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Stable, Water-Borne Silane Coupling Agents

ABSTRACT

The bonding of organosilane coupling agents to inorganic surfaces through stable oxane bonds requires hydrolysis. In many commercial applications this is accomplished by preparation of aqueous treating solutions. For many aminofunctional silanes this is relatively simple since stable aqueous solutions of these materials are easily formed. For most other functionalities, however, stabilization techniques are required to form even dilute solutions with limited pot lives. In addition, the hydrolysis by-products, normally alcohols, represent potential health and flammability hazards and an environmental concern.

This paper reviews kinetic and mechanistic aspects of silane hydrolysis and describes a new series of water-borne silanes. These new coupling agents have been prepared with a wide range of functionality for compatibility with most common resin systems. Performance data which compares these aqueous-borne silanes with conventional silane coupling agents, in both thermoset and thermoplastic applications, is presented.

SILANOL CHEMISTRY—BACKGROUND AND NEW DATA

In the vast majority of silane surface treatment applications, the alkoxy groups of the silane 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 silane alkoxy groups may occur during the formal preparation of aqueous solutions or the reaction of the silane with absorbed 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 silanols. Silanols usually condense with themselves or alkoxy silanes to form siloxanes. Alkoxy silanes are stable sources for silanols, but they have low intrinsic reactivity, low solubility in aqueous situations and by-products of hydrolysis which may be undesirable from a flammability and toxicity perspective.

The general mechanism for siloxane bond formation, depicted below, has been reviewed [1,2] (Figure 1). Alkoxy silanes undergo hydrolysis by both base and acid catalyzed mechanisms. In contact with water under neutral, low ionic conditions, alkoxy silanes bearing no autocatalytic functionality are stable for weeks or months. The products of hydrolysis do not propagate the hydrolysis reaction. In contact with "tap" water, hydrolysis is usually substantial within hours. The same factors which accelerate the hydrolysis of alkoxy silanes also accelerate the condensation of silanols with other silanols and their alkoxy silane precursors. The overall path-

way for the hydrolysis and full condensation of an alkoxy silane is complicated. If effects beyond the next nearest neighbor during condensation are ignored, there are 6 possible hydrolysis paths, 15 possible water producing condensations, and 30 possible alcohol producing reactions. Assink has presented a model for tetraalkoxy silane hydrolysis and condensation [3]. Presented in Figure 2 is a version of the Assink model for trialkoxy silanes used on surface treatments. Like the model for tetraalkoxy silanes, extended condensation or polymerization which results in phase separation and its kinetic consequences are not considered.

The overall complexity of hydrolysis and condensation has not allowed determination of kinetic or equilibrium data for silanol formation or reaction. In this context, it is useful to review observations and present new data which support silanol formation as the critical intermediate of silane surface treatment.

Alkoxy silane Hydrolysis

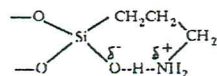
A series of hydrolysis studies [4,5,6], indicate that under basic conditions the hydrolysis of alkoxy groups usually takes place in a stepwise manner. Carbon bonded substituents can have profound effects on the rate of hydrolysis. With the exception of amino silanes, most silanes are employed in surface 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 rate of hydrolysis of the alkoxy groups are generally related to their steric bulk: $\text{CH}_3\text{O} > \text{C}_2\text{H}_5\text{O} > \text{tC}_4\text{H}_9\text{O}$. A methoxy silane, for example, hydrolyzes 6-10 times the rate of an ethoxy silane. Under acid conditions the hydrolysis of the first alkoxy group is rate limiting. We have proposed [7] that after the formation of the first silanol group, hydrolysis of the remaining alkoxy groups is facilitated by proton transfer from the initially formed silanol group as shown in Equations (1-3).

The salient characteristics of acid catalyzed hydrolysis of alkoxy silanes is illustrated by a series of new FTIR experiments, the results of which are given below (Figures 3-8). Vinyl and isobutyl triethoxy, trimethoxy and mixed ethoxymethoxy silanes were hydrolyzed with 0.1M HCl. Vinyltrimethoxy silane and isobutyltrimethoxy silane hydrolyze 7.7 \times and 8.2 \times faster, respectively, than their ethoxy analogs. In the case of the mixed ethoxymethoxy silane, the overall rate of hydrolysis is 87% of that of the methoxy group, a consequence of the fact that while the hydrolysis of the methoxy group is slowed 30% by the steric effects of the ethoxy groups, the hydrolysis of the methoxy group hydrolysis promotes the hydrolysis of the slower ethoxy group by 40%.

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Persistence of Silanols

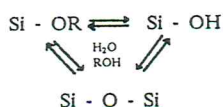
Individual examples of monomeric silanols such as triethylsilanol [8] and phenylsilanetriol [9] have been prepared under regimens different from those used for surface treatments and exhibit extended stability. To date, no monomeric trisilanols have been isolated from aqueous hydrolysates of alkoxysilanes employed as surface treatments. Since 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 has been observed empirically [10] and by Si [29] nmr [11,12]. In the reaction mixtures, silanol persistence can be favored by steric, electronic or equilibrium conditions.



While condensed silanols or siloxanes are typically not regarded as participating in a reversible reaction with water or alcohol, this is, in fact, not the case. Iler [13] has shown that even hydrated amorphous silicon dioxide has an equilibrium solubility in methanol. The phase separation that results from highly condensed systems will continuously remove material from the equilibrium, depleting all soluble silane species. On the other hand, condensation can create steric restraints which retard extended polymerization.

In order to provide insight into the extent of condensation of silanols and their phase separation as a function of time, we have studied the hydrolysis of propyltrimethoxysilane and present this data. The aqueous hydrolysis of propyltrimethoxysilane (10%) was catalyzed with 0.1% acetic acid and followed by GPC. It can be observed that the formation of dimeric species proceed much faster than trimeric species, with dimer appearing within 5 minutes and trimer appearing after 15 minutes. At 90 minutes, tetramer was observed by GPC and the solution was observed to become hazy, indicating phase separation (Figure 9).

A special case exists for many aminosilanes such as amino-propyltriethoxysilane, where a stable zwitterionic silonate forms that is stable in solution [14,15,16].



NEW WATER-BORNE SILANES WITH STABLE SILANOLS

The following factors enhance the stability of silanols:

1. Neutral conditions
2. Limited condensation
3. Presence of hydroxylic species
4. Silanes forming stable zwitterions

A number of schemes were developed which incorporated these factors in synthetic design. A series of water-borne silanes were developed having high active silanol contents which are stable in water for periods of greater than six months. Their properties are described below.

Silane Type	Name	Specific Gravity	Viscosity, cSt
Amine	Hydrosil™ 2627	1.1	5-10
	Hydrosil™ 2628	1.1	5-12
	Hydrosil™ 2774	1.1	65-75

Silane Type	Name	Specific Gravity	Viscosity, cSt
Epoxy Mercapto Methacrylate Vinyl-amino	Hydrosil™ 2776	1.1	10-20
	Hydrosil™ 2775	1.1	35-50
	Hydrosil™ 2759	1.0	3-6
	Hydrosil™ 2788	1.2	10-15
	Hydrosil™ 2789	1.1	3-9
	Hydrosil™ 2781	1.1	4-9

PERFORMANCE DATA OF WATER-BORNE SILANES

Experimental

ADDITIVE FOR ACRYLIC LATEX SEALANTS

Basic acrylic latex sealant formulations were compounded in a sigma blade mixer. The water-borne silanes were then incorporated into base. Standard wet and dry peel adhesion determinations on carbon steel were performed periodically.

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 minutes

Latex (Rhoplex 1785)	534.4 parts
Ammonia (28%)	4.5 parts
Silane	31.0 parts

Mix 15 minutes

RESULTS

Adhesive bonding on carbon steel after 3 months sealant storage (0.5% silane added) was evaluated.

Peel strength pli	Control	AMEO ¹	Hydrosil 2627	DAMO ²	Hydrosil 2774	Hydrosil 2776
Dry	30	40	35	30	30	34
Wet	<1	10	13	3	5	12

Circled values are highest observed

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

Pretreatment for Kaolin in Nylon 6/6

Kaolin (Burgess) was treated with the appropriate silane in a Patterson Kelly 8-qt twin shell blender with intensifier bar. Treatment

¹Aminopropyltriethoxysilane.

²Aminoethylaminopropyltrimethoxysilane.

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.

RESULTS

40% CLAY FILLED NYLON 6/6

Surface Treatment	Tensile Strength, psi
Control	9400
AMEO-40 ³	10400 (+11%) ⁵
HS ⁴ 2627	11000 (+17%)
HS 2628	11300 (+18%)
HS 2781	11700 (+24%)
HS 2774	10700 (+14%)
HS 2776	11200 (+19%)
HS 2775	11200 (+19%)

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

CONCLUSIONS

New data has been presented in the context of a review of the aqueous behavior of silanes which elucidates their behavior. Based on observations of silanol stability, a new series of silanes were developed 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 silanes was studied. While comparable in most cases to conventional silanes, in several cases, notably acrylic latices, the new silanes excelled. In particular, the data obtained suggests that the new amine functional materials may exhibit superior performance to conventional silanes in moist environments.

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BIOGRAPHIES

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B. Arkles is currently Vice President of Corporate Development for Huls America. Previously he was co-founder and President of Petrarch Systems, Inc.

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³40% solution of aminopropyltriethoxysilane in water.

⁴Hydrosil.

⁵Percent improvement over control.

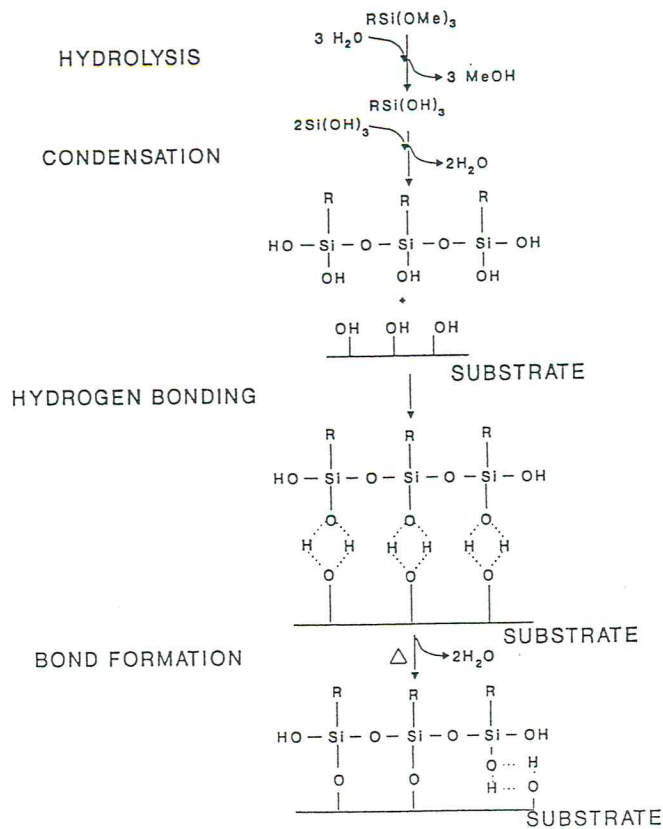


FIGURE 1. Mechanism of bond formation.

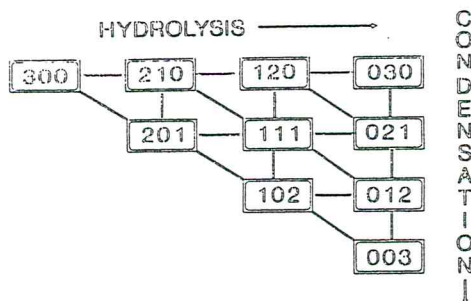


FIGURE 2a.

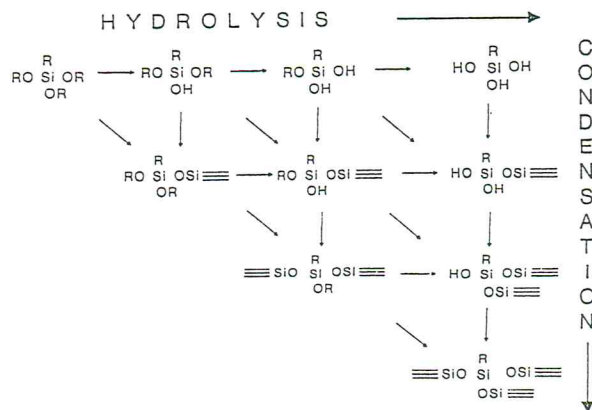


FIGURE 2b.

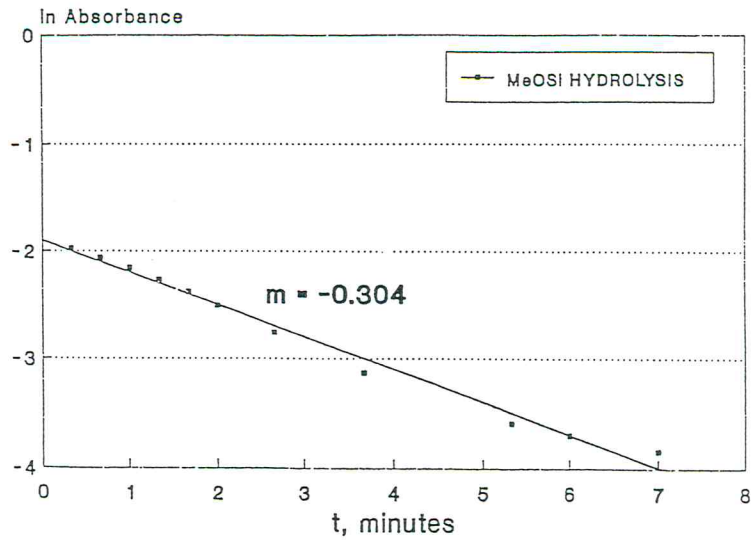


FIGURE 3. Hydrolysis of i-butyltrimethoxy silane with 0.1N HCl.

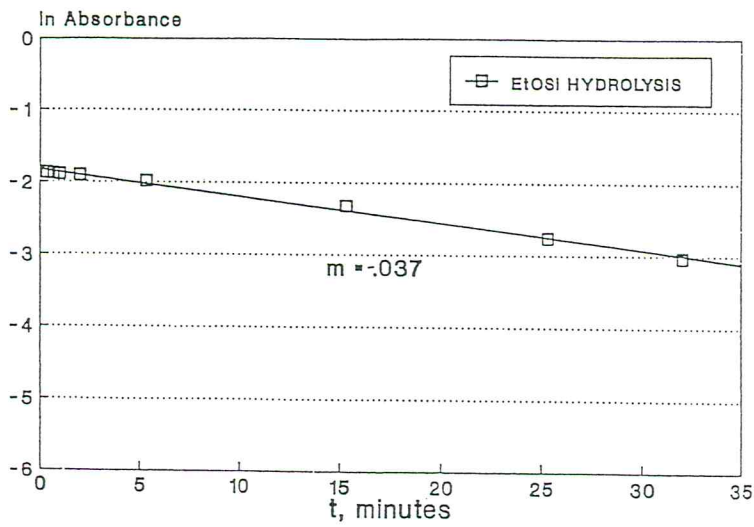


FIGURE 4. Hydrolysis of i-butyltriethoxy silane with 0.1N HCl.

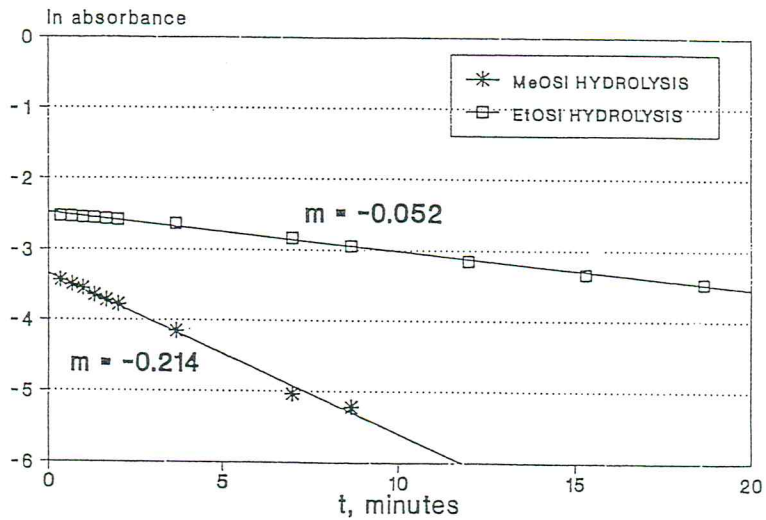


FIGURE 5. Hydrolysis of i-butyl mixed alkoxy silanes with 0.1N HCl.

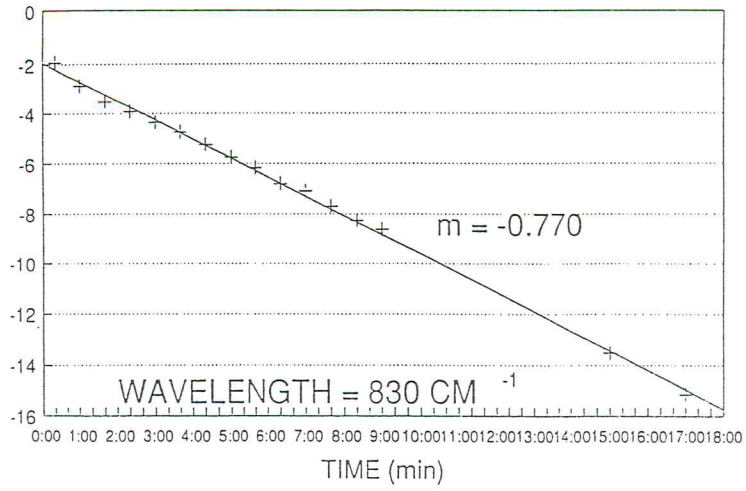


FIGURE 6. Hydrolysis of vinyltrimethoxysilane with 0.1N HCl.

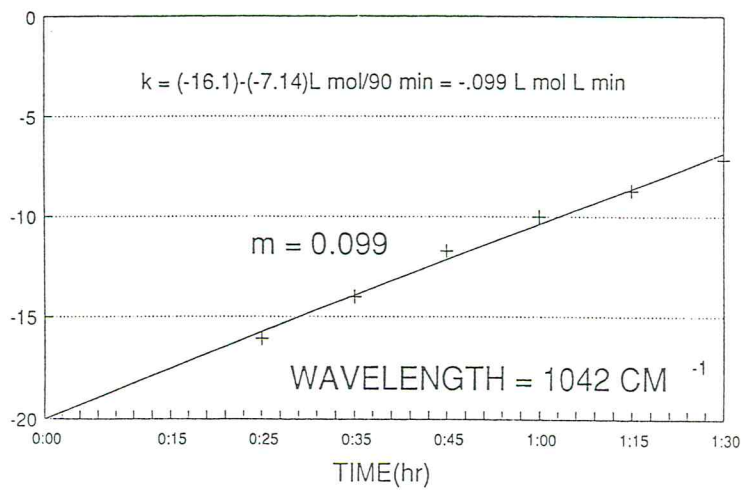


FIGURE 7. Hydrolysis of vinyltriethoxysilane with 0.1N HCl.

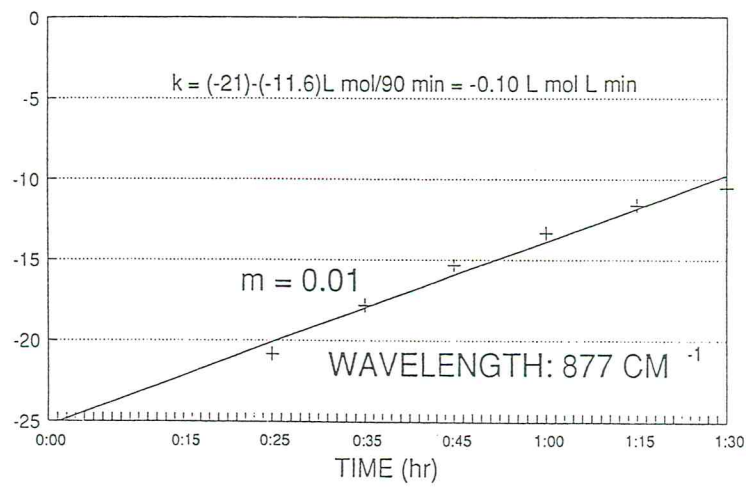


FIGURE 8. Hydrolysis of vinyltriethoxysilane with 0.1N HCl.

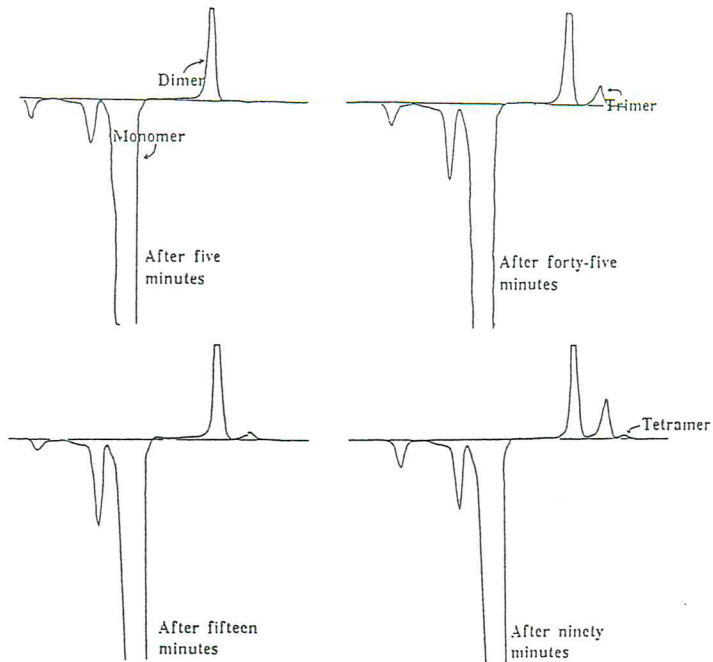
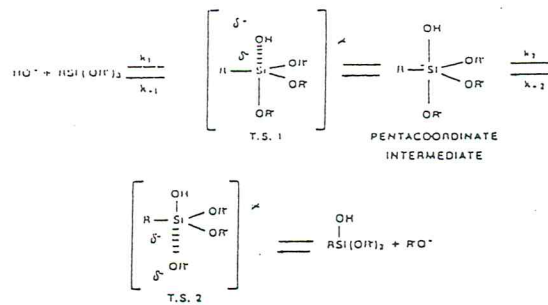
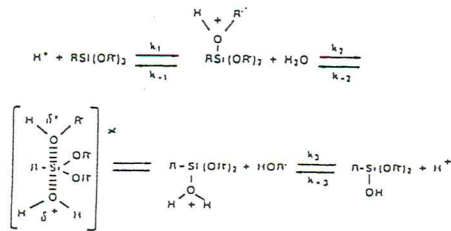


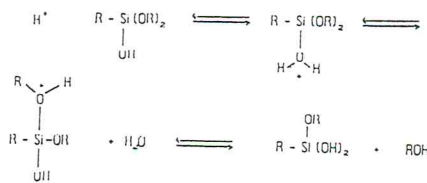
FIGURE 9. Hydrolysis of propyltrimethoxysilane. Analysis by GPC.



EQUATION 1.



EQUATION 2.



EQUATION 3.