times higher. These ratios are comparable to those of the monomer silicates.

DISCUSSION

The graphs in Figures 1 and 2 are plotted on viscosity-temperature charts modified from ASTM (D 341-39). The petroleum oil is identified as a modified aircraft hydraulic oil: AN-VVO-366B.

From Figures 1 and 2, it can be seen that all lines are parallel and flat, reflecting the low viscosity temperature coefficient (VTC) of organosilicon fluids $\mathrm{VTC}\text{-}1 - \dfrac{n210^\circ\mathrm{F.}}{n100^\circ\mathrm{F.}}$ (*5,12*). For liquids of the same viscosity at 77°F. (25°C.), the smaller the viscosity temperature coefficient, the flatter the slope of change in viscosity with temperature. The viscosity temperature coefficient of the disiloxanes is generally lower than that of the monomer silicates.

All three classes of compounds are colorless mobile fluids which boil without decomposition, with the exception of 1,1,9-trihydrononaforyl silicate and hexa-1,1,9-trihydrononaforyloxy disiloxane, which are white crystalline solids. The former melts at 47–9°C. and the latter at 55–7°C.,

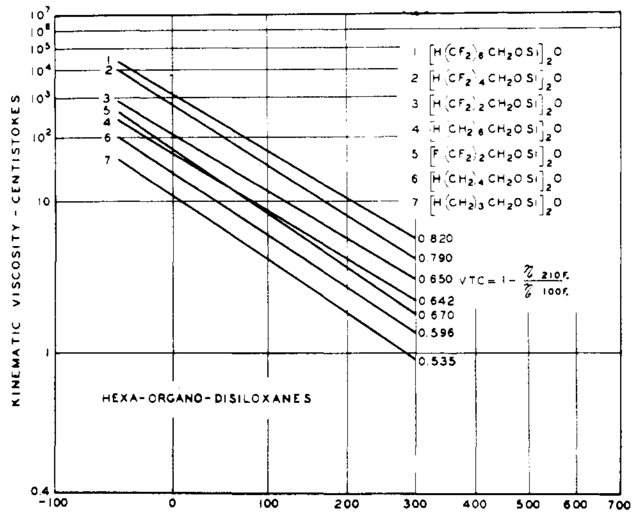


Figure 2. Viscosity-temperature chart for hexaorganodisiloxanes

both uncorrected. All boiling points and vapor pressures are corrected.

The odor of the alkyl silicates approximates that of the parent alcohol, the 1,1($n + 2$)-trihydroalkforyl silicates have a fruity esterlike odor, and the 1,1-dihydroalkforyl silicates have an odor somewhere between the two.

While all three classes are subject to hydrolysis in neutral aqueous media, the rate sequence is 1,1-dihydro > 1,1($n + 2$)-trihydro > alkyl. This was observed by simply shaking three parts of silicate with one part of water at room temperature and waiting for the formation of a white precipitate. The first compound took approximately 8 hours, the second 24 hours, and the last 4 days.

The alkyl silicates are miscible in all proportions with organic solvents, while both alkforyl silicates are only very slightly soluble in aromatic and aliphatic hydrocarbons but completely miscible with oxygen-containing organic solvents.

METHOD OF PREPARATION

In all cases, silicon tetrachloride in a graduated dropping funnel, fitted with a calcium chloride drying tube, was added dropwise to the appropriate alcohol using a Tru-bore glass paddle stirrer. A dry ice-packed reflux condenser helped prevent the loss of silicon tetrachloride by entrainment in the by-product. Hydrogen chloride was removed via the condenser to a fume hood or through a series of water bottles.

In the case of exothermic reactions, external cooling of the reaction flask prevented loss of the volatile silicon tetrachloride. After the complete addition of silicon tetrachloride, heat was applied slowly until reflux was attained. The mixture was then refluxed for 24 hours, cooled, and fractionated under reduced pressure. Yields were generally greater than 80% based on silicon tetrachloride.

When an endothermic reaction occurred, heat was gently supplied, to hasten the liberation of hydrogen chloride. Once the silicon tetrachloride addition was over, more heat was applied until reflux occurred.

When the starting alcohol was a solid, it was warmed to just beyond its melting point, and silicon tetrachloride was slowly added.

STARTING MATERIALS, INSTRUMENTS, AND APPARATUS

n-Aliphatic alcohols, pure-dried before use.
n-1,1 ($n + 2$)-Trihydroalkforyl alcohols, as received.
n-1,1-Dihydropropforyl alcohol, as received.
n-1,1-Dihydrobutforyl alcohol, as received.
Silicon tetrachloride, distilled.

Instruments. Boiling point and vapor pressure, Cottrell boiling point apparatus. Melting point, capillary in Thiele tube. Specific gravity, pycnometers in constant temperature bath ±0.05 °F. Viscosity, Fenske viscosity pipet in constant temperature bath ±0.05 °F. Refractive index, Bausch & Lomb refractometer using sodium *D* lamp.

	Boiling Point, °C.	
n-Propyl alcohol	96–8	Eastman Kodak
n-Butyl alcohol	116–8	Eastman Kodak
n-Amyl alcohol	136–8	Eastman Kodak
n-Hexyl alcohol	155–8	Eastman Kodak
n-Heptyl alcohol	174–6	Eastman Kodak
n-Nonyl alcohol	211–4	Matheson, Coleman, Bell
1,1,3-trihydro-*n*-propforyl alcohol	109–10	Du Pont
1,1,5-trihydro-*n*-pentforyl alcohol	140–1	Du Pont
1,1,7-trihydro-*n*-heptforyl alcohol	169–70	Du Pont
1,1,9-trihydro-*n*-nonforyl alcohol	m.p. 65–7	Du Pont
1,1-Dihydropropforyl alcohol	72	Caribou Chemicals
1,1-Dihydrobutforyl alcohol	95–6.5	Minnesota Mining & Mfg. Co.
Phenol	m.p. 42	Dow Chemical
Silicon tetrachloride	57–8	Stauffer

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