

Tetraalkylsilanes: A New Class of Wide Liquid Range Fluids

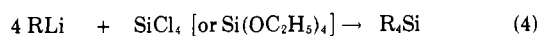
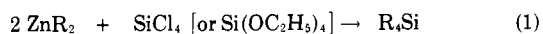
GEORGE BAUM and CHRIST TAMBORSKI

Materials Central, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio

THE ADVENT of new, higher performance jet aircraft has created a pressing need for heat-stable lubricants and fluids. High speed and high load operation of aircraft components have imposed upon the lubricant the additional burden of dissipating considerable amounts of frictional heat.

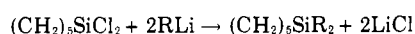
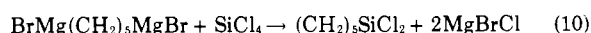
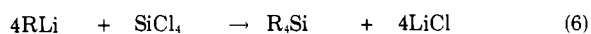
This laboratory began a general investigation of the synthesis and properties of tetraalkylsilanes in 1954. Although the materials are principally hydrocarbon in nature, the relatively simple synthetic methods available for producing a wide variety of pure, related materials allow a systematic study of the effect of molecular structure on such important fluid properties as liquid range, viscosity, volatility, and lubricity.

Low molecular weight tetraalkylsilanes have been known for many years (6) and have since been prepared by a variety of procedures (4, 6-8, 11). Some of the synthetic procedures reported in the literature for various tetraalkylsilanes are summarized below.



Synthesis procedures and physical properties of high molecular weight, high boiling tetraalkylsilane fluids have been investigated in this laboratory as part of a general synthesis program (14, 16).

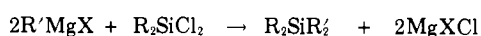
The general procedures for the synthesis of small quantities of various types of tetraalkylsilanes in this laboratory are:



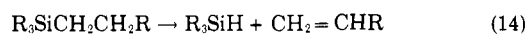
The alkyllithium procedure was preferred over other reported synthesis procedures because the organolithium intermediate is more reactive than the corresponding Grignard reagent and is easier to handle than the organozinc intermediates. Being more reactive, the organolithium intermediate produced tetraalkylsilanes in excellent yields (73 to 89%) and in purer quality than by the Grignard method. Since the Grignard reagent is not as reactive as the organolithium reagent, it is useful in the synthesis of partially alkylated chlorosilane intermediates as shown in Equations 7, 8, and 10, where complete alkylation is undesirable.

The preparation of larger quantities (1 to 15 gallons) of high molecular weight, high boiling tetraalkylsilane fluids was later reported by Harris and others (10). They preferred

the Grignard procedure because of the relatively lower cost of Grignard reagents to organolithium reagents. The various types of tetraalkylsilanes were prepared by the following procedures:



Generally the Grignard route produced silanes containing various impurities as Si-H, Si-OH, and Si-O-Si-containing compounds. These impurities are due to the less reactive Grignard reagent which does not completely react with all the chlorosilane starting material. The unreacted chlorosilane in the work-up of the product yields the Si-OH type impurities which later can be converted partially to Si-O-Si type impurities through condensation. The Si-H type impurity is believed to be formed through some reductive action of the Grignard reagent on chlorosilanes or through thermal cleavage of the Si-C bond during distillation to yield an olefin and an Si-H compound.



Excess Grignard reagent is converted to a hydrocarbon during work-up of the reaction.

Detection of the silicon containing impurities is readily accomplished by infrared spectroscopy. Si-H compounds show a strong sharp band at 2100 cm^{-1} and Si-O compounds have a strong broad band at 1055 to 1024 cm^{-1} (2).

Purification of a reaction product containing the above contaminants is difficult. Fractional distillation will often concentrate the hydrocarbon in early fractions and siloxanes in tail fractions. Hydrocarbons may also be removed by fractional crystallization. Current work at this laboratory indicates that column chromatography may be used for purification.

PROPERTIES

Viscosity and Pour Point. The alkyl groups in the three series prepared were varied from methyl to octadecyl. In the dodecyltri(alkyl)silanes, a minimum pour point below -76°F . exists between dodecyltri(pentyl)silane and dodecyltri(heptyl)silane. The first nine members of the series all poured below -60°F . The viscosities of the cyclopentamethylenedialkylsilanes were higher than those of the other two series with equivalent molecular weights. A minimum pour point of -35°F . in the didodecyltrialkylsilane series was observed for di(dodecyl)di(octyl)silane. The liquid properties of these three series are given in Tables I to II.

As insufficient quantities of the silanes were prepared in the laboratory for extensive evaluation studies, 11 silane fluids were obtained from commercial sources. The physical properties of these fluids are given in Table III and some general properties are given in Tables IV to V.

Viscosities and pour points of commercially prepared fluids were comparable to those obtained on laboratory samples. Cyclopentamethylene derivatives obtained from commercial sources were about 10% more viscous than

Table I. Liquid Properties of Alkylsilanes

Alkyl	Pour Point, ° F.	Kinematic Viscosity, Centistokes					
		-65° F.	-40° F.	0° F.	100° F.	210° F.	400° F.
Dodecyltrialkylsilanes							
CH ₃ ^a	48	3.23	1.34	...
C ₂ H ₅	12	24.2	4.16	1.58	...
n-C ₃ H ₇	-49	...	192.2	44.8	5.63	2.33	...
n-C ₄ H ₉	-56	...	470.5	91.1	8.37	2.35	...
n-C ₅ H ₁₁	<-76	2720	671.2	123.0	10.49	2.80	0.87
n-C ₆ H ₁₃	<-76	3465	875.5	160.8	13.23	3.35	0.99
n-C ₇ H ₁₅	<-76	5345	1294	225.8	16.44	3.90	1.21
n-C ₉ H ₁₉	-34.6	343.8	21.9	4.89	1.56
n-C ₁₀ H ₂₁	8.6	27.0	5.66	1.57
n-C ₁₁ H ₂₃	35.6	31.0	6.25	1.62
n-C ₁₂ H ₂₅	55.4	35.1	6.96	1.84
n-C ₁₄ H ₂₇	71.6	44.7	8.44	2.16
Cyclopentamethylenedialkylsilanes							
C ₂ H ₅ ^b	<-60	9.93	5.98	3.35	1.22	0.68	...
n-C ₃ H ₇	<-60	26.6	12.24	4.95	1.50	0.77	...
n-C ₄ H ₉	<-60	131.2	41.6	11.61	2.28	0.97	...
n-C ₅ H ₁₁	<-60	314.4	91.1	21.0	3.17	1.22	...
n-C ₆ H ₁₃	<-60	553.0	...	32.7	4.31	1.50	...
n-C ₇ H ₁₅	<-60	1081.0	278.4	54.4	5.70	1.80	0.72
n-C ₈ H ₁₇	<-60	1739.5	418.3	82.8	7.26	2.19	0.81
n-C ₉ H ₁₉	<-60	2751.8	630.4	108.1	9.16	2.56	0.89
n-C ₁₀ H ₂₁	<-60	3870	829.4	138.2	11.42	2.90	1.02
n-C ₁₁ H ₂₃	-26	199.4	13.90	3.42	1.09
n-C ₁₂ H ₂₅	-31	428.5	16.92	4.00	1.28
n-C ₁₄ H ₂₉	-12	23.9	5.25	1.51
n-C ₁₆ H ₃₃	-1	31.5	6.37	1.81
n-C ₁₈ H ₃₇	21	40.5	7.80	2.18

^a Also reported (17).^b Also reported (9).

samples prepared in this laboratory. The average deviation of the 100° F. viscosity between commercial and laboratory samples was 2.5%. At 210° F. the average deviation was 5%. A comparison of pour points is possible for only two of the samples. Commercial samples which contained more siloxane contaminant than laboratory samples, as shown by infrared spectroscopy, possessed lower pour points. Completely symmetrical silanes tetradodecylsilane and tetraundecylsilane have the highest pour points. A small amount of a siloxane will drastically lower the pour point of the fluid and is believed to account for the discrepancies noted.

The viscosity index (*I*) of the silanes in Table IV ranged from 124 to 155. Diphenyldi(dodecyl)silane possessed the lowest viscosity index, completely symmetrical silanes possessed intermediate values, and mixed symmetrical silanes possessed values ranging from 152 to 155.

High temperature viscosities were measured using the

Cannon-Fenske viscometer immersed in a well-stirred silicone oil bath. At 700° F. the temperature of the bath was controlled to $\pm 1.0^\circ$ F. The viscometer constant was corrected for the thermal expansion of fluid. The kinetic energy coefficient was not evaluated. At 700° F., the viscosity of the higher molecular weight silanes shown in

Table II. Liquid Properties of Didodecylalkylsilanes

Alkyl	Pour Point, ° F.	Kinematic Viscosity, Centistokes			
		0° F.	100° F.	210° F.	400° F.
CH ₃	75	...	9.96	2.95	1.03
C ₂ H ₅	68	...	11.28	3.19	1.06
n-C ₃ H ₇	41	...	14.76	3.68	1.10
n-C ₄ H ₉	39	...	17.27	4.08	1.16
n-C ₅ H ₁₁	30	...	18.77	4.29	1.23
n-C ₆ H ₁₃	7	...	21.22	4.72	1.42
n-C ₈ H ₁₇	-9	355.8	21.91	4.86	1.43
n-C ₉ H ₁₉	-35	407.8	24.80	5.36	1.57
n-C ₁₀ H ₂₁	9	...	29.50	6.10	1.66
n-C ₁₁ H ₂₃	28	...	32.10	6.68	1.75
n-C ₁₂ H ₂₅	55	...	35.10	6.96	1.84
n-C ₁₄ H ₂₉	54	...	41.80	8.14	2.11
n-C ₁₈ H ₃₇	54	...	47.40	8.90	2.34

Table III. Physical Properties of Commercially Prepared Silanes

Silane	Boiling Point, ° C./Mm. Hg	Refractive Index, n_D^{25}	Density, 25°/4° C.
(C ₆ H ₅) ₂ Si(C ₁₂ H ₂₅) ₂ ^a	237-243/0.035	1.5060	0.905
(C ₁₂ H ₂₅) ₄ Si ^a	280/0.13	1.4622	0.8276
C ₁₈ H ₃₇ Si(C ₈ H ₁₇) ₃ ^b	208/0.075	1.4620	0.834
C ₁₈ H ₃₇ Si(C ₁₀ H ₂₁) ₃ ^b	255/0.06	1.4649	0.8357
C ₁₂ H ₂₅ Si(C ₁₀ H ₂₁) ₃ ^b	200/0.10	1.4608	0.8220
(C ₁₂ H ₂₅) ₃ Si(C ₈ H ₁₇) ₂ ^b	170/0.075	1.4601	0.8191
C ₁₂ H ₂₅ Si(C ₆ H ₁₃) ₃ ^b	165/0.06	1.4558	0.814
C ₁₂ H ₂₅ Si(C ₅ H ₁₁) ₃ ^b	148/0.06	1.4543	0.812
C ₈ H ₁₇ Si(C ₈ H ₁₇) ₂ ^b	140/0.1	1.4631	0.8344
C ₅ H ₁₀ Si(C ₁₀ H ₂₁) ₂ ^b	160/0.1	1.4649	0.8637

^a Metal and Thermit Corp.^b Olin-Mathieson Chemical Corp.

Table IV ranged from 0.62 to 0.66 cs. The viscosity of the lighter silanes was not measured above 400° F. because of their volatility.

Thermal Stability. Tetraalkylsilanes show good resistance to thermal degradation up to temperatures of 700° F. After exposure at 700° F. for 9 hours in sealed borosilicate glass ampoules, the silanes exhibited minor changes in viscosity of 4 to 6%.

The temperature where decomposition reactions are detectable is about 600° F. This value was obtained from a

discontinuity occurring in a plot of the log of the vapor pressure vs. the reciprocal of the absolute temperature (Figure 1).

Vapor pressure was determined in an isoteniscope of the Smith and Menzies design (15). Blake and coworkers (3) have reported 660° to 670° F. as the thermal decomposition point based on the isothermal rate of pressure rise in a similar apparatus.

Oxidative Stability. Uninhibited silane fluids showed only moderate resistance, at 500° F., to oxidation in the presence of metal catalysts which included copper, aluminum, silver, steel, and titanium. Although metal corrosion was not observed, considerable darkening of the fluid occurred as well as neutralization number changes of 1 to 3 and viscosity increases of 25 to 50% have been observed as shown in Table VI. The procedure used was a small scale modification of the apparatus described in MIL-L-9236 (13).

Some success in the inhibition of the oxidation of silanes was reported by Cole (5) using organoselenium compounds. However, these materials were corrosive to copper and silver.

The lack of a suitable oxidation inhibitor restricts considerably the use of silane fluids where a severe thermal-oxidative environment exists.

Flammability. The silanes exhibit very high flash and fire points. Even the light cyclopentamethylenedioctylsilane has a flash point of 380° F. The other fluids possessed flash points up to 555° F. The autogenous ignition temperatures ranged from 610° to 775° F. ASTM D 9252 and D 286-30 procedures were used (1).

Lubricity. The ability of the silanes to lubricate sliding surfaces in plane contact was investigated in the 4-ball wear machine (12). The effect of varying speed, load, and temperature was studied. The resulting data are given in

Table VII. At low loads, up to 10 kg., effective thin film lubrication is provided by the fluids. At 40-kg. load, however, the wear scars exceed 1.0 mm. in diameter and are elongated, indicating that seizure and tearing of the wearing surfaces occurred. At 400° F. and 10-kg. load, the border line between film collapse and thin film lubrication is

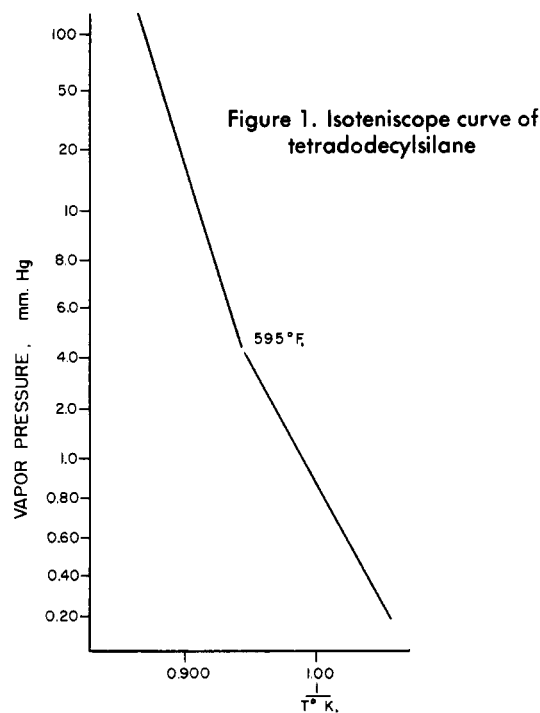


Table IV. General Properties of Commercially Prepared Silanes

Laboratory Tests	(C ₁₂ H ₂₅) ₄ Si	(C ₈ H ₁₇) ₂ Si (C ₁₂ H ₂₅) ₂	C ₁₈ H ₃₇ Si (C ₈ H ₁₇) ₃	C ₁₈ H ₃₇ Si (C ₁₀ H ₂₁) ₃	(C ₁₀ H ₂₅) ₂ Si (C ₁₂ H ₂₅) ₂	(C ₁₂ H ₂₅) ₂ Si (C ₈ H ₁₇) ₂	(C ₁₁ H ₂₃) ₄ Si
Spontaneous ignition temp., ° F.	775	690	790	750	750	750	760
Flash point, ° F.	555	530	520	545	535	520	545
Fire point, ° F.	625	580	590	595	575	565	600
Pour point, ° F.	20	-25	-30	-20	-35	-45	0
Viscosity, centistokes							
0° F.		1024.9	516.9	689.1	665.1	442.8	
100° F.	34.58	37.2	27.5	33.9	26.4	23.1	29.26
210° F.	6.37	6.2	5.76	6.8	5.6	5.0	6.11
400° F.	1.66	1.6	1.58	1.79	1.56	1.41	1.57
550° F.	0.90	0.91	0.90	0.95	0.91	0.89	0.95
700° F.	0.63	0.65	0.66	0.69	0.64	0.63	0.62
ASTM slope 210/100° F.	0.66	0.69	0.62	0.62	0.61	0.66	0.62
Viscosity index	139	124	154	152	154	155	148
Thermal stability, 700° F., 9 hr., sealed tube, viscosity change at 210° F.	-6.9%	-8.1%	-5.03%	-6.0%	-5.7%	-4.0%	-5.7%
Neut. No. change	0.09	0.07	0.0	0.0	0.0	0.0	0.0
Appearance after test	No change	No change	No change	No change	No change	No change	No change

Table V. General Properties of Commercially Prepared Silanes

Test	C ₁₂ H ₂₅ Si(C ₆ H ₁₃) ₃	C ₁₂ H ₂₅ Si(C ₈ H ₁₇) ₃	C ₈ H ₁₇ Si(C ₁₀ H ₂₁) ₂	C ₈ H ₁₇ Si(C ₈ H ₁₇) ₂
Flash point, ° F.	435	395	450	380
Fire point, ° F.	465	425	490	415
Pour point, ° F.	-85	-85	-70	-85
Spontaneous ignition temp., ° F.	665	650	700	610
Viscosity, centistokes				
-65° F.	5463.4	3158.4	8987.7	2317.8
-40° F.			1743.2	546.3
100° F.	14.34	10.95	15.0	8.5
210° F.	3.65	2.73	3.7	2.4
400° F.	0.84	0.89	1.08	0.80

Table VI. Oxidative Stability of Commercially Prepared Silanes

Laboratory Tests	$(C_{12}H_{25})_4Si$	$(C_6H_5)_2Si$ $(C_{12}H_{25})_2$	$C_{18}H_{37}Si$ $(C_8H_{17})_3$	$C_{18}H_{37}Si$ $(C_{10}H_{21})_3$	$C_{12}H_{25}Si$ $(C_{10}H_{21})_3$	$(C_{12}H_{25})_2Si$ $(C_8H_{17})_2$	$(C_{11}H_{23})_4Si$
	Oxidation-Corrosion, 500° F., 24 Hr., 5 Liters Air/Hr., Wt. Change, Mg./Sq. Cm.						
Copper			0.104	0.056	0.114	0.064	0.072
Aluminum	0.02	0.06	0.032	0.016	0.016	0.0	0.088
Silver	0.14	0.04	0.048	0.024	0.032	0.009	0.184
Titanium	0.06	0.0	0.0	0.0	0.0	0.006	0.136
Steel	0.06	0.08	0.018	0.104	0.104	0.152	0.0
Appearance of Metals							
Copper			Slight corrosion	Stain	Slight corrosion	Tarnish	Tarnish
Aluminum	No change	No change	No change	No change	No change	No change	No change
Silver	Tarnish	Tarnish	Stain	Stain	Tarnish	Tarnish	Coated
Titanium	Tarnish	Slight tarnish	Tarnish	Tarnish	Tarnish	Tarnish	Tarnish dark
Steel	Dark stain	Slight tarnish	Slight corrosion	Slight corrosion	Slight corrosion	Slight corrosion	Coated
Appearance of oil after test	Solid	Black, no solids	Dark green, no solids	Dark green, no solids	Green-brown, no solids	Green-brown, no solids	Black, solids
% vis. change at 210° F.		48.3	47.5	33.9	26.3	34.2	45.7
Neut. No. change		0.0	1.4	2.8	1.9	1.5	2.9
% evaporation loss		-6.7	-5.8	-5.8	-10.8	-6.6	-5.0

approached. Perhaps there is some contribution to film strength by lubricant viscosity. Increasing the running speed of the machine to 1200 r.p.m. at 40-kg. load results in drastic wearing of the stationary M-10 bearings. A common antiwear agent, tricresyl phosphate, adequately reduced wear at 167° F., but at 400° F. it was not very effective. The M-10 steel bearings are, however, more difficult to lubricate by chemically active agents.

CONCLUSIONS

Tetraalkylsilanes may be conveniently prepared in a wide range of molecular weights and structures. Optimum physical properties are reached in the molecular weight region of 600. Completely symmetrical substitution yields silanes of too high a pour point to be of practical value in

and additive susceptibility at 500° F. are poor. Thermal degradation is first observed at 600° F. It is not yet clear whether the Si-C bond cleavage or the C-C bond cleavage is the predominant degradation reaction. Silane fluids provide effective thin film lubrication under moderate operating conditions. At high speed and high load conditions, film collapse occurs and antiwear agents are required.

Additional structural modification may bring about improved low temperature properties in high molecular weight silanes.

ACKNOWLEDGMENT

The authors acknowledge the assistance of the Lubricants Branch, Materials Central, Wright Air Development Division, in the determination of many physical properties reported.

LITERATURE CITED

- (1) Am. Soc. Testing Materials, Philadelphia, "ASTM Standards on Petroleum Products and Lubricants," 1955.
- (2) Bellamy, L.J., "Infrared Spectra of Complex Molecules," Wiley, New York, 1954.
- (3) Blake, E.S., Edwards, J.W., Hammann, W.C., Reichard, T.E., *WADC Tech. Rept. 57-437*, ASTIA No. 142188, 36 (1957).
- (4) Bygdén, Arthur, *Ber. 44B*, 2640 (1911).
- (5) Cole, J.W., *WADC Tech. Rept. 53-293*, Part VIII, ASTIA No. 150994, 9 (1958).
- (6) Friedel, Charles, Craft, J.M., *Ann. Chem.* **259**, 334 (1870).
- (7) Gilman, Henry, Clark, R.N., *J. Am. Chem. Soc.* **68**, 1675 (1946).
- (8) Gilman, Henry, Massie, S.P., Jr., *Ibid.*, **68**, 1128 (1946).
- (9) Gruttner, Gerhard, Wiernik, Maximilian, *Ber.* **48**, 1474 (1915).
- (10) Harris, E.E., Milnes, F.J., Rayner, R.J., Dombchewsky, R., *WADC Tech. Rept. 57-181*, ASTIA No. 151074 (1958).
- (11) Kipping, F.S., *Proc. Chem. Soc.* **20**, 15 (1904).
- (12) Larsen, R.G., *Lubrication Eng.* **1**, 35 (1945).
- (13) Military Specification MIL-L-9236, Lubricating Oil, Aircraft Gas Turbine, High Temperature (1954).
- (14) Rosenberg, Harold, Groves, J.D., Tamborski, Christ, *J. Org. Chem.* **25**, 243 (1960).
- (15) Smith, Alexander, Menzies, A.W.C., *J. Am. Chem. Soc.* **32**, 1413 (1910).
- (16) Tamborski, Christ, Rosenberg, Harold, *J. Org. Chem.* **25**, 246 (1960).
- (17) Whitmore, F.C., *et al.*, *J. Am. Chem. Soc.* **68**, 475 (1946).

RECEIVED for review March 8, 1960. Accepted August 23, 1960.

Table VII. Four-Ball Wear Machine Data on Octadecyltridecylsilane

Conditions	Load, Kg. ^a		
	4	10	40
Av. Wear Scar Diameter, Mm.			
167° F., 1200 r.p.m., SAE 52100 bearings			
Silane	0.39	0.39	0.97
Silane, 3% TCP	...	0.31	0.51
400° F., 600 r.p.m., M-10 bearings			
Silane	0.42	0.58	1.34
Silane, 3% TCP	1.22
400° F., 1200 r.p.m., M-10 bearings			
Silane	...	0.87	3.75
Silane, 3% TCP	1.41

^aRunning time, 2 hr.

fluid applications. The cyclopentamethylenedialkylsilanes require very long alkyl chains to reduce volatility, thus resulting in high pour point compounds. The didodecyl-dialkylsilanes possess the lowest pour points of the three series studied in the molecular weight region of interest.

There is little difference in the oxidative, thermal, and lubricating character of the silanes. Oxidative resistance