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Factors contributing to the stability of alkoxysilanes in aqueous solution

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Abstract—Parameters controlling intrinsic stability and reactivity of organosilanols generated from alkoxysilanes in aqueous environments have been elucidated in several experiments. Data involving kinetics, equilibrium, phase separation, and bonding studies of alkyl and organofunctional alkoxysilanes are presented. The studies indicate that the rates of hydrolysis of alkoxysilanes are generally related to their steric bulk, but demonstrate that after rate-limiting hydrolysis of the first alkoxy group steric effects are much less important. Aqueous hydrolysis of alkylalkoxysilanes was studied to determine equilibrium constants and the extent of oligomerization up to phase separation. In the case of propyltrialkoxysilane, phase separation is coincident with the formation of tetramer. The equilibrium constant for esterification of silanols is

$$K_{eq} = \frac{[R_3SiOCH_3][H_2O]}{[R_3SiOH][CH_3OH]} = 2.5 \pm 0.3 \times 10^{-2}.$$

Also, the performance properties of new water-borne silanes were evaluated and in most cases, their performance equalled or exceeded their traditional silane counterparts.

Keywords: Aqueous solution; hydrolysis; alkoxysilanes.

1. INTRODUCTION

The silanes employed in improving adhesion and surface modification are usually alkoxysilanes. Before or during application and bonding processes, alkoxysilanes are hydrolyzed, initiating a complex cascade of reactions. A simplified view of the reaction cascade is depicted in Fig. 1. In most application protocols, a catalyst which initiates alkoxysilane hydrolysis but which also affects silanol condensation and substrate interaction dictates reaction paths. In order to achieve inherent control and reproducibility of silane modification of surfaces, it would appear necessary to control the rate and path of reactions leading to the formation and consumption of silanol-rich species, particularly silanol-rich oligomers. Maximizing the availability of silanol-rich species, in terms of both time and concentration, should lead to improved reproducibility and greater surface interaction.

The objective of the studies presented in this paper was to develop fundamental information for silanol intermediates concerning their kinetics of formation, equilibrium with other silicon-containing species, and phase separation behavior. Based on these results, it was the further objective of the studies

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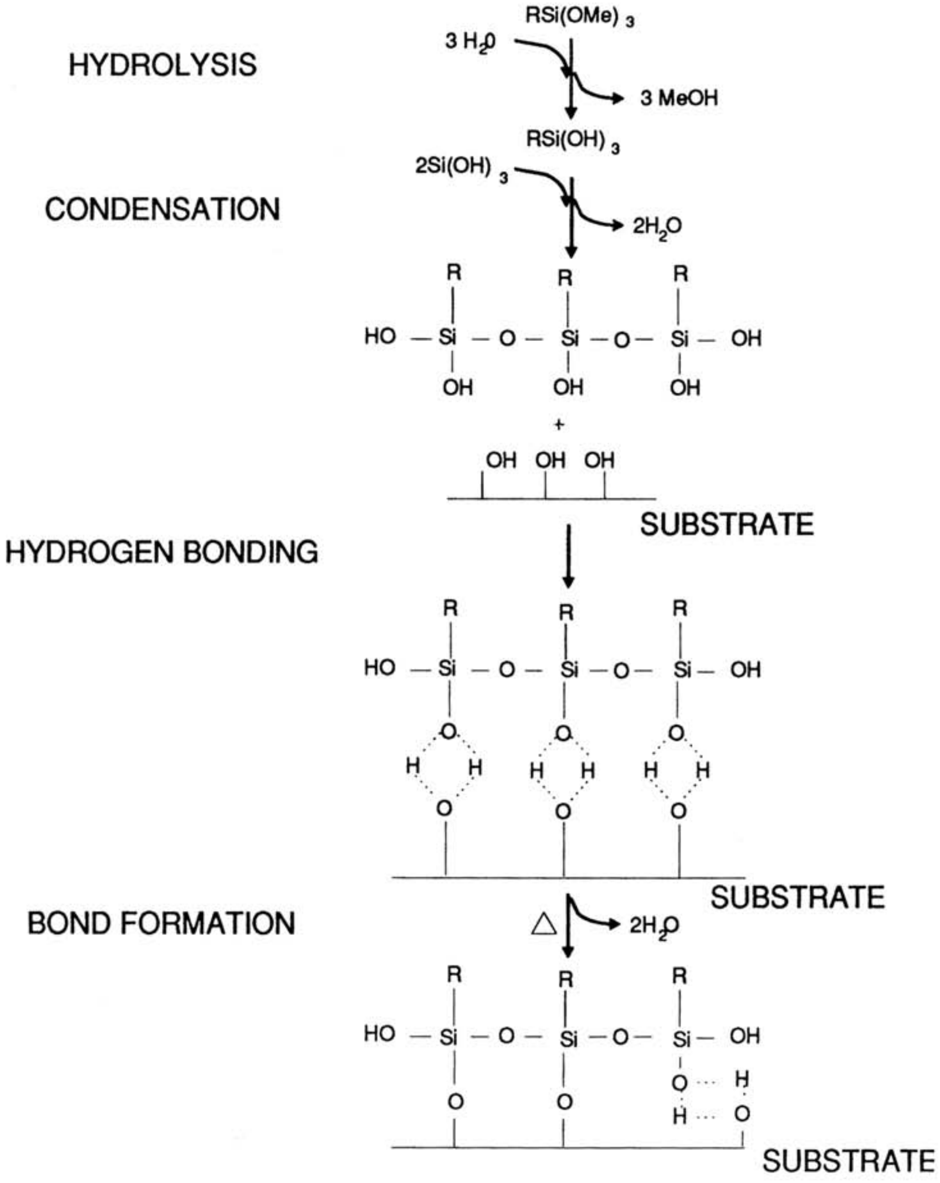

Figure 1. Reaction and bonding mechanism of alkoxysilanes.

to develop a series of stable silanol-rich oligomers and to evaluate their performance in sealant and composite systems.

2. SILANE HYDROLYSIS CHEMISTRY

In the vast majority of silane surface treatment applications, the alkoxy groups of trialkoxysilanes are hydrolyzed to form silanol-containing species. The silanol-containing species are highly reactive intermediates which are responsible for bond formation with the substrate. Hydrolysis of trialkoxysilane alkoxy groups may occur during the formal preparation of aqueous solutions or the reaction of the silane with adsorbed moisture on substrate surfaces. In principle, if silanol materials were stable, they would be preferred for surface treatments. Most silanes employed in surface treatments do not form stable monomeric silanols. Silanols usually condense with themselves or with alkoxysilanes to form siloxanes. Trialkoxysilanes are stable sources for silanols, but they have low intrinsic reactivity, low solubility in aqueous solutions, and by-products of hydrolysis which may be undesirable from a flammability and toxicity perspective.

The general mechanism for silane bond formation, depicted in Fig. 1, has been reviewed in detail [1, 2]. Alkoxysilanes undergo hydrolysis by both base- and acid-catalyzed mechanisms. In contact with high-purity (18×10^6 Ω cm) water under neutral, low ionic conditions in non-glass containers, alkoxysilanes bearing no autocatalytic functionality are stable for weeks or months. In contrast to chlorosilanes and acetoxysilanes, the products of alkoxysilane hydrolysis do not propagate the hydrolysis reaction. In contact with 'tap' water, hydrolysis of alkoxysilanes is substantial, if not complete, within hours. The same factors which accelerate the hydrolysis of alkoxysilanes also accelerate the condensation of silanols with other silanols and their alkoxy precursors. The overall pathway for the hydrolysis and full condensation of an alkoxysilane is complicated. If effects beyond the next nearest neighbor during condensation are ignored, there are six possible hydrolysis paths, 21 possible water-producing condensations, and 36 possible alcohol-producing reactions. Kay and Assink have presented a model for tetraalkoxysilane hydrolysis and condensation [3]. Presented in Fig. 2 is a scheme derived for trialkoxysilanes from that model. The numeric presentation indicates the number of alkoxy (OR) substitution in the first digit, the number of hydroxyl (OH) substitutes in the second digit, and the number of siloxane substitutions (OSi) in the third digit. Thus, a trialkoxysilane is 300 and a silanetriol is 030. Like the model for tetraalkoxysilanes, extended condensation or polymerization which results in phase separation and its kinetic consequences are not considered. Figure 3 shows the gross changes in silane condensation and polymerization in an acid vs. base condition. It can be related to the Kay and Assink model by observing that base hydrolysis favors a 300 to 003, where acid hydrolysis favors a 300 to 030 pathway.

It is important to note that catalysts for alkoxysilane hydrolysis are usually catalysts for condensation. In typical silane surface treatment applications, alkoxysilane reaction products are removed from equilibrium by phase separation and deposition of condensation products. The overall complexity of hydrolysis and condensation has not allowed simultaneous determination of the kinetics of silanol formation and reaction. Eqiulibrium data for silanol formation and condensation, until now, have not been reported.

2.1. Silane hydrolysis—background

2.1.1. Alkoxysilane hydrolysis—effects of substituents. A series of hydrolysis studies [4–9] have elucidated general trends. Under basic conditions, the hydrolysis of alkoxy groups usually takes place in a stepwise manner. Carbon-bonded substituents can have profound effects on the rate of hydrolysis. With the

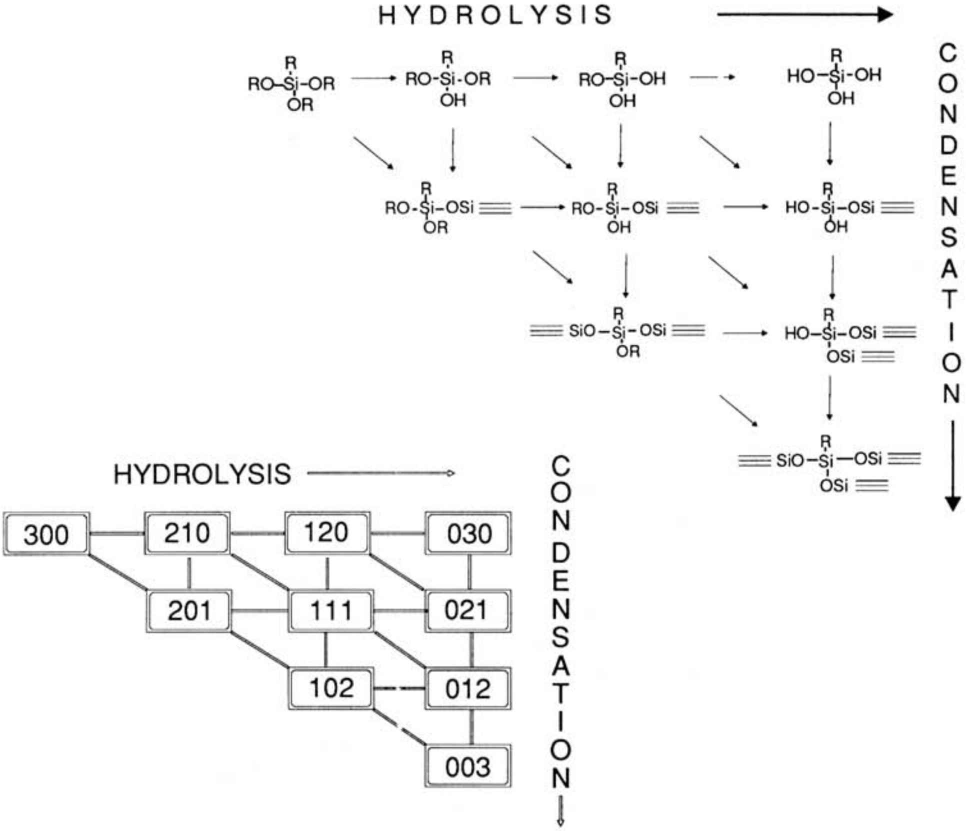

Figure 2. Numeric equivalents for the alkoxysilane hydrolysis cascade reaction.

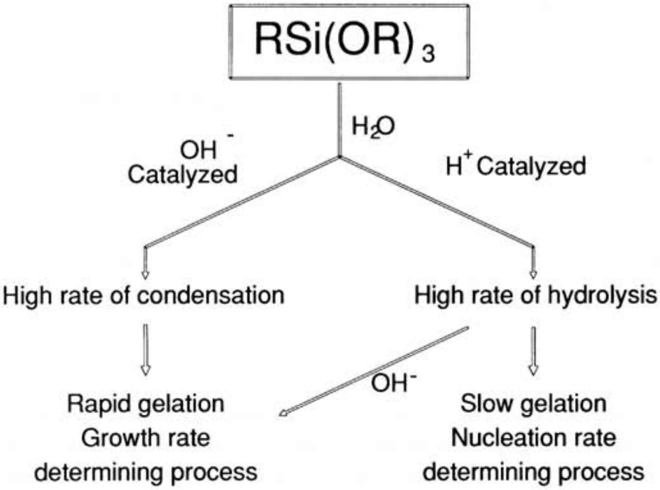

Figure 3. Effect of pH on alkoxysilane hydrolysis, adapted from Prassas [20].

exception of aminosilanes, most silanes are employed in surface treatment applications under acid-catalyzed conditions. The rate of acid hydrolysis is significantly greater than base hydrolysis and is minimally affected by other carbon-bonded substituents. The hydrolysis is preceded by protonation of the OR group. The rates of hydrolysis of the alkoxy groups are generally related to their steric bulk: $CH_3O > C_2H_5O > t\text{-}C_4H_9O$. A methoxysilane, for example, hydrolyzes at 6–10 times the rate of an ethoxysilane. As for base condensation, the hydrolysis of alkoxy groups is stepwise; however, the differential in hydrolysis rate between the first and second alkoxy group is greater. Finally, increased organic substitution enhances the hydrolysis rate, i.e. $Me_3SiOMe > Me_2Si(OMe)_2 > MeSi(OMe)_3$ [7]. The difficulty in straightforward application of the conclusions of the various hydrolysis studies to alkoxysilanes employed in surface treatments is that most of the studies employ non-functional silanes and provide data at pH extremes, i.e. outside the range of normal surface treatment regimens. Moreover, many of the studies incorporate solvents. In most normal surface treatment regimens, there are consequences of the insolubility of alkoxysilanes.

2.1.2. Condensation and persistence of silanols. In terms of devising a stable water-borne silane system, the silanol form of silanes is desirable since the silanols have greater solubility and reactivity than their alkoxy precursors and much greater solubility and reactivity than their siloxane products. One avenue for enhancing silanol persistence is to devise a system in which the rate of hydrolysis is substantially greater than that of condensation. A second avenue is to allow condensation of the polyhydroxylic silanol only to the extent that water solubility is maintained, allowing steric factors to preclude further condensation. Another consideration is that while silanols undergo S_N2 reactions rapidly with other silanols and methoxysilanes, their reaction with ethoxysilanes and higher alkoxysilanes is slow.

Individual examples of monomeric silanols such as triethylsilanol [10] and phenylsilanetriol [11] have been prepared under regimens different from those used for surface treatments and they exhibit extended stability. To date, no monomeric silanetriols have been isolated from aqueous hydrolysates of alkoxysilanes. The kinetics of silanetriol condensation have been studied [12]. The conditions which promote the hydrolysis of alkoxysilanes also promote condensation of silanols; the persistence of monomeric silanetriols for more than a few hours in typical solutions is unlikely. However, the persistence of silanols in reaction mixtures containing condensed structures have been observed empirically [13] and by ^{29}Si-NMR [14, 15].

The fact that silanol persistence can be favored by equilibrium conditions rather than control of condensation kinetics by steric or electronic factors is usually not considered. The phase separation which results from highly condensed systems continuously removes material from deposition solutions, depleting soluble silane species. While condensed silanols or siloxanes are typically not regarded as participating in a reversible reaction with water or alcohol, they do indeed participate in an equilibrium reaction. Iler [16] has shown that even hydrated amorphous silicon dioxide has an equilibrium solubility in methanol, which implies the formation of soluble low molecular weight species. The equilibrium concentration of SiO-containing species in methanol is 7 ppm, compared with 70–120 ppm in water.

The equilibrium reactions for alkoxysilane hydrolysis mixtures are given in equations (1)–(3). Data on equilibrium constants for these reactions have not been reported.

$$R_3SiOR + H_2O \rightleftharpoons R_3SiOH + ROH \tag{1}$$

$$2\,R_3SiOH \rightleftharpoons R_3SiOSiR_3 + H_2O \tag{2}$$

$$R_3SiOSiR_3 + ROH \rightleftharpoons R_3SiOR + R_3SiOH. \tag{3}$$

The equilibrium as well as the kinetics of hydrolysis and condensation of trialkoxysilanes is influenced by the organic substitution. A special case exists for many aminosilanes such as aminopropyltriethoxysilane, where a stable zwitterionic silanolate forms that is stable in solution [17–19]. It has been reported that at concentrations lower than 0.2% the aminosilane exists as a monomeric silanetriol [19].

2.2. *Silane hydrolysis—experimental*

All silanes were obtained from commercial production at Huls America. Ultrapure water was prepared in a Millipore purification unit. FTIR studies were conducted with a Nicolet Model 740 Spectrometer using ATR (attenuated total reflectance) of samples in a zinc selenide cell. NMR spectra were obtained using a General Electric QE-plus 300 MHz NMR Spectrometer.

2.3. *Silane hydrolysis—results and discussion*

A series of studies were conducted to define parameters related to reactivity, solubility, and stability of alkoxysilane hydrolysis mixtures for the purpose of generating model compounds stable in water solution and maintaining coupling agent activity.

2.3.1 Mixed alkoxysilane hydrolysis kinetics. Since the displacement of an alkoxy group with a hydroxyl group enhances water solubility, the possibility of generating mixed trialkoxysilanes which would react with water to form stable dialkoxysilanols was considered. If the kinetic differential of stepwise hydrolysis of alkoxy groups could be extended 'practically' stable silane–water solutions might be possible. The salient characteristics of acid-catalyzed hydrolysis of alkoxysilanes are illustrated by a series of FTIR experiments, the results of which are given in Figs 4–6. Isobutyltriethoxy, trimethoxy, and mixed ethoxymethoxysilanes were hydrolyzed by adjusting mixtures with 0.1 M HCl to 6 mM H^+ concentration. Isobutyltrimethoxysilane hydrolyzes 7.7 times faster than its ethoxy analog. In the case of the mixed ethoxymethoxysilane, the overall rate of hydrolysis is 87% of that of the trimethoxysilane group. The nearly equivalent hydrolysis rates are a consequence of the fact that while the hydrolysis of the methoxy group is slowed down by 30% by the steric effets of the ethoxy groups, the hydrolysis of the methoxy group promotes the hydrolysis of the slower ethoxy group by 40%. Thus, under acidic conditions the hydrolysis of the first

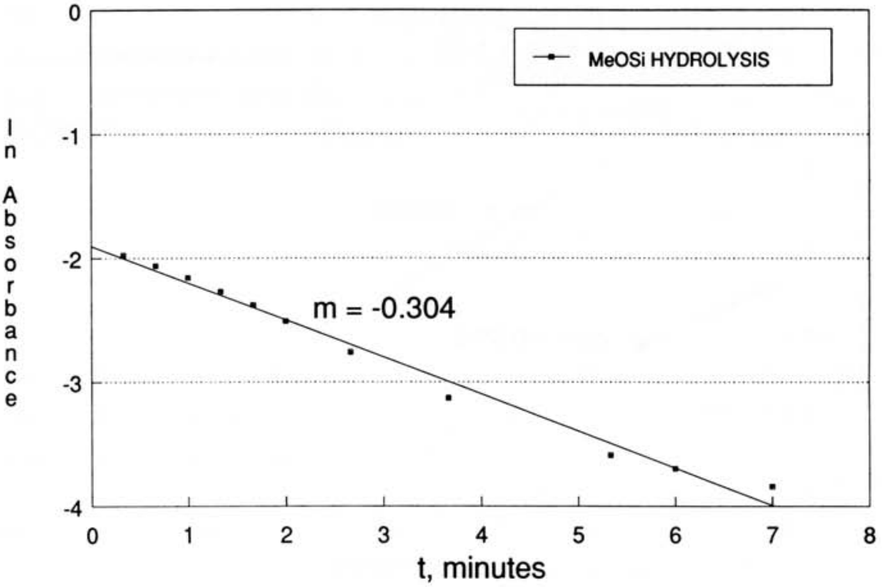

Figure 4. Hydrolysis of *i*-butyltrimethoxysilane.

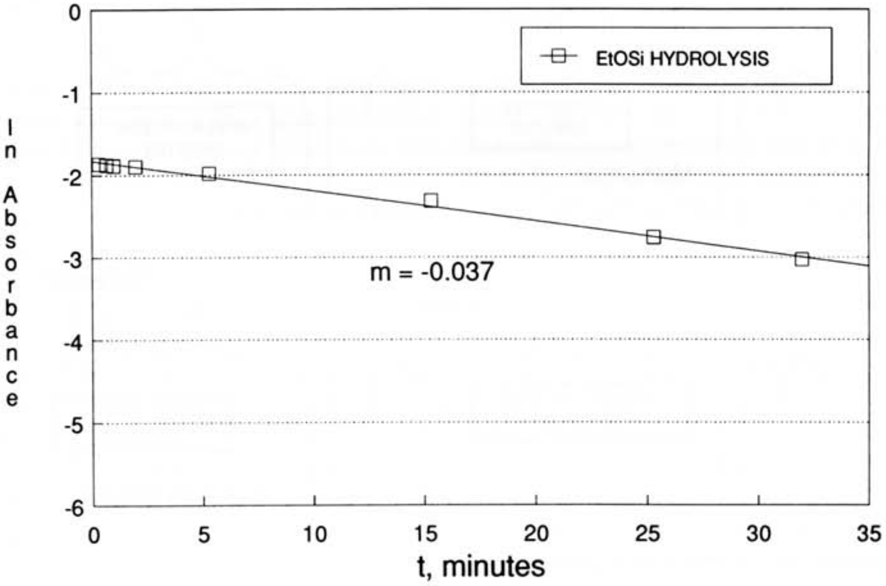

Figure 5. Hydrolysis of *i*-butyltriethoxysilane.

alkoxy group is rate-limiting. Preparing mixed alkoxysilanes would have no substantial benefit to extending silane aqueous solution stability.

2.3.2. Extent of silane condensation (degree of polymerization). In order to provide insight into the extent of condensation of silanols and their phase separation as a function of time, the hydrolysis of propyltrimethoxysilane was

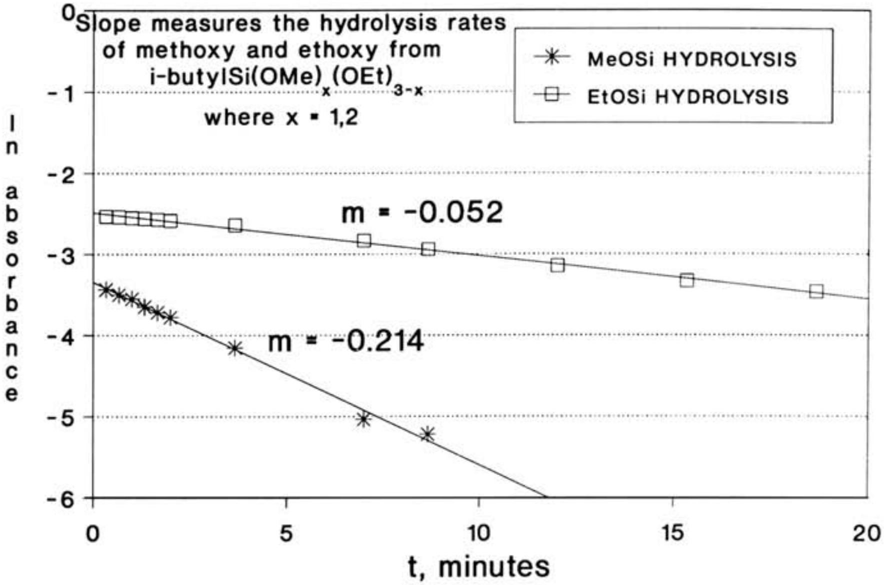

Figure 6. Hydrolysis of *i*-butyl mixed alkoxysilanes.

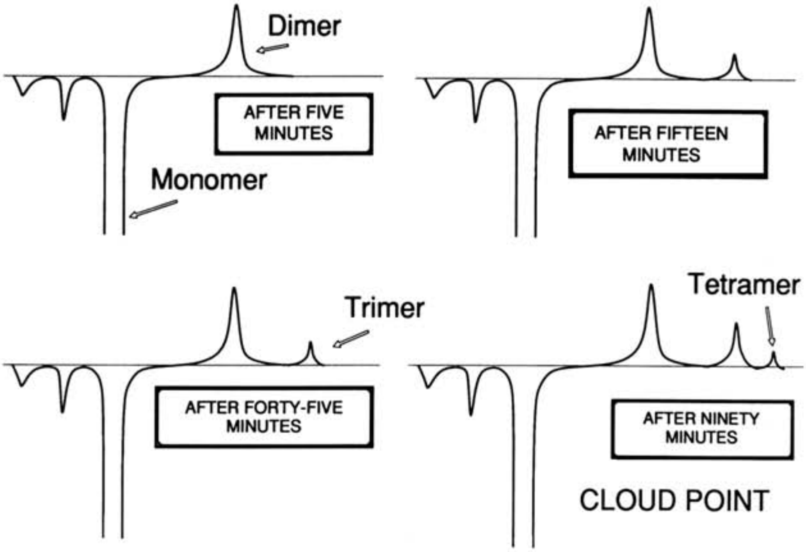

Figure 7. Hydrolysis of propyltrimethoxysilane.

studied. The aqueous hydrolysis of propyltrimethoxysilane was catalyzed with HCl and followed by HPLC, as shown in Fig. 7. It can be observed that the formation of dimeric species proceeds much faster than that of trimeric species. By the time tetramer was observed by HPLC, the solution had become hazy, indicating phase separation. The generalized model of propyltrimethoxysilane condensation is shown in Fig. 8.

It is interesting to note that the appearance of haze or onset of phase separation is coincident with the first opportunity for branching or cyclic

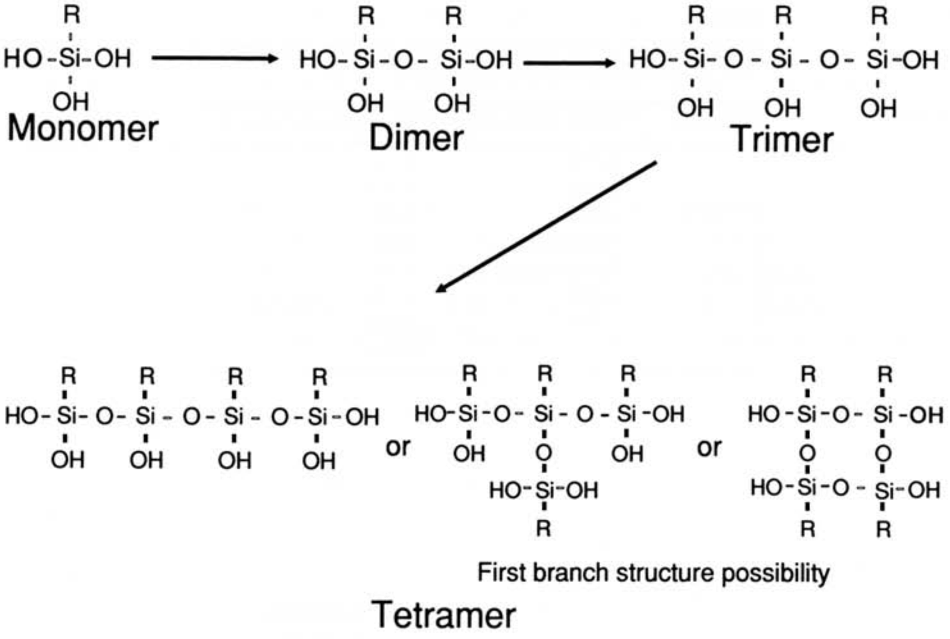

Figure 8. Oligomerization of silanes.

formation. More rapid molecular weight growth is possible in branched vs. linear systems due to the fact that silanediol chain ends are preferred for polymer growth. It may be argued, therefore, that the formation of the branched structure presages phase separation. In terms of preparing aqueous silane-treating solutions, it is clear that the maximum degree of polymerization for alkyltrialkoxysilanes should be limited to 3.

2.3.3. Equilibrium constant determination for alkoxysilane hydrolysis. Triethylsilanol was selected as a model compound for determination of the equilibrium constant for equation (1), since under neutral conditions the condensation to disiloxane was observed to take place only over an extended period of time (i.e. years), eliminating equilibria (2) and (3) as interfering factors.

A series of triethylsilanol/methanol/water mixtures were prepared as shown in Table 1 and stored in clean high-density polyethylene containers at room temperature. They were monitored for changes in component concentration and it was determined that after 100 days they had reached equilibrium.

2.3.4. NMR—results. All spectra were taken using a GE QE-plus 300 MHz NMR spectrometer. ^{13}C-NMR spectra (H decouple) were relatively easy; however, to eliminate the nuclear Overhauser effect, spectra were obtained in a reverse gated decouple mode. The T_1 spin lattice relaxation times for the samples were between 3 and 5 s. Therefore, all spectra were taken with a 30 s delay sequence. A typical spectrum with assignments is given in Fig. 9. The average equilibrium constant $[Et_3SiOMe][H_2O]/[Et_3SiOH][MeOH]$ for the series of mixtures was $2.7 \pm 0.4 \times 10^{-2}$.

Table 1.
Initial reactant concentrations in the equilibrium study of the triethylmethoxysilane–H_2O system

Sample no.	Moles methanol	Moles triethylsilanol
1	0.000	0.101
2	0.006	0.045
3	0.010	0.041
4	0.021	0.031
5	0.062	0.044
6	0.089	0.022
7	0.095	0.010
8	0.112	0.000

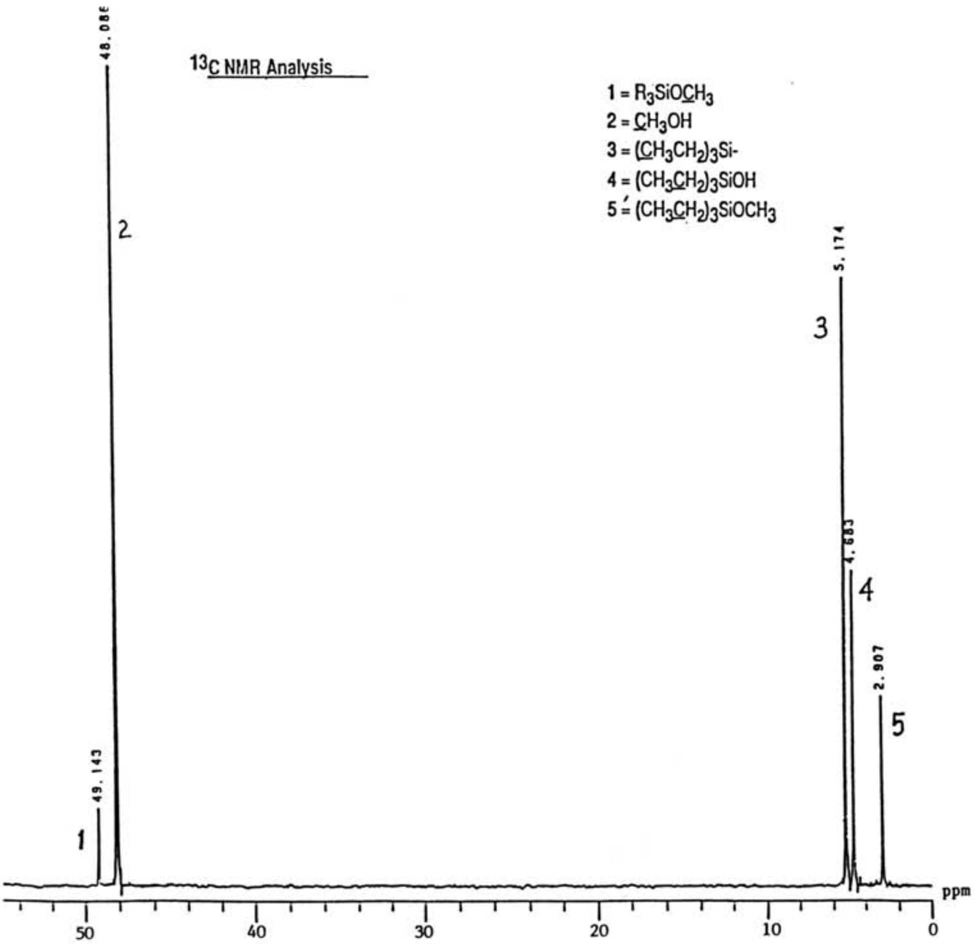

Figure 9. ^{13}C-NMR analysis of the concentrations of triethylsilanol/methanol/water in equilibrium mixture.

2.3.5. FTIR—results. All spectra were obtained using a Nicolet Model 740 FTIR spectrophotometer. A typical spectrum is given in Fig. 10. The spectra were deconvoluted using Lab Calc software, from Galactic Industries. The concentrations were derived by applying Beer's Law. The average equilibrium constant $[Et_3SiOMe][H_2O]/[Et_3SiOH][MeOH]$ for the series of mixtures was $2.3 \pm 0.3 \times 10^{-2}$.

Together, the NMR and IR results indicate that the equilibrium constant for $[R_3SiOR'][H_2O]/[R_3SiOH][R'OH]$ can be taken as $2.5 \pm 0.3 \times 10^{-2}$. There is, of course, some question as to how the results of monoalkoxysilanes can be translated to trialkoxysilanes. It is clear, however, that the equilibrium, while favoring hydrolysis, is not so large that stabilization by alcoholic species is precluded.

2.4. Silane hydrolysis—conclusions

New data have been presented in the context of a review of the aqueous behavior of silanes which elucidate their behavior, including mixed alkoxysilane hydrolysis kinetics, silane solubility, and the determination of the equilibrium constant for the alkoxy hydrolysis reaction.

The following factors enhance the stability of silanols:

(1) neutral conditions;
(2) limited condensation;

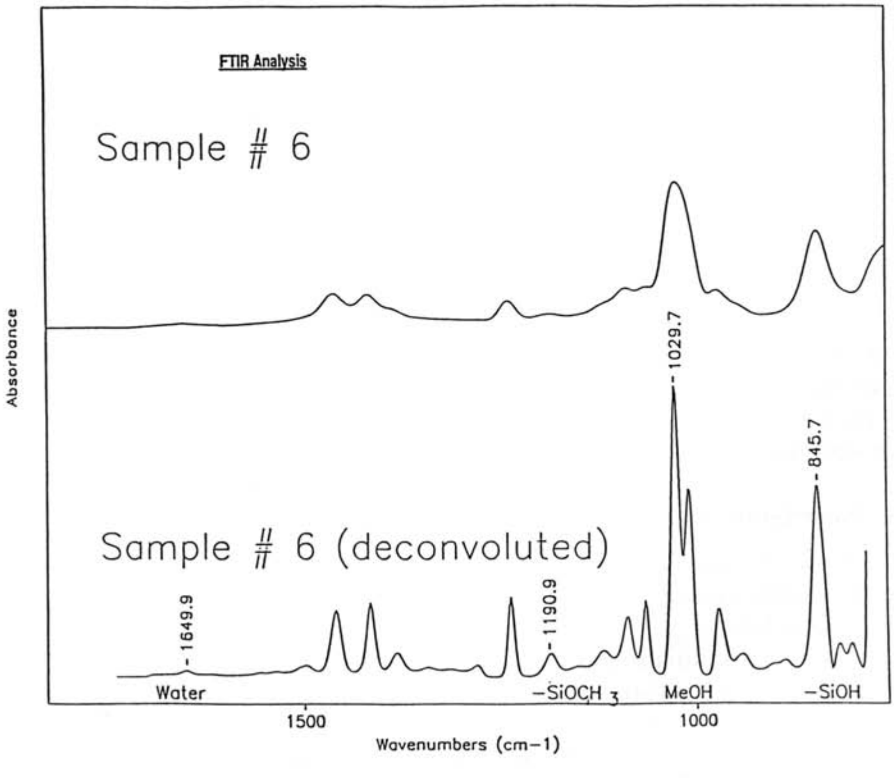

Figure 10. FTIR analysis of triethylsilanol/methanol/water in equilibrium mixture.

(3) the presence of hydroxylic species; and
(4) silanes forming stable zwitterions.

On the other hand, simply substituting different alkoxy groups on a silane or preparing mixed alkoxy-substituted silanes appears to offer little advantage in preparing stable water-borne silanes.

3. WATER-BORNE SILANES WITH STABLE SILANOLS

3.1. Water-borne silanes—background

A number of schemes were developed which incorporated the conclusions of the alkoxysilane hydrolysis studies in the first part of this paper. A series of water-borne silanes were developed having high active silanol contents which are stable in water for periods of more than 6 months. Low molecular weight alcohols were not incorporated in the solutions since even at concentrations as low as 1% they contribute to flammability.

Hydrosil® is the name used to designate a stable water-borne silane. The properties of various Hydrosil silanes are described in Table 2.

Table 2.
Physical properties of water-borne silanes

Silane type	Designation	Specific gravity	pH	Viscosity (mPa s)
Amine	Hydrosil 2627	1.1	10–10.5	5–10
Amine	Hydrosil 2628	1.1	10.5–11	5–10
Diamine	Hydrosil 2776	1.1	10–11	10–20
Diamine	Hydrosil 2774	1.1	10–11	65–70
Triamine	Hydrosil 2775	1.1	10–11	35–50
Epoxy	Hydrosil 2759	1.0	6–8	3–6
Mercapto	Hydrosil 2788	1.2	6–8	10–15
Vinyl	Hydrosil 2810	1.1	3.5–4.5	6–12
Vinyl-amino	Hydrosil 2781	1.1	10.5–11	4–9

3.2. Water-borne silanes—experimental

3.2.1. Acrylic latex sealants. Basic acrylic latex sealant formulations were compounded in a sigma blade mixer, as shown in Table 3. The water-borne silanes were then incorporated into a base. Standard wet and dry peel adhesion determinations from various substrates were performed periodically in accordance with ASTM C794-8.

3.3. Water-borne silanes—results and discussion

3.3.1. Acrylic latex sealants. Adhesion strengths on three substrates after 3 months sealant storage (0.5% silane added) were evaluated and the results are presented in Table 4.

The data substantiate that the silanes significantly enhance acrylic sealant bonding to various substrates. The significant results are the wet bond strength. Without silane addition there is virtually no wet bond strength. All silanes impart a substantial wet bond strength. The water-borne silanes, however, give wet bond strengths up to 30% greater than conventional silane coupling agents.

Table 3.
Latex sealant formulation

Latex (Rhoplex 1785 Rohm & Haas)	1915.0 parts
Non-ionic surfactant (TDET N407, Thompson Hayward)	59.4 parts
Dispersant (Calgon T)	49.9 parts
Plasticizer (Santicizer 160—Monsanto)	54.9 parts
Biocide (Fungitrol 234—Huls)	9.1 parts
Mineral spirits	59.2 parts
Ethylene glycol	63.2 parts
Calcium carbonate	3401.9 parts
Mix 30 min	
Latex (Rhoplex 1785)	534.4 parts
Ammonium hydroxide (28%)	4.5 parts
Silane	3.1 parts
Mix 15 min	

Table 4.
Effect of silanes on adhesion strength of latex formulations

(A) Adhesion to carbon steel

Peel strength (N/m)	Control	AMEO^a	Hydrosil 2627	DAMO^b	Hydrosil 2774	Hydrosil 2776
Dry	5254	7000	6130	5254	5254	5954
Wet	< 100	1750	2277^c	525	876	2100^c

(B) Adhesion to glass

Peel strength (N/m)	Control	AMEO^a	Hydrosil 2627	Hydrosil 2628	Hydrosil 2775
Dry	1750	2627	3152	4378	4378
Wet	< 100	2627	3152^c	2977^c	2100

(C) Adhesion to aluminum

Peel strength (N/m)	Control	AMEO^a	Hydrosil 2628	Hydrosil 2775	Hydrosil 2776
Dry	2627	3327	5954	2627	2977
Wet	< 100	525	875^c	1400^c	700

[a] Aminopropyltriethoxysilane.
[b] Aminoethylaminopropyltrimethoxysilane.
[c] Highest values observed.

3.3.2. Mineral-filled nylon 6/6 composites. Kaolin (Burgess) was treated with the appropriate silane in a Patterson Kelly 8-qt. twin shell blender with intensifier bar. Treatment levels were 1% active silane. The kaolin was compounded with nylon 6,6 (Vydyne 21x—Monsanto) in a Leistritz twin screw extruder. The compounds were tested in a 'dry as molded' condition in accordance with ASTM D-638 (see Table 5).

In virtually all the cases tested, the water-soluble silane hydrosil gave values better than that from a conventional control silane in solution.

3.4. Water-borne silanes—conclusions

Based on observations of silanol stability, a new series of silanes were developed

Table 5.
Tensile strength of 40% clay-filled nylon 6/6 as a function of treatment

Surface treatment	Tensile strength (MPa)	% of control
Control	64.8	100
AMEO-40[a]	71.7	111
HS2627[b]	75.8	117
HS2628	77.90	118
HS2781	80.66	124
HS2774	73.76	114
HS2776	77.2	119
HS2775	77.2	119

[a] 40% solution of aminopropyltriethoxysilane in water.
[b] Hydrosil.

with long-term stability in aqueous systems. These materials offer intrinsic process flexibility due to the elimination of volatile by-products and reduced flammability.

The performance of the new water-borne silanes was studied. The water-borne silanes were comparable to conventional silanes in most cases. In several cases, notably with acrylic latices, the new silanes excelled. In particular, the data obtained suggest that the new amine functional materials may exhibit superior performance to conventional silanes in moist environments.

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