Silicate Esters and Related Compounds

Physical Properties of Certain Tetraalkoxysilanes, Polyalkoxypolysiloxanes, Bis(trialkoxysilyl)ethanes, Bis(trialkoxysiloxy)alkanes, and Compounds Containing Nitrogen, Phosphorus, and Halogens

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CERTAIN SILICATE ESTERS exhibit good viscosity-temperature characteristics and hydrolytic stability. As a result, these materials are finding increasing use as high temperature hydraulic fluids and lubricants (*3*). Such silicates were discovered by extensive work on the synthesis of new compounds and the study of their properties.

The first article of this series (*14*) describes the methods used to synthesize the silcate esters. The second (*12*) presents a convenient empirical method for the calculation of normal boiling points of certain of these materials. This third article gives data of physical and chemical properties of the old as well as new compounds.

SYNTHESIS

The compounds in Table I were synthesized, as noted in the last column, by the methods previously described (*14*). These procedures, as applied to the silicates in Table I, are typified by the following equations:

Method IA (symmetrical tetraalkoxysilanes)

$$4\ \mathrm{ROH} + \mathrm{SiCL_4} \rightarrow \mathrm{(RO)_4Si} + 4\ \mathrm{HCl}\uparrow \qquad (1)$$

where R = *sec*-alkyl; also applicable to ROH + $\mathrm{(CH_2SiCl_3)_2}$.

Method IB (unsymmetrical tetraalkoxysilanes, disiloxanes, and trisiloxanes)

$$\mathrm{(RO)_3SiCl} + \mathrm{R'OH} + \mathrm{C_5H_5N} \rightarrow \mathrm{(RO)_3R'OSi} + \mathrm{C_6H_5N \cdot HCl}\downarrow \qquad (2)$$

R = *sec*- or *tert*-alkyl and R′ = *p*- or *sec*-alkyl; or R =*p*- or *sec*-alkyl and R′ = *tert*-alkyl; also applicable to $\mathrm{(RO)_2SiCl_2}$ + 2 R′OH. Or

$$2\mathrm{(RO)_3SiCl} + 2\ \mathrm{C_5H_5N} \rightarrow \mathrm{[(RO)_3Si]_2O} + 2\ \mathrm{C_5H_5N \cdot HCl}\downarrow \qquad (3)$$

R = *p*- or *sec*-alkyl (*13*). Or

$$\mathrm{(RO)_2SiCl_2} + \mathrm{(R'O)_3SiOH} + 2\mathrm{C_5H_5N} \rightarrow \mathrm{[(R'O)_3SiO]_2Si(OR)_2} + 2\mathrm{C_5H_5N \cdot HCl}\downarrow \qquad (4)$$

R and R′ = *p*- or *sec*-alkyl (*15*); also applicable to $\mathrm{R_2SiCl_2}$ + $\mathrm{(R'O)_3SiOH}$ where R = ethyl or phenyl.

Method IIA (tetraalkoxysilanes with *tert*-alkyl group)

$$\mathrm{(RO)_3SiOH} + \mathrm{R'NH_2} \xrightarrow{\mathrm{NaOMe}} \mathrm{(RO)_3R'OSi} + \mathrm{NH_3}\uparrow \qquad (5)$$

R = *p*- or *sec*-alkyl and R′ = *tert*-alkyl.

Method IIB (tetrabenzyloxysilane)

$$\mathrm{(EtO)_4Si} + \mathrm{ROH} \xrightarrow{\mathrm{Na}} \mathrm{(RO)_4Si} + 4\mathrm{EtOH}\uparrow \qquad (6)$$

R = $\mathrm{PhCH_2}$.

The silicate derivatives of aliphatic and aromatic diols in Table II [bis(trialkoxysiloxy)alkanes or benzenes], were synthesized by Method IB according to Equation 7:

$$2\mathrm{(RO)_3SiCl} + \mathrm{R'(OH)_2} + 2\mathrm{C_5H_5N} \rightarrow \mathrm{R'[OSi(OR)_3]_2} + 2\mathrm{C_5H_5N \cdot HCl}\downarrow \qquad (7)$$

R = *sec*- or *tert*-alkyl and R′ = alkyl or aryl diradical (*1*).

The miscellaneous silicate derivatives in Table III were prepared by a somewhat more complicated synthesis than the compounds in Tables I and II. The materials containing phosphorus (compounds 1, 2, and 3) involved the following reactions:

$$2\mathrm{(RO)_2P(O)H} + 2\ \mathrm{Na} \rightarrow 2\mathrm{(RO)_2P(O)Na} + \mathrm{H_2}\uparrow \qquad (8)$$

$$\mathrm{(RO)_2P(O)Na} + \mathrm{R'\ (OH)\ (Cl)} \rightarrow \mathrm{(RO)_2P(O)R'OH} + \mathrm{NaCl}\uparrow \qquad (9)$$

$$\mathrm{(RO)_2P(O)R'OH} + \mathrm{(R''O)_3SiCl} \rightarrow \mathrm{(RO)_2P(O)R'OSi\ (OR'')_3} + \mathrm{HCl} \rightarrow \qquad (10)$$

R = Bu, R′ = alkyl diradical, R″ = *sec*- or *tert*-alkyl.

The materials containing nitrogen in Table III (compounds 4 and 5) were prepared by alcoholysis of tetraethoxysilane with a dialkylamino alcohol (Method IIA). The aromatic silicate derivatives (compounds 6, 7, and 8) were made by reacting the trialkoxychlorosilane with the appropriate halogen-containing aromatic diol (Method IB). The last compound in Table III, tetra(1-carbethoxyethoxy) silane, was prepared by reacting silicon tetrachloride with ethyl lactate (Method IA).

IDENTIFICATION OF COMPOUNDS

Relatively large laboratory preparations were made of all the compounds studied, so that ample quantities of "plateau" distillation fractions were available for analysis. Identities of most of the compounds in Tables I, II, and III were established by elemental analyses. Molar refractions were also used. Theoretical values were calculated from the bond refraction values of Denbigh (*4*) and Warrick (*11*). With few exceptions, agreement was excellent between the experimental and calculated molar refractions for all classes of compounds.

PHYSICAL PROPERTIES

Boiling Points. A convenient method for determining the normal boiling points of silicate esters using the Kinney equation (*6*) was given previously (*12*). The same technique is applicable to many of the compounds shown in Tables I, II, and III.

Viscosity-Temperature Characteristics. These relationships with the silicate derivatives are affected by the structure of the alkyl group in a manner similar to that observed with hydrocarbons (*10*). In tetraalkoxysilanes, the dependence of viscosity on temperature increases markedly with increased degree of branching:

Compound	ASTM Slope (100–210° F.)
tetra(1-butoxy)silane (*8*)	0.74
tetra(2-butoxy)silane	0.87
2-Butoxytri(*tert*-butoxy)silane	0.92

The transition from silanes to disiloxanes and trisiloxanes is marked by a significant decrease in the viscosity-temperature slope:

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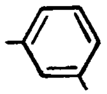
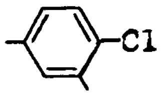
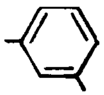
Table I. Physical Properties of Tetraalkoxysilanes, Hexaalkoxydisiloxanes, Polyalkoxytrisiloxanes, and Bis(trialkoxysilyl)ethanes

	Compounds	Density, d_4^{20}	Refractive Index, n_D^{20}	Molar Refraction, MR_D^{20}		Boiling Point		Viscosity, Cs. at ° F.				ASTM Slope^b			Silicon, %		Method of Synthesis^c
				Found	Calcd.^{a}	° C.	Mm. Hg	−65	−40	100	210	100–210° F.	−40–210° F.	−65–210° F.	Calcd.	Found	
	Silanes																
1	Tetra(2-propoxy)^d	0.8746	1.3852	70.9	70.4	70.5	10	Solid	...	1.03	0.56	0.93	...	...	...	...	Ia
2	Tetra(2-butoxy)^d	0.8871	1.4075	89.0	88.9	105	5	46.0	...	2.01	0.91	0.87	...	0.82	...	...	Ia
3	*tert*-Butoxytri(2-butoxy)^e	0.8877	1.4075	89.0	88.9	120	5	41.9	18.3	2.01	0.91	0.87	0.81	0.81	8.76	8.74^f	IIa
4	2-Butoxytri(*tert*-butoxy)^d	0.8806	1.4024	88.7	88.9	89	5	747	...	4.62	1.44	0.92	...	0.84	...	...	Ib
5	1-Butoxytri(*tert*-butoxy)^d	0.8718	1.4012	89.4	88.9	97.5	5	...	...	3.09	1.21	0.86	...	...	...	...	Ib
6	2-Heptoxytri(*tert*-butoxy)	...	1.4179	...	...	140–141	1	279	...	4.75	1.55	0.83	...	0.75	...	...	Ib
7	Tetra(1-pentoxy)^d	...	...	...	...	144	1	65.5	...	2.6	1.2	0.74	...	0.73	...	...	Ia
8	Tetra(1-methoxy-2-propoxy)	1.0114	1.4172	95.7	96.0	124–127	1	315	...	3.19	1.25	0.84	...	0.85	...	...	Ia
9	Tetra(3-pentoxy)^d	...	...	...	...	121	1	326	...	3.79	1.43	0.81	...	0.79	...	...	Ia
10	Tetra(3-methyl-2-butoxy)^d	0.8880	1.4182	106.7	107.4	132–135	5	472	129	4.04	1.44	0.85	0.81	0.81	...	...	Ia
11	Di(2-ethyl-1-hexoxy)-di(*tert*-pentoxy)^d	0.8842	1.4312	135.0	135.2	153	1	1250	315	6.79	2.05	0.79	0.75	0.75	6.10	6.11	Ib
12	Di(1-hexoxy)-di(*tert*-pentoxy)	0.8850	1.4328	118.8	116.7	142	1	222	77.3	3.88	1.49	0.78	0.75	0.75	6.94	6.84	Ib
13	Di(4-methyl-2-pentoxy)-di(*tert*-pentoxy)^d	...	1.4207	...	...	146	5	1380	243	4.62	1.56	0.85	0.83	0.84	6.94	6.75	Ib
14	*tert*-Pentoxytri(1-hexoxy)^d	...	1.4261	...	...	160	1	172	62.1	3.65	1.45	0.77	0.74	0.74	6.71	6.61	Ib
15	Tetra(4-methyl-2-pentoxy)^d	0.8669	1.4205	126.5	125.9	136	1	846	146	3.88	1.44	0.81	0.82	0.84	...	...	Ia
16	1-Dodecoxytri(2-butoxy)	0.8739	1.4360	129.5	125.9	141–145	1	2835	545	7.43	2.17	0.80	0.78	0.77	...	...	Ia
17	Tetra(benzyloxy)^e	...	...	...	...	217–221^g	0.2	...	...	7.1	2.3	0.71	...	...	...	...	IIb
18	2-Ethyl-1-hexoxytri-(2-ethyl-1-butoxy)^d	0.8885	1.4328	134.7	135.2	176	1.1	325	102	4.56	1.73	0.73	0.72	0.72	...	...	Ib
19	*tert*-Pentoxytri(2-heptoxy)	0.8759	1.4278	135.3	135.2	146	0.5	891	223	5.28	1.77	0.79	0.77	0.77	6.10	6.00	IIa
20	Di(1-octoxy)-di(*tert*-pentoxy)	0.8808	1.4302	135.2	135.0	171	0.2	611	183	5.77	1.95	0.75	0.73	0.72	...	...	Ib
21	*tert*-Butoxytri(2-octoxy)	...	1.4285	...	...	160	0.2	1600	371	6.40	1.96	0.79	0.77	0.77	5.72	5.53	Ib
22	Tetra(4-methyl-1-cyclohexoxy)	0.9755	1.4663	136.6	135.9	210–211	1	...	...	64.6	6.44	0.84	...	...	...	...	Ia
23	Tetra(2-heptoxy)^d	0.8715	1.4296	144.8	144.4	176	1	867	215	5.07	1.73	0.78	0.78	0.78	...	...	Ia
24	*tert*-Butoxytri(2-ethyl-1-hexoxy)	0.8785	1.4322	144.4	144.4	155–157	0.1	1160	286	6.39	2.02	0.78	0.75	0.75	...	...	IIa
25	Di(2-ethyl-1-hexoxy)-di(2-ethyl-1-butoxy)	0.8859	1.4348	143.9	144.4	175–177	1	555	143	5.20	1.89	0.71	0.72	0.75	...	...	Ib
26	*tert*-Pentoxytri(1-octoxy)	0.8829	1.4347	148.5	149.1	182	0.2	621	191	6.28	2.15	0.72	0.70	0.70	...	...	IIa
27	Tetra(2-octoxy)^d	0.8692	1.4340	163.3	163.0	204	1	1720	410	7.12	2.20	0.76	0.75	0.70	...	...	Ia
28	Tetra(2-ethyl-1-hexoxy)^d	0.8803	1.4388	162.8	163.0	194	1	1400	319	6.89	2.27	0.71	0.72	0.72	...	...	Ia
29	Tetra(3-phenyl-1-propoxy)	1.0620	1.5380	167.5	167.9	165–170	^{h}	...	...	20.7	4.41	0.71	...	...	...	...	Ia
30	Tetra(2-butoxy-1-ethoxy)	0.9653	1.4309	133.2	133.0	193–194	0.2	359	104	4.35	1.67	0.73	0.74	0.74	...	...	Ia
31	Ethyltri(2-ethyl-1-hexoxy)	0.8698	1.4371	134.0	134.4	171	1	545	151	4.97	1.79	0.75	0.74	0.74	...	...	Ia

	Compounds	Density, d^{20}_{4}	Refractive Index, n^{20}_{D}	Molar Refraction, MR$^{20}_{D}$		Boiling Point		Viscosity, Cs. at ° F.				ASTM Slope[b]			Silicon, %		Method of Synthesis[c]
				Found	Calcd.[a]	° C.	Mm. Hg	-65	-40	100	210	100 210° F.	40- 210° F.	-65- 210° F.	Calcd.	Found	
32	Diethyldi(2-butyl-1-octoxy)	0.8514	1.4440	142.5	142.9	193	1	1552	406	...	2.43	0.71	0.71	0.69	...	...	Ia
	Disiloxanes																
33	Hexa(2-propoxy)[d]	0.9281	1.3930	109.7	109.0	96	1	...	...	3.04	1.34	0.73	...	...	...	...	Ib
34	Hexa(2-butoxy)[e]	0.9285	1.4133	136.8	136.8	145.5–146.5	1.5	...	...	7.38	3.11	0.51	...	...	11.00	10.52	Ib
35	Hexa(2-methyl-1-pentoxy)	0.9153	1.4323	192.4	192.4	217–219	1	1770	396	11.0	3.70	0.57	0.60	0.61	...	...	Ib
36	Hexa(4-methyl-2-pentoxy)[d]	0.9048	1.4252	192.0	192.4	194	1	4430	761	11.4	3.53	0.62	0.66	0.67	...	...	Ib
37	Hexa(2-ethyl-1-hexoxy)	...	1.4411	...	...	252–254	0.1	3010	693	13.2	4.09	0.58	0.61	0.62	6.63	6.67	Ib
38	Hexa(1-methoxy-2-propoxy)	...	...	...	...	182	1	1210	...	7.38	2.57	0.65	...	0.68	...	...	Ib
	Trisiloxanes																
39	1,1,1,5,5,5-Hexa(2-butoxy)-3,3-diethyl	0.9463	1.4194	163.8	164.7	177–178	1	450	171	10.1	3.4	0.59	0.56	0.56	13.75	14.17	Ib
40	Octa(2-butoxy)[e]	...	1.4178	...	...	187–188	1	...	...	25[i]	6.80	0.53	...	...	...	...	Ib
41	1,1,1,5,5,5-Hexa(2-butoxy)-3,3-di(4-methyl-2-pentoxy)	...	...	...	...	199	1	...	...	Solid	8.10	...	...	...	11.62	10.97	Ib
42	1,1,1,5,5,5-Hexa(4-methyl-2-pentoxy)-3,3-di(2-butoxy)	0.9157	1.4260	243.3	240.3	209	0.1	10360	1760	24.3	6.74	0.52	0.56	0.58	9.67	9.87	Ib
43	1,1,1,5,5,5-Hexa-(2-heptoxy)-3,3-diethyl	0.9152	1.4345	246.5	248.1	252–255	0.1	2763	624	11.55	3.44	0.64	0.65	0.65	9.74	9.41	Ib
44	Octa(2-ethyl-1-butoxy)	0.9384	1.4350	257.4	258.8	241–243	0.1	2000	594	23.7	7.77	0.45	0.47	0.48	9.10	9.17	Ib
45	1,1,1,5,5,5-Hexa(2-butoxy)-3,3-diphenyl[e]	1.0013	1.4638	195.4	195.1	256–258[h]	1	10750	2060	31.6	8.18	0.52	0.53	0.55	11.88	11.99	Ib
	Bis[trialkoxysilyl]ethanes																
46	1,2-Bis[tri(2-ethyl-1-butoxy)silyl]	...	1.4414	...	...	213	0.1	2367	501	11.7	3.62	0.61	0.62	0.63	8.13	8.12	Ia
47	1,2-Bis[tri(2-butoxy)silyl][f]	0.9124	1.4248	146.5	146.3	155	1	864	210	7.06	2.37	0.69	0.68	0.69	10.74	10.76	Ia
48	1,2-Bis[tri(2-methyl-1-butoxy)silyl]	...	1.4346	...	...	190	0.1	1097	325	9.25	2.92	0.66	0.65	0.65	9.25	9.28	Ia
49	1,2-Bis[tri(3-methyl-1-butoxy)silyl]	0.9094	1.4320	173.1	174.1	185	0.1	578	185	7.29	2.47	0.67	0.65	0.65	9.25	9.47	Ia

[a] Calculations based on bond refraction values (*11*). Agreement: Average and standard deviations = ±0.42 and 0.60%, respectively. [b] Measured slope of line plotted on ASTM kinematic viscosity–temperature chart D-341 (*2*). [c] Refer to Table II of (*14*). [d] Some properties given in (*12*). [e] Some properties given in (*14*). [f] % C calculated, 60.0, found 59.75; % H calculated, 11.25, found 11.21. [g] Boiling point reported in (*14*) is in error. [h] Distillation carried out at pressure of 1 micron. % C calculated, 50.67, found 50.41; % H calculated, 9.92, found 9.87. [i] Supercooled.

Table II. Physical Properties of Silicate Derivatives of Aliphatic and Aromatic Diols

(RO)$_3$SiOR′OSi(OR)$_3$			Density, d_4^{20}	Refractive Index, n_D^{20}	Molar Refraction,[a] MR_D^{20}		Boiling Point		Viscosity, Cs. at ° F.				ASTM Slope[b]			Silicon, %	
No.	R	R′			Calcd.[b]	Found	° C.	Mm. Hg	−65	−40	100	210	100–210° F.	−40–210° F.	−65–210° F.	Calcd.	Found
1	2-Butyl	CH_2CH_2	0.9523	1.4172	147.9	146.6	147–148	1	480	145	6.50	2.37	0.65	0.65	0.65	10.12	10.41
2	*tert*-Butyl	CH_2CH_2	0.9261	1.4074	147.9	147.6	149	1	...	...	19.7	3.96	0.76	...	...	10.12	9.94
3	2-Ethyl-1-butyl	CH_2CH_2	0.9049	1.4320	203.4	207.3	138–139	0.002	315	98	4.89	1.86	0.70	0.69	0.70	...	...
4	2-Butyl	$CH_2CH(CH_3)$	0.9380	1.4158	152.5	152.2	162	1	476	121	5.88	2.22	0.64	0.65	0.66	9.87	9.74
5	2-Butyl	$CH_2CH_2CH_2$	0.9449	1.4171	152.5	151.5	162–164	1	347	98	5.15	1.96	0.68	0.67	0.68	9.87	9.66
6	2-Butyl	$CH_2CH_2CH_2CH_2$	0.9340	1.4184	157.1	157.4	188	1	407	127	5.92	2.18	0.67	0.66	0.66	9.64	9.61
7	2-Butyl	$(CH_3)CHCH(CH_3)$	0.9368	1.4180	157.1	156.8	161–162	1	1900	455	9.61	2.84	0.70	0.68	0.68	9.64	9.58
8	2-Ethyl-1-butyl	$(CH_3)CHCH_2CH(CH_3)$	0.9223	1.4349	217.3	216.5	232–234	0.6	3680	572	11.1	3.45	0.62	0.64	0.66	7.34	7.42
9	2-Propyl	$(CH_3)CHCH_2CH_2CH(CH_3)$	0.9244	1.4040	138.6	139.4	144–146	1.3	246	78	4.26	1.65	0.72	0.71	0.72	10.66	10.81
10	2-Butyl	$CH_2CH_2CH_2CH_2CH_2CH_2$	0.9305	1.4208	166.4	166.5	197–198	1	673	184	6.88	2.44	0.65	0.66	0.66	9.19	9.21
11	2-Ethyl-1-butyl	$(CH_3)CHCH_2CH_2CH(CH_3)$	0.9226	1.4359	221.9	220.8	170	0.1	2790	616	11.8	3.66	0.61	0.63	0.63	7.21	7.39
12	2-Butyl	$CH_2CH(CH_3)CH(CH_2CH_3)$	0.9329	1.4212	166.4	166.2	182–184	1	1510	392	9.35	2.95	0.65	0.65	0.65	9.19	9.14
13	2-Butyl	$(CH_2CH_2CH_2CH_2CH_2)_2$	0.9229	1.4258	184.9	185.1	204–205	0.4	1530	382	9.96	3.24	0.62	0.63	0.63	8.42	8.42
14	2-Butyl	$CH_2CH_2OCH_2CH_2$	0.9592	1.4202	158.9	158.1	177–178	1	490	144	5.76	2.13	0.68	0.68	0.68	9.38	9.19
15	2-Butyl	$CH_2CH_2SCH_2CH_2$	0.9636	1.4318	165.0	165.5	194	1	704	191	6.65	2.40	0.65	0.66	0.67	9.13	9.18
16	2-Propyl		0.9858	1.4325	135.2	136.8	139–140	0.5	Solid	Solid	5.38	1.96	0.70	...	...	10.84	10.88
17	2-Butyl		0.9757	1.4430	163.0	163.8	184–186	0.2	1380	310	8.48	2.83	0.64	0.65	0.66	9.32	9.42
18	2-Propyl		0.9857	1.4338	135.2	137.0	156	1	320	96	4.63	1.74	0.73	0.71	0.72	10.84	10.86
19	2-Propyl		1.0297	1.4420	140.0	142.2	166	1	1170	248	6.23	2.09	0.73	0.73	0.73	10.14	10.20
20	2-Butyl		0.9749	1.4431	163.0	164.0	179–180	0.3	1150	280	7.53	2.55	0.66	0.67	0.68	9.32	9.24

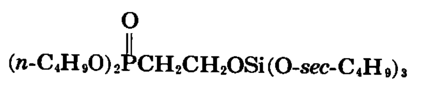
[a] Calculations based on bond refraction values (*11*). Agreement: Average and standard deviations = ±0.35 and 0.63%, respectively.

[b] Measured slope of line plotted on ASTM kinematic viscosity–temperature chart D-341 (*2*).

Table III. Physical Properties of Miscellaneous Silicate Derivatives

No.	Compound	Density, d_4^{20}	Refractive Index, n_D^{20}	Molar Refraction, MR_D^{20}		Boiling Point		Viscosity, Centistokes at ° F.				ASTM Slope[a]			Analysis, %		
				Found	Calcd.[b]	° C.	Mm. Hg	−65	−40	100	210	100–210° F.	−40–210° F.	−65–210° F.	Element	Calcd.	Found
1	Dibutyl-2-[tri(2-butoxy)-siloxy]ethane phosphonate	0.9675	1.4251	...	...	154–158	1	420	128	4.88	1.79	0.75	0.72	0.70	P	6.41	6.61
2	Dibutyl-4-[tri-(isopropoxy)-siloxy]-butane phosphonate	...	1.4128	...	...	141–144	0.5	79.9	30.0	2.8[c]	1.30	0.72	0.70	0.72	P	6.60	6.62
3	Bis(dibutylphosphono-di-(*tert*-pentoxy)silane	...	1.4280	...	...	127–129	0.1	83.2	31.6	2.2[c]	1.03	0.81	0.81	0.81	P	10.6	11.9
4	Tetra(1-diethylamino)-2-propoxy)-silane	0.9096	1.4413	159.5	159.7	190–192	1.2	...	...	6.79	2.17	0.74	...	...	...	...	...
5	Tetrakis(5-diethylamino-2-pentoxy)silane	0.9038	1.4508	171.8	168.9	225	0.3	...	2860	13.4	3.32	0.73	0.75	...	...	...	...
6	1-[Tri(2-butoxy)siloxy]-4-bromobenzene	1.1307	1.4704	103.6	102.4	146	1	574	121	3.44	1.34	0.82	0.83	0.84	...	...	...
7	1-[Tri(2-butoxy)siloxy]-2,4-dibromobenzene	1.2866	1.4880	111.6	110.1	173	2.5	3500	462	5.03	1.64	0.81	0.86	0.88	Si	5.62	5.68
8	1-[Tri(2-butoxy)siloxy]-4-methoxybenzene	0.9887	1.4550	101.7	101.2	140–142	1	526	124	3.82	1.42	0.82	0.81	0.82	...	...	...
9	Tetrakis(1-carbethoxy-ethoxy)-silane	1.1220	1.4265	113.5	114.5	167–169	0.6	24800	1570	6.60	0.90	1.67	1.20	1.18	C H	48.40 7.30	48.15 7.29

[a] Measured slope of line plotted on ASTM kinematic viscosity–temperature chart D-341 (2). [b] Calculations based on bond refrac- ±0.95 and 1.20%, respectively. [c] Values obtained from plot of viscosities at 210°, −40°, and −65° F.

1

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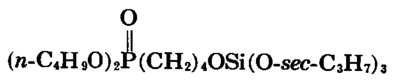
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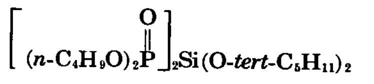
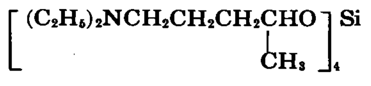

$\left[(n\text{-}C_4H_9O)_2\overset{O}{\overset{\|}{P}}\right]_2Si(O\text{-}tert\text{-}C_5H_{11})_2$

4

$\left[(C_2H_5)_2NCH_2\underset{CH_3}{\underset{|}{C}}HO\right]_4Si$

5

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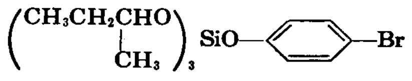
6


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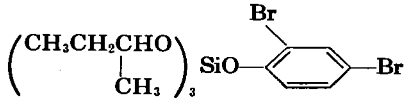

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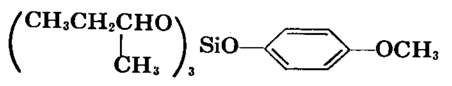

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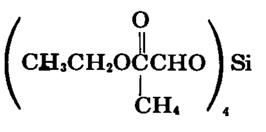
$\left(CH_3CH_2O\overset{O}{\overset{\|}{C}}\underset{CH_4}{\underset{|}{C}}HO\right)_4Si$

Table IV. Effect of Alkoxy Group and Siloxane Chain on Viscosity-Temperature Properties of Silicate Esters

Alkoxy Group	ASTM Slope (100-210° F.)		
	Silane	Disiloxane	Trisiloxane
2-Propoxy	0.93	0.73	...
2-Butoxy	0.87	0.64	0.53
4-Methyl-2-pentoxy	0.82	0.62	0.52
2-Ethyl-1-butoxy (9)	0.75	0.56	0.45
2-Ethyl-1-hexoxy	0.71	0.58	...

Compound	ASTM Slope (100–210° F.)
Tetra(2-butoxy)silane	0.87
Hexa(2-butoxy)disiloxane	0.64
Octa(2-butoxy)trisiloxane	0.53
Dimethyl silicone (20-cs. Dow Corning-200)	0.38

This effect of the growing -Si-O-Si "backbone" is further illustrated by the outstanding viscosity-temperature behavior of the silicone polymers. As the backbone becomes larger, its influence on the slope overshadows the effect of the alkyl groups, as can be seen in Table IV. These results are in agreement with, and extend, the findings of Morgan and Olds (*8*).

HYDROLYTIC STABILITY

Test Method. The hydrolytic stability test was conducted in the presence of air as follows: A borosilicate glass vial of 10-ml. capacity, fitted to a 4-mm. diameter glass tube condenser by a standard-taper joint, was charged with 2 ml. of silicate ester and 2 ml. of distilled water or acid solution. The vial was then placed on a steam plate operating at 110° C. The briskly boiling water bubbled through the supernatant layer of silicate, thus establishing good contact between the two phases.

The beginning of the hydrolysis was marked by a drop in viscosity and, simultaneously, by haze formation. This was ordinarily followed, after a short time, by voluminous precipitation of gelatinous silica, a sign of massive decomposition. The time (in hours) required to produce the latter was the criterion of relative hydrolytic stability. The reproducibility of the test was ±10%.

Results. Tetraalkoxysilanes containing more than one *tert*-alkoxy group are remarkably stable (*7, 9*). This stabilizing effect is not limited to *tert*-alkoxy groups. As shown in Table V, all the alkyl groups which impart some degree of steric hindrance give a corresponding degree of resistance to hydrolysis. Thus, the structural features which make certain silicate esters more difficult to synthesize also promote their hydrolytic stability. This effect is attributed to shielding of the Si-O bond by nearby alkyl groups.

Straight-chain *p*-alkyl silicates were easily hydrolyzed. Primary alkyl groups with branching on the second carbon atom from the Si-O bond impart a significantly higher stability. Secondary alkyl silicates and compounds containing two or three *tert*-alkyl groups can withstand prolonged contact with boiling water. These considerations apply equally well to the alkoxysilanes, disiloxanes, and trisiloxanes. The increase in the number of Si-O units has little or no effect on hydrolytic stability; the important factor is the nature of the alkyl group.

The gelation of silicates in contact with water is accelerated by acid and atmospheric oxygen. Times to gelation were longer when air was excluded from the system, and aromatic amine oxidation inhibitors did not delay gelation under this condition (*5*). When air was present, these oxidation inhibitors retarded gelation, as shown in Table VI for phenyl-1-naphthylamine.

A similar effect was observed with phenothiazine. The accelerated rate of decomposition in the presence of acid is illustrated by Table VII.

Table V. Stability of Silicate Esters in Boiling Water in Presence of Air

Compound	Hours to Gelation
Silanes	
Tetra(ethoxy)	<2
Tetra(1-butoxy) (*8*)	32
Tetra(1-hexoxy) (*8*)	25
Tetra(1-octoxy) (*8*)	30
Tetra(2-methyl-1-butoxy) (*9*)	88
Tetra(2-ethyl-1-butoxy) (*9*)	75
Tetra(2-ethyl-1-hexoxy)	72
Di(2-butoxy)di(2-ethyl-1-butoxy)	150
Tetra(2-butoxy)	>500
Tetra(2-octoxy)	700
Tetra(4-methyl-2-pentoxy)	1150
1-Butoxytri(*tert*-butoxy)	>236
2-Butoxytri(*tert*-butoxy)	>236
tert-Butoxytri(2-butoxy)	>600
Di(*tert*-butoxy)di(2-ethyl-1-hexoxy)	1850
tert-Butoxytri(2-ethyl-1-hexoxy)	700
tert-Butoxytri(2-octoxy)	>750
Disiloxanes	
Hexa(2-butoxy)	>300
Hexa(2-ethyl-1-butoxy) (*9*)	120
Hexa(2-ethyl-1-hexoxy)	95
Others	
Octa(2-butoxy)trisiloxane	1600
Octa(2-ethyl-1-butoxy)trisiloxane	126
1,2-Bis[tri(2-ethyl-1-butoxy) silyl]ethane	140
Tri(*tert*-butoxy)silanol (*14*)	>300

Table VI. Effect of 1% Phenyl-1-naphthylamine on Stability of Silicate Esters in Boiling Water in Presence of Air

	Hours to Gelation	
Compounds	No additive	With additive
Di(2-butoxy)di(2-ethyl-1-butoxy)silane	150	280
Tetra(2-ethyl-1-butoxy)silane (*9*)	75	240
Tetra(2-ethyl-1-hexoxy)silane	72	180

Table VII. Stability of Silicate Esters in Presence of Air in Boiling 0.5*N* Hydrochloric Acid and in Water

	Hours to Gelation	
Compounds	Water	Acid
Tetra(2-butoxy)silane	>500	21
2-Butoxytri(*tert*-butoxy)silane	>236	45
tert-Butoxytri(2-butoxy)silane	>600	45

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