Kirk-Othmer Encyclopedia of Chemical Technology.

SILICON COMPOUNDS, SILICON ESTERS

Silicon esters are silicon compounds that contain an oxygen bridge from silicon to an organic group, ie, Si–OR. The earliest reported organic silicon compounds contain four oxygen bridges and are often named as derivatives of orthosilicic acid, $Si(OH)_4$. The most conspicuous material is tetraethyl orthosilicate [78-10-4], $Si(OC_2H_5)_4$. The advent of organosilanes that contain silicon–carbon bonds, Si–C, initiated an organic nomenclature by which compounds are named as alkoxy derivatives. For example $Si(OC_2H_5)_4$ becomes tetraethoxysilane. The compound $CH_3Si(OCH_3)_3$ is named methyltrimethoxysilane. Whereas the latter usage is preferred, the literature even in the mid-1990s, particularly in ceramics (qv) technology, contains the older terms. Acyloxysilanes, eg, tetraacetoxysilane, $Si(OOCCH_3)_4$, are also members of this class. The chemistry and applications of acyloxysilanes are significantly different from those of the alkoxysilanes.

Applications for tetraalkoxysilanes cover a broad range. These compounds are classified roughly according to whether the Si–OR bond is expected to remain intact or to be hydrolyzed in the final application. Applications in which the Si–OR bond is hydrolyzed include binders for foundry-mold sands used in investment and thin-shell castings, binders for refractories (qv), resins, coatings (qv), sol–gel glasses, cross-linking agents, and adhesion promoters. Applications in which the Si–OR bond remains intact include heat-transfer and hydraulic fluids (qv). In general, the lower molecular weight compounds, eg, tetraethoxysilane and tetramethoxysilane, are used in reactive applications, whereas compounds such as tetra-2-ethylhexoxysilane are associated with mechanical applications. Methyl- and phenyltrialkoxysilanes are primarily used in the production of silicone resins and coatings. Longer-chain materials, eg, propyl-, isobutyl-, and octyltrialkoxysilanes, are used in hydrophobic coatings, primarily for masonry and concrete. The hydridoalkoxysilanes, triethoxysilane and trimethoxysilane, are intermediates for the production of organofunctional silanes. Organosilane esters in which there is a functional or reactive substitution of the organic radical are used as coupling agents. Tetraethoxysilane and its polymeric derivatives account for $>75\%$ of all production of nonfunctional silane esters.

1. Properties

The tetraalkoxysilanes possess excellent thermal stability and liquid behavior over a broad temperature range that widens with length and branching of the substituents. The physical properties of the silane esters, particularly the polymeric esters containing siloxane bonds, ie, Si–O–Si, are often likened to the silicone oils. These have low pour points and similar temperature–viscosity relationships. The alkoxysilanes generally have sweet, fruity odors that become less apparent as molecular weight increases. With the exception of tetramethoxysilane, trimethoxysilane, triethoxysilane, and a few closely related compounds that can be absorbed into corneal tissue, causing eye damage, the alkoxysilanes generally exhibit low levels of toxicity.

The physical properties of commercial alkoxysilanes are provided in Table 1. Two classes of silane esters have very distinct properties and are generally considered apart from alkoxysilanes. Silatranes are compounds derived from trialkanolamines and have silicon–nitrogen coordination. These are generally hydrolytically

Table 1. Physical Properties of Silane Esters[a]

Compound	CAS Registry Number	Formula	Boiling point[b], °C
		Monoorganoalkoxysilanes	
methyltrimethoxysilane	[1185-55-3]	$CH_3Si(OCH_3)_3$	102–103
methyltriethoxysilane	[2031-67-6]	$CH_3Si(OC_2H_5)_3$	141–143
ethyltrimethoxysilane	[5314-55-6]	$C_2H_5Si(OCH_3)_3$	124–125
ethyltriethoxysilane	[78-07-8]	$C_2H_5Si(OC_2H_5)_3$	158–159
propyltrimethoxysilane	[1067-25-0]	$C_3H_7Si(OCH_3)_3$	142
propyltriethoxysilane	[141-57-1]	$C_3H_7Si(OC_2H_5)_3$	179–180
isobutyltrimethoxysilane	[18395-30-7]	$i\text{-}C_4H_9Si(OCH_3)_3$	154
pentyltriethoxysilane	[2761-24-2]	$C_5H_{11}Si(OC_2H_5)_3$	95–$6_{1.3}$
octyltriethoxysilane	[2943-75-1]	$C_8H_{17}Si(OC_2H_5)_3$	98–$99_{0.27}$
octadecyltrimethoxysilane	[3069-42-9]	$C_{18}H_{37}Si(OCH_3)_3$	$170_{0.013}$
octadecyltriethoxysilane	[112-04-9]	$C_{18}H_{37}Si(OC_2H_5)_3$	165–$169_{0.27}$
phenyltriethoxysilane	[780-69-8]	$C_6H_5Si(OC_2H_5)_3$	112–$113_{1.3}$
		Tetraorganoxysilanes and polyorganoxysiloxanes	
tetramethoxysilane	[681-84-5]	$Si(OCH_3)_4$	121–122
tetraethoxysilane	[78-10-4]	$Si(OC_2H_5)_4$	169
tetrapropoxysilane	[682-01-9]	$Si(O\text{-}n\text{-}C_3H_7)_4$	224–225
tetraisopropoxysilane[e]	[1992-48-9]	$Si(O\text{-}i\text{-}C_3H_7)_4$	185–186
tetrabutoxysilane	[4766-57-8]	$Si(O\text{-}n\text{-}C_4H_9)_4$	$115_{0.4}$
tetrakis(*s*-butoxy)silane	[5089-76-9]	$Si(O\text{-}sec\text{-}C_4H_9)_4$	$87_{0.27}$
tetrakis(2-ethyl-butoxy)silane	[78-13-7]	$Si(OCH_2CH(C_2H_5)_2)_4$	166–$172_{0.27}$
tetrakis(2-ethyl-hexoxy)silane	[115-82-2]	$Si(OCH_2CH(C_2H_5)(C_4H_9))_4$	$194_{0.13}$
tetrakis(2-methoxy-ethoxy)silane	[2157-45-1]	$Si(OCH_2CH_2OCH_3)_4$	179–$182_{14.7}$
tetraphenoxysilane[e]	[1174-72-7]	$Si(OC_6H_5)_4$	236–$237_{0.13}$
hexaethoxydisiloxane[e]	[2157-42-8]	$(C_2H_5O)_3SiOSi(OC_2H_5)_3$	230–232
ethylsilicate 40[i]	[18954-71-7]	ca $(OSi(OC_2H_5)_2)_{4--5}$	290–310
		Acyloxysilanes	
tetracetoxysilane	[5623-90-3]	$Si(OOCCH_3)_4$	$148_{0.8}$
methyltriacetoxysilane	[4253-34-3]	$CH_3Si(OOCCH_3)_3$	87–$88_{0.4}$
ethyltriacetoxysilane	[17689-77-9]	$C_2H_5Si(OOCCH_3)_3$	107_1
di-*t*-butoxydiacetoxysilane	[13170-23-5]	$(t\text{-}C_4H_9O)_2Si(OOCCH_3)_2$	$102_{0.7}$

[a] Ref. 1.

[b] Subscript denotes pressure, other than atmospheric, in kPa. To convert kPa to psi, multiply by 0.145.

[c] To convert kJ to kcal, divide by 4.184.

[d] Ref. 2. Value may be questionable.

[e] Model compound; not of commercial significance.

[f] At 38°C.

[g] At 60°C.

[h] At 55°C.

[i] Nominal values; commercial values may vary. Properties given are for the average compound containing 40 wt % silicon dioxide.

stable and have unique physiological properties (3). A second special class of monomeric esters are cyclic diesters of polyethyleneoxide glycols designated sila-crowns, which have application as catalysts (4). Neither silatranes nor sila-crowns are considered herein.

Aryloxy- and acyloxysilanes are often solids. The aryloxysilanes have excellent thermal stability. Acyloxy and mixed acyloxyalkoxysilanes have poor thermal stability. Thermal decomposition has been noted at temperatures as low as 110°C and is generally observed by 170°C.

The most significant difference between the alkoxysilanes and silicones is the susceptibility of the Si–OR bond to hydrolysis (see Silicon compounds, silicones). The simple alkoxysilanes are often operationally viewed as liquid sources of silicon dioxide (see Silica). The hydrolysis reaction, which yields polymers of silicic acid

Table 2. (Continued)

Melting point, °C	Density, g/cm^3	Refractive index, n_D	ΔH_{vap}, kJ/mol^c	Viscosity, mm^2/s(=cP)	Flash-point, °C	LD$_{50}$ (oral, rat), mg/kg
Monoorganoalkoxysilanes						
	0.955	1.3646		0.5	8	
	0.895	1.3832		0.6	23	12,500^d
	0.949	1.3838		0.5	27	
	0.896	1.3955	32.6	0.7	40	13,720
	0.939	1.3880			34	7,420
	0.892	1.3956			57	
	0.933	1.3960			42	>2,000
	0.895	1.4059			68	
< −40	0.875	1.4160		1.9	100	
13–17	0.885	1.4391			140	
10–12	0.870	1.4386				>5,000
	0.996	1.4718	47.7		96	2,830
Tetraorganoxysilanes and polyorganoxysiloxanes						
2	1.032	1.3668	46.8	0.5	20	700
−85	0.934	1.3838	46.0	0.7	46	6,270
< −80	0.916	1.4012		1.7	95	
< −22	0.887	1.3845	46.8	1.2	60	
< −80	0.899	1.4128	61.9	2.3	110	
	0.885	1.4000		2.1^f	104	
< −70	0.892	1.4309		4.4^f	116	22,130
< −80	0.88	1.4388	70.6	6.8^f	188	>22,000
< −70	1.079	1.4219		4.4	140	
48–49	1.141	1.554^g		6.6^h		
	0.998	1.3914				
−90	1.05–1.06	1.3914		4–5	43	
Acyloxysilanes						
110 sub	1.06	1.4220				
40	1.175	1.4083			85	
7–9	1.143	1.4123			106	
−4	1.0196	1.4040			95	

that can be dehydrated to silicon dioxide, is of considerable commercial importance. The stoichiometry for hydrolysis for tetraethoxysilane is

$$Si(OC_2H_5)_4 + 2\ H_2O \xrightarrow{\text{acid or base}} SiO_2 + 4\ C_2H_5OH$$

Silicon dioxide never forms directly during hydrolysis. Intermediate ethoxy derivatives of silicic acid and polysilicates form as hydrolysis progresses. The polysilicates grow in molecular weight until most or all of the ethoxy groups are removed and a nonlinear network of Si–O–Si remains. The development of cyclic and cube structures containing 3–8 silicon atoms also occurs (5–7). A numerical modeling system for the hydrolysis of tetraethoxysilane has been developed (8). The viscosity of the solution increases until gelation or precipitation. Partially hydrolyzed materials of this type often contain more than enough silanols, Si–OH, to displace most of the remaining ethoxy groups in an acid- or base-catalyzed condensation. The stoichiometric equation for partial hydrolysis is

$$n\ Si(OC_2H_5)_4 + 2x\ H_2O \xrightarrow{\text{acid or base}} \left(Si(OC_2H_5)_{4(1-x)}O_{2x} \right)_y + 4x\ ROH$$

where x is the mol % partial hydrolysis. If the alkoxysilane is an organoalkoxysilane, eg, methyltriethoxysilane or phenyltriethoxysilane, the hydrolysis proceeds analogously to give the organosilsesquioxanes, $(RSiO_{1.5})_n$, instead of the dioxides, $(SiO_2)_n$. Likewise diorganodialkoxysilanes yield silanediols upon hydrolysis. Whereas the hydrolysis process is not usually considered to be an equilibrium reaction, the equilibrium constant for the reaction is $\sim 2 \times 10^{-3}$. The reversibility of the reaction only plays a significant role when the hydrolysis products are soluble (9).

Redistilled tetraethoxysilane containing less than 1 ppm chloride added to neutral $18 \times 10^6\ \Omega$ water purged with nitrogen in fluorocarbon bottles does not hydrolyze to a gel for over 6 months (10). Without special precautions, tetraethoxysilane hydrolyzes to a gel in ~10 d; tetramethoxysilane hydrolyzes in ~2 d; and tetra-*n*-butoxysilane in ~25 d. The hydrolysis reaction is catalyzed by acid or base. Acid-catalyzed hydrolysis generally proceeds more rapidly than base hydrolysis, and leads to more linear polymers than base hydrolysis. In contrast to base-catalyzed hydrolysis, there is a significant rate difference between the rate of hydrolysis of the first and second alkoxy groups in the presence of acid (see Table 1).

For binder preparation, dilute hydrochloric or acetic acids are preferred, because these facilitate formation of stable silanol condensation products. When more complete condensation or gelation is preferred, a wider range of catalysts, including moderately basic ones, is employed. These materials, which are often called hardeners or accelerators, include aqueous ammonia, ammonium carbonate, triethanolamine, calcium hydroxide, magnesium oxide, dicyclohexylamine, alcoholic ammonium acetate, and tributyltin oxide (11, 12).

2. Sol–Gel Process Technology and Chemistry

The complete hydrolysis of tetraalkoxysilanes under highly controlled conditions, usually without the presence of fillers, is associated with sol–gel technology (qv). Sol–gel is a method for preparing specialty metal oxide glasses and ceramics by hydrolyzing a chemical precursor or mixture of chemical precursors that pass sequentially through a solution state and a gel state before being dehydrated to a glass or ceramic. The use of sol–gel technology has increased dramatically since 1980. A variety of techniques have been developed to prepare fibers, microspheres, thin films (qv), fine powders, and monoliths. Applications for this technology include protective coatings, catalysts, piezoelectric devices, wave-guides, lenses, high strength ceramics, superconductors, insulating materials, and nuclear waste encapsulation. The flexibility of sol–gel technology allows unique access to multicomponent oxide systems and low temperature process regimes. An excellent review of sol–gel chemistry is available (13).

Preparation of metal oxides by the sol–gel route proceeds through three basic steps: (*1*) partial hydrolysis of metal alkoxides to form reactive monomers; (*2*) the polycondensation of these monomers to form colloid-like oligomers (sol formation); and (*3*) additional hydrolysis to promote polymerization and cross-linking leading to a three-dimensional matrix (gel formation). Although presented herein sequentially, these reactions occur simultaneously after the initial processing stage.

Monomer formation or partial hydrolysis

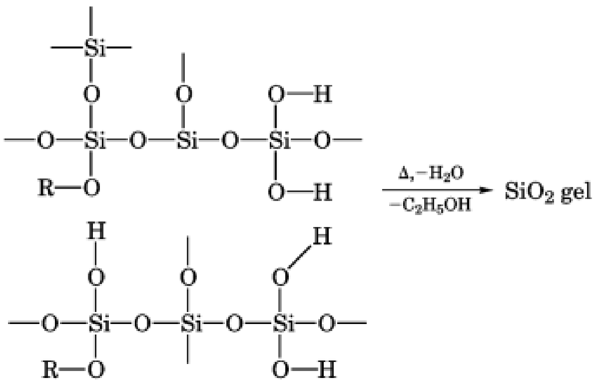
$$Si(OC_2H_5)_4 + H_2O \longrightarrow (C_2H_5O)_3SiOH + C_2H_5OH$$

Sol formation or polycondensation

$$y\ (C_2H_5O)_3SiOH \xrightarrow[\text{dimers}]{\text{monomers}} (C_2H_5O)_3Si(OSi(OC_2H_5)_2)_nOH + n\ C_2H_5OH$$

Gelation or cross-linking

$$(C_2H_5O)_3Si(OSi(OC_2H_5)_2)_nOH \xrightarrow{n\ H_2O} (C_2H_5O)_3Si(OSi(OC_2H_5)OH)_nOH + n\ C_2H_5OH \xrightarrow{-H_2O}$$



where R is C_2H_5.

As polymerization and cross-linking progress, the viscosity of the sol gradually increases until the sol–gel transition point is reached. At this point the viscosity abruptly increases and gelation occurs. Further increases in cross-linking are promoted by drying and other dehydration methods. Maximum density is achieved in a process called densification in which the isolated gel is heated above its glass-transition temperature. The densification rate and transition (sintering) temperature are influenced primarily by the morphology and composition of the gel.

Nonhydrolytic methods for the formation of silicon dioxide from tetraalkoxysilanes have been reported (14, 15). Others have been reinvestigated (16):

$$2\ \mathrm{HCOOH} + \mathrm{Si(OC_2H_5)_4} \longrightarrow \mathrm{SiO_2} + 2\ \mathrm{C_2H_5OH} + 2\ \mathrm{HCOOC_2H_5}$$

$$\mathrm{Si(OCH_2C_6H_5)_4} + \mathrm{SiCl_4} \longrightarrow \mathrm{SiO_2} + 4\ \mathrm{C_6H_5CH_2Cl}$$

The Si–OR bond undergoes a variety of reactions apart from hydrolysis and condensation. In one of the more important aspects of reactivity, it is associated with the production of silicone intermediates and with cross-linking reactions for silicone room temperature vulcanizing materials (RTVs) (17). The reactivity of the Si–OR bond is in many cases analogous to the Si–Cl bond, except that the reactions are more sluggish. These reactions become increasingly more sluggish with greater bulk and steric screening of the alkoxy group. Reactions that have been reviewed (18–20) include the following:

$$\text{—}\mathrm{SiOR} + \mathrm{R'MgCl} \longrightarrow \text{—}\mathrm{SiR'} + \mathrm{Mg(OR)Cl}$$

$$\text{—}\mathrm{SiOR} + \mathrm{HOSi} \longrightarrow \text{—}\mathrm{Si}\text{—}\mathrm{O}\text{—}\mathrm{Si}\text{—} + \mathrm{ROH}$$

$$\text{—}\mathrm{SiOR} + \mathrm{HOB} \longrightarrow \text{—}\mathrm{SiOB}\text{—} + \mathrm{ROH}$$

$$—SiOR + (R'\overset{O}{\overset{\|}{C}})_2O \longrightarrow —SiO\overset{O}{\overset{\|}{C}}R' + R'\overset{O}{\overset{\|}{C}}OR$$

$$2—SiOR + R'CHO \xrightarrow{H_2SO_4} —Si—O—Si— + R'CH(OR)_2$$

$$—SiOR + ClSi \xrightarrow{\text{catalyst}} —Si—O—Si— + RCl$$

$$—SiOR + HON{=}R' \xrightarrow{\text{catalyst}} —Si—ON{=}R' + ROH$$

$$—SiOR + R'COCl \longrightarrow —SiCl + R'COOR$$

In comparison to the Si–OR bond, the Si–C bond can be considered essentially unreactive if the organic moiety is a simple unsubstituted hydrocarbon. If the organic moiety is substituted as in the case of a trialkoxysilane, the chemistry is more appropriately considered elsewhere (see Silicon compounds, silanes; Silicon compounds, silylating agents).

Simple alkyl- and aryltrialkoxysilanes have three rather than four matrix coordinations in the polymeric hydrolysates, leading to less rigid structures than those derived from tetraalkoxysilanes. These and other changes in physical characteristics, eg, wetting and partition properties, make these materials more appropriate in a variety of coating applications, where tetraalkoxysilanes are not acceptable. These materials are variously referred to as T-resins, organosilsesquioxanes, and ormosils, from the term organic modified silicas. Methylsilsesquioxanes are stable to 400°C. Phenylsilsesquioxanes are stable to 475°C.

3. Preparation

The principal method of silicon ester production is described by Von Ebelman's 1846 synthesis (21):

$$SiCl_4 + 4\ C_2H_5OH \longrightarrow Si\,(OC_2H_5)_4 + 4\ HCl$$

The reaction is generalized to

$$R_{(4-n)}SiCl_n + n\ R'OH \longrightarrow R_{(4-n)}Si\left(OR'\right)_n + n\ HCl$$

Process considerations must not only take into account characteristics of the particular alcohol or phenol to be esterified, but also the self-propagating by-product reaction, which results in polymer formation.

$$ROH + HCl \longrightarrow RCl + H_2O$$

$$H_2O + SiCl_4 \longrightarrow \left[SiCl_2O\right] + 2\ HCl$$

Methods used to remove hydrogen chloride include the use of refluxing solvents or reaction mixtures, sparging dry air or nitrogen through the reaction mixture, and conducting the reaction in vapor phase or under applied vacuum. Amines can be employed as base-acceptors, but generally this is not practical commercially. In batch processes, the alcohol is always added to the chlorosilane. Continuous processes involve (*1*) pumping the alcohol and chlorosilane together in a mixing section, (*2*) introducing the chlorosilane vapor countercurrent to liquid alcohol, or (*3*) introducing chlorosilane vapor in a two-column reaction distillation scheme in which substoichiometric alcohol is introduced center-column to a chlorosilane, removing HCl and unreacted alcohol in the overhead, and in the second stage a slight excess of the alcohol is introduced center-column, recovering the excess overhead and removing product from the bottom. All processes provide a method for removal of by-product hydrogen chloride. The energy of activation for the reaction of ethanol with silicon tetrachloride in the vapor phase is 64.9 kJ/mol (15.5 kcal/mol) (22). The initial stages of the esterification processes are endothermic because the heat of evaporation of HCl cools the reaction mixture. In the last stages of esterification, the mixtures are usually heated during the final addition of alcohol. Tertiary alkoxides cannot be formed in this manner.

In the batch production of tetraethoxysilane from silicon tetrachloride, the initial reaction product contains at least 90 wt % tetraethoxysilane with a 28 wt % SiO_2 content. Distillation removes alcohol and high boiling impurities, and the distilled product contains at least 98% tetraethoxysilane and is called pure ethyl silicate. Partially hydrolyzed or polymeric versions where substantial portions have an average of 4–5 silicon atoms and 40 wt % SiO_2 or have an average of 5–8 silicon atoms and a 50 wt % SiO_2 content are referred to as ethylsilicate 40 and ethylsilicate 50, respectively. Ethylsilicate 50 has a branched structure with approximately 30–35% of all silicon atoms bonded to two others by oxygen bridges; 35–38% are bonded to three silicon atoms; and 12–16% are bonded to four silicon atoms. Model systems for hydrolyzed tetraethoxysilane which include cube as well as cyclic structures have been prepared (4).

Although known since the 1940s and 1950s (23, 24), catalyzed direct reactions of alcohols using silicon metal have become important commercial technology in the 1990s for production of lower esters. Patents have reported the reactions of methanol and ethanol with silicon in high boiling solvents, or in contained reaction products to give high yields of trialkoxysilanes and tetraalkoxysilanes (25, 26). It has been demonstrated that in the presence of a methoxy compound, where M is a metal, and under moderate pressure, substantial improvements in yield can be achieved (27).

$$Si + 4\ ROH \xrightarrow[Si(OR)_4]{Fe,\ CH_3OM} Si(OR)_4 + 2\ H_2$$

The synthesis of triethoxysilane (28) and trimethoxysilane (29) has also been achieved by direct process. In 1980 there were no direct processes for the production of alkoxysilanes. In 1995 Silbond in Weston, Michigan, and Carboline in St. Louis, Missouri, operated processes for the production of tetraethoxysilane in the United States, and OSi/Witco announced start-up of a process to produce triethoxysilane and tetraethoxysilane in Termoli, Italy.

Apart from the direct action of an alcohol on a chlorosilane or silicon, the only other commercial method used to prepare alkoxysilanes is transesterification.

$$Si(OR)_4 + 4\ R'OH \overset{catalyst}{\rightleftharpoons} Si(OR')_4 + 4\ ROH$$

Transesterification, an equilibrium reaction, is practical only when the alcohol to be esterified has a high boiling point and the leaving alcohol can be removed by distillation. The most widely used catalysts are sodium alcoholates and organic titanates, although amines are also used (30, 31).

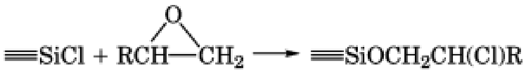
A provocative reaction of ethylene glycol directly with silicon dioxide that leads to a complex mixture of oligomeric and cyclic ester species has been reported (32). This reaction proceeds in the presence of sodium hydroxide or in the presence of high boiling tertiary amines (33).

Other preparative methods for alkoxysilanes, in approximate order of declining utility, are given by the following equations (34–40):

$$\equiv SiCl + (RO)_3CH \longrightarrow \equiv SiOR + RCl + RO\overset{\overset{\displaystyle O}{\|}}{C}H$$

$$\equiv SiCl + NaOR \longrightarrow \equiv SiOR + NaCl$$

$$\equiv SiH + HOR \xrightarrow{\text{catalyst}} \equiv SiOR + H_2$$

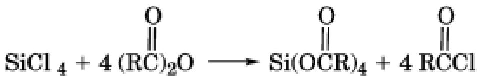


$$\equiv SiOH + HOR \longrightarrow \equiv SiOR + H_2O$$

$$\equiv SiCl + CH_3NO_2 \longrightarrow \equiv SiOCH_3 + NO_2Cl$$

$$\equiv SiSR + HOR \longrightarrow \equiv SiOR + H_2S$$

The acyloxysilanes are produced by the reaction of an anhydride and a chlorosilane.



$$SiCl_4 + 4\,(R\overset{\overset{\displaystyle O}{\|}}{C})_2O \longrightarrow Si(O\overset{\overset{\displaystyle O}{\|}}{C}R)_4 + 4\,R\overset{\overset{\displaystyle O}{\|}}{C}Cl$$

The analogous reaction between anhydrides and alkoxysilanes also produces acyloxysilanes. The direct reaction of acids with chlorosilanes does not cleanly lead to full substitution. Commercial production of methyltriacetoxysilane directly from methyltrichlorosilane and acetic acid has been made possible by the addition of small amounts of acetic anhydride or EDTA, or acceptance of dimethyltetraacetoxydisiloxane in the final room temperature vulcanizing (RTV) application (41–43). A reaction that leads to the formation of acyloxysilanes is the interaction of acid chlorides with silylamides.

4. Economic Aspects

Tetraethoxysilane and its polymeric derivatives account for >90% of the dollar value of nonaryl- or alkyl-substituted esters. The leading U.S. suppliers are Silbond and Hüls America. Silbond manufacture is limited to ethylsilicates. Hüls imports ethylsilicate produced at its Rheinfelden and Dresden, Germany, facilities. Eagle-Picher announced start-up of an electronic-grade tetraethoxysilane unit at Miami, Oklahoma, in September 1995. Yamanaka operates a similar facility in Japan. The U.S. market for the ethylsilicates is estimated at 3000–3500 metric tons. Pricing ranges from $2.40 to $6.00/kg, depending on grade and quantity.

Nonethyl ester prices are $3–$100/kg. Hüls, Gelest, and Harris Specialty Chemical are U.S. producers. Alkyltrialkoxysilanes are produced by Hüls at Mobile, Alabama, Harris Specialty Chemical at Gainesville, Florida, and OSi/Witco in Sistersville, West Virginia. In 1996, AlliedSignal announced the sale of its Jayhawk facility, which produced alkylalkoxysilanes, to Allco/Inspec, and the future production of alkylalkoxysilanes at the facility was not certain. Gelest manufactures specialty alkylsilane esters at its Tullytown, Pennsylvania, facility. Shin-etsu and Dai-Hachi produce alkylalkoxysilanes in Japan.

The bulk of acyloxysilanes is produced and used by the principal U.S. silicone rubber producers, ie, Dow Corning and General Electric (see Silicon compounds, silicones).

5. Toxicity

The alkoxysilanes generally have a low order of toxicity, which may be associated with their alcoholic products of hydrolysis. Notable exceptions are tetramethoxysilane and two hydridosilanes, trimethoxysilane and triethoxysilane. Triethoxymethoxysilane is the lowest member of the series in which the hazard is substantially reduced. Vapors of these materials may be absorbed directly into corneal tissue, causing blindness (44). The onset of corneal damage is noted by a scratchy feeling in the eyes, usually 2–4 h after exposure. The effects of exposure to the methoxysilanes are rarely reversible. This is a significant consideration for worker safety. Especially because of the pleasant minty or fruity fragrance, warnings of exposure to silicon esters are frequently ignored.

6. Uses

6.1. Precision Casting

The ethoxysilanes are used as binders in precision casting for investment and thin-shell processing (45–47). Ethylsilicate 40 and its partial hydrolysates are preponderant. In the investment process, 3–10% excess water is added to a prehydrolyzed silicate binder. This is mixed with refractory material. If the refractory material contains magnesium oxide or calcium hydroxide, gelation occurs in 40–60 min. If these additives are not present or an accelerated cure is required, catalysts are added to the binder prior to mixing with the refractory. In the thin-shell process, fusible patterns are dipped into slurries made of a refractory and ethylsilicate binder. Curing is accomplished by air drying or exposure to ammonia vapor. Ethanol from hydrolysis is either allowed to evaporate or is burned off before firing. The utilization of silicate esters has diminished since the 1980s, owing to their partial replacement by colloidal silicas.

6.2. Cements and Ceramics

Refractory cements and ceramics (qv) are prepared from slurries of silica, zirconia, alumina, or magnesia and a prehydrolyzed silicate (see Cement). Calcining at 1000°C yields cured refractory shapes (48, 49).

6.3. Glass Frosting

Deposition of silicon dioxide is used to impart a translucent coating on glass (qv) (50). The surfaces are either exposed to tetraethoxysilane or tetramethoxysilane under high moisture conditions, or the alkoxysilanes are ignited and the resulting powder is applied to the surface.

6.4. Paints and Coatings

Ethoxysilanes are used in high temperature, zinc-rich paints (see Paint) (51, 52). Methyl- and phenyltrialkoxysilanes are used to prepare abrasion-resistant coatings for plastics (53), particularly polycarbonate (54, 55), and dielectric coatings and seals for high voltage electrical components, including television tubes.

6.5. Sol–Gel Glasses and Ceramics

Although sol–gel is actually a process, not a product, several classes of materials are associated with the sol–gel process. Sol–gel-derived materials include fine powders, coatings and monoliths, and aerogels (qv). Sol–gel-derived powders are produced by the Stöber process (56) and variations of it. The products are used in catalysis and chromatography. Unmodified silica coatings are employed in the preparation of ion-free coatings on glass used in liquid crystal displays (LCDs), coatings for eyewear, and industrial and automotive plastic glazing. Small-diameter lenses and gradient index (GRIN) optics are in commercial development, as of 1996. Aerogels derived from tetraethoxysilane have extremely great potential as insulating materials. BASF has introduced a product based on this technology called Basogel.

6.6. Water Repellents

Protective and consolidating coatings for masonry and other applications are produced from methyl-, propyl-, isobutyl-, and octyltrialkoxysilanes (57). Applications for these materials are in two principal markets: vertical, ie, buildings; and horizontal, ie, bridge decks, parking garages, etc. Performance characteristics such as substrate penetration often make use of lower alkyltrialkoxysilanes, important where salt penetration is a concern. A water repellent based on isobutyltrimethoxysilane is marketed under the trade name of Chem-Trete by Hüls. The ability of longer alkyls to form stable emulsions makes them preferred for cost and safety (58). A product based on octyltriethoxysilane is marketed under the trade name Enviroseal by Harris Specialty Chemical.

6.7. Bonded Phases

Substrate-bond hydrocarbon coatings for high pressure liquid chromatography (hplc) and flash chromatography are prepared from octyltrialkoxysilanes and other long-chain alkyltrialkoxysilanes (see Chromatography).

6.8. Hydraulic and Heat-Transfer Fluids

Hydraulic fluids (qv) for high altitude supersonic aircraft and thermal exchange applications including solar panels employ fluids such as tetrakis(2-ethylhexoxy)silane. These products have been marketed under the trade name Coolanol by Monsanto .

6.9. Silicone Room Temperature Vulcanizing Cross-Linking

Condensation-cured polydimethylsiloxanes contain terminal silanol groups which condense with the silanols produced by ambient moisture hydrolysis of acyloxysilanes. Methyltriacetoxysilane, ethyltriacetoxysilane, and tetraacetoxysilane are the most commonly used cross-linking agents.

6.10. Spin-On Glass

In microelectronic applications, films of silicon dioxide are deposited on silicon substrates by the application of a partially hydrolyzed solution of tetraethoxysilane or methyltriethoxysilane (59, 60). A product based on this technology is marketed under the name Accuspin by AlliedSignal.

6.11. Chemical Vapor Deposition

Chemical vapor deposition (CVD) of silicon dioxide from tetraethoxysilane assisted by the presence of oxygen and a plasma is an important technology for the deposition of pure and modified dielectrics for microelectronics (61). An alternative method for the deposition of silicon dioxide utilizes di-*t*-butoxydiacetoxysilane (62).

BIBLIOGRAPHY

“Silicon Esters and Ethers” under “Silicon Compounds” in *ECT* 1st ed., Vol. 12, pp. 371–372, by E. G. Rochow, Harvard University; in *ECT* 2nd ed., Vol. 18, pp. 216–221, by A. R. Anderson, Anderson Development Co.; in *ECT* 3rd ed., Vol. 20, pp. 912–921, by B. Arkles, Petrarch Systems, Inc.

Cited Publications

1. B. Arkles, *Silicon, Germanium, Tin, and Lead Compounds: A Survey of Properties and Chemistry*, Gelest, Inc., Tullytown, Pa., 1995.
2. N. Sax and R. Lewis, *Dangerous Properties of Industrial Materials*, Van Nostrand Reinhold Co., Inc., New York, 1989.
3. M. G. Voronkov, in G. Bendz and I. Lindqvist, eds., *Biochemistry of Silicon and Related Problems*, Plenum Publishing Corp., New York, 1977, p. 395.
4. B. Arkles, R. Anderson, and K. King, *Organometallics* **2**, 454 (1983).
5. J. F. Brown Jr., *J. Am. Chem. Soc.* **87**, 4317 (1965).
6. P. Cagle and co-workers, in B. Zelinski and co-workers, eds., *Better Ceramics Through Chemistry IV, MRS Proc. 180*, 1990, p. 961.
7. F. Feher, D. Newman, and J. Walzer, *J. Am. Chem. Soc.* **111**, 1741 (1989).
8. B. D. Kay and R. A. Assink, *J. Non Cryst. Sol.* **104**, 112 (1988).
9. B. Arkles, J. Steinmetz, J. Zazyczny, and P. Mehta in K. L. Mittal, ed., *Silanes & Other Coupling Agents*, VSP, 1993, p. 91.
10. Technical data, Gelest, Inc., Tullytown, Pa., 1992.
11. U.S. Pat. 2,550,923 (May 1, 1951), C. Shaw, J. E. Hocksford, and W. E. Smith (to Shaw and Langish-Smith); U.S. Pat. 2,795,022 (June 11, 1957), N. Shaw (to Shaw Process).
12. H. G. Emblem and T. R. Turger, *Trans. Br. Ceram. Soc.* **78**(5), 1979.
13. C. J. Brinker, G. W. Scherer, *Sol-Gel Science*, Academic Press, Orlando, Fla., 1990.
14. U.S. Pat. 4,950,779 (Aug. 21, 1990), J. H. Wengrovius and V. M. VanValkenburgh (to General Electric).

15. U.S. Pat. 5,441,718 (Aug. 15, 1995), K. Sharp (to E. I. du Pont de Nemours & Co., Inc.).
16. S. Acosta and co-workers, in S. Acosta and co-workers, *Better Ceramics Through Chemistry VI, MRS Proc. 346*, 1994, p. 43.
17. E. L. Warrick, O. R. Pierce, K. E. Polmanteer, and J. C. Saam, *Rubber Chem. Tech. Revs.* **52**, 437 (1979).
18. B. Arkles, in G. Silverman and P. Rackita, eds., *Grignard Reagents*, Marcel Dekker, New York, 1996, p. 667.
19. R. C. Mehrotra, V. D. Gupta, and G. Srivastiva, *Rev. Silicon, Germanium, Tin Lead Comp.* **1**, 299 (1975).
20. M. G. Voronkov, V. P. Mileshevich, and Yu. A. Yuzhelevski, *The Siloxane Bond*, Plenum Publishing Corp., New York, 1978.
21. J. Von Ebelman, *Ann. Chem.* **57**, 319 (1846).
22. V. G. Ukhtomshii, *Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhnol.*, **19**(7), 146 (1976).
23. U.S. Pat. 2,473,260 (June 26, 1946), E. G. Rochow (to General Electric).
24. U.S. Pat. 3,072,700 (Jan. 8, 1963), N. de Wit (to Union Carbide).
25. B. Kanner and K. M. Lewis, in K. M. Lewis and D. G. Rethwisch, eds., *Catalyzed Direct Reactions of Silicon*, Elsevier Science, Inc., New York, 1993, p. 39.
26. U.S. Pat. 4,323,690 (Apr. 6, 1982), J. F. Montle, H. J. Markowsi, P. D. Lodewyck, and D. F. Schneider (to Carboline).
27. U.S. Pat. 4,113,761 (Sept. 12, 1978), G. Kreuzberg, A. Lenz, and W. Rogher (to Dynamit Nobel).
28. Jpn. Kokai Tokkyo Koho 80 28,929 (Feb. 29, 1980), S. Suzuki, T. Imaki, and T. Yamamura (to Mitsubishi).
29. U.S. Pat. 5,084,590 (Jan. 28, 1992), J. S. Ritscher and T. E. Childress (to Union Carbide).
30. P. D. George and J. R. Ladd, *J. Am. Chem. Soc.* **75**, 987 (1953).
31. H. Steimann, G. Tschernko, and H. Hamann, *Z. Chem.* **17**, 89 (1977).
32. R. M. Laine, *Nature* **353**, 640 (1991).
33. R. M. Laine, *Chem. Mat.* **6**, 2177 (1994).
34. L. M. Shore, *J. Am. Chem. Soc.* **76**, 1390 (1959).
35. U.S. Pat. 2,381,137 (May 14, 1942), W. I. Patnode and R. O. Sauer (to General Electric).
36. D. Seyferth and E. G. Rochow, *J. Org. Chem.* **20**, 250 (1955).
37. V. Day, W. Klemperer, V. Mainz, and D. Millar, *J. Am. Chem. Soc.* **107**, 8262 (1985).
38. A. Weiss and G. Reiff, *Z. Anorg. Allg. Chem.* **311**, 151 (1961).
39. M. E. Havill, I. Jofee, and H. W. Post, *J. Org. Chem.* **13**, 280 (1948).
40. U.S. Pats. 2,569,455 and 2,459,746 (1949), J. B. Culbertson, H. D. Erasmus, and F. M. Fowler (to Union Carbide).
41. U.S. Pat. 3,9784,198 (Aug. 10, 1976), B. Ashby (to General Electric).
42. U.S. Pat. 4,329,484, L. P. Peterson (to General Electric).
43. U.S. Pat. 4,332,956 (June 1, 1982), L. A. Tolentino (to General Electric).
44. H. F. Smith, *The Effect of Tetramethylorthosilicate on the Eyes*, Carbide and Carbon Chemicals Industrial Fellowship 274-1, Mellon Institute, Pittsburgh, Pa.
45. A. Dunlop, *Foundry Trade J.* **75**, 107 (1945).
46. A. E. Focke, *Met. Prog.* **49**, 489 (1945).
47. U.S. Pat. 2,678,282 (May 11, 1954), C. Jones (to Pilkington Bros. Ltd.).
48. H. G. Emblem and I. R. Walters, *J. Appl. Chem., Biotechnol.* **27**, 618 (1977).
49. U.S. Pat. 2,678,282 (May 11, 1954), C. Jones (to Pilkington Bros. Ltd.).
50. U.S. Pat. 2,596,896 (Mar. 20, 1951), M. Pipken (to General Electric).
51. U.S. Pat. 3,056,684 (Oct. 11, 1962), S. L. Lopata (to Carboline).
52. D. M. Berger, *Met. Finishing* **72**(4), 27 (1979).
53. U.S. Pat. 4,197,230 (Apr. 8, 1980), R. H. Baney and L. A. Harris (to Dow Corning).
54. U.S. Pat. 4,495,360 (Jan. 22, 1985), B. T. Anthony (to General Electric).
55. U.S. Pat. 4,491,508 (Jan. 1, 1985), D. R. Olson and K. K. Webb (to General Electric).
56. W. Stöber and co-workers, *J. Coll. Interface Sci.* **26**, 62 (1968).
57. U.S. Pat. 2,916,461 (Dec. 8, 1959), K. W. Krantz (to General Electric).
58. U.S. Pat. 4,648,904 (Mar. 10, 1987), R. Depasquale and M. Wilson (to SCM).

59. U.S. Pat. 3,915,766 (Oct. 28, 1975), G. F. Pollack and J. G. Fish (to Texas Instruments).
60. U.S. Pat. 4,103,065 (July 25, 1978), D. Gagnon (to Owens-Illinois).
61. S. Fisher and co-workers, *Solid State Technol.*, 55 (Sept. 1993).
62. G. Smolinsky and R. Dean, *Mat. Lett.* **4**, 256 (1986).

BARRY ARKLES
Gelest, Inc.

Related Articles

Silicon compounds, silanes; Silicones; Heat-exchange technology; Paint