



# Using Silanes as Adhesion Promoters

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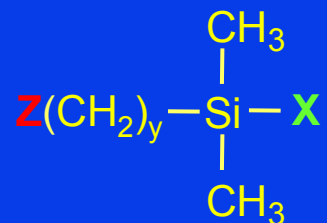
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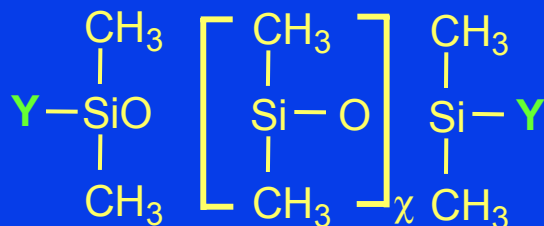
# UCT'S PETRARCH® PRODUCTS

## Silanes



**Z = NH<sub>2</sub>, SH, C-H,**  
And Other Reactive  
Functional Groups

## Silicones



**Y=H, Vinyl, Amino**  
And Other Reactive  
Functional Groups

## Platinum Catalysts



# PRODUCT APPLICATIONS

## Silanes

- Adhesion Promoters
- Hydrophobic Coatings
- Surface Modifying Reagents
- Lenses Monomers
- Chromatographic Stationary Phases

## Silicones

- Lubricants
- Adhesives
- Electronic Coatings
- Dental Fillings
- Fiber Optic Coatings
- Releasing Agents
- Medical Coatings
- High Performance Coatings

## Platinum Catalysts

- Hydrosilylation
- Room Temperature Silicone Curing Agent
- High Temperature Silicone Curing Agent



Adhesion (“sticking”) of resins to surfaces is often marginal, especially if the polymeric resin has no chemical affinity to bond to the substrate surface. Evidence of poor adhesion is seen as manual de-lamination when mechanical force is applied to the laminate or often as partial spontaneous de-lamination, especially at the edges of the device. Often moisture, acid or base promote this adhesive failure.

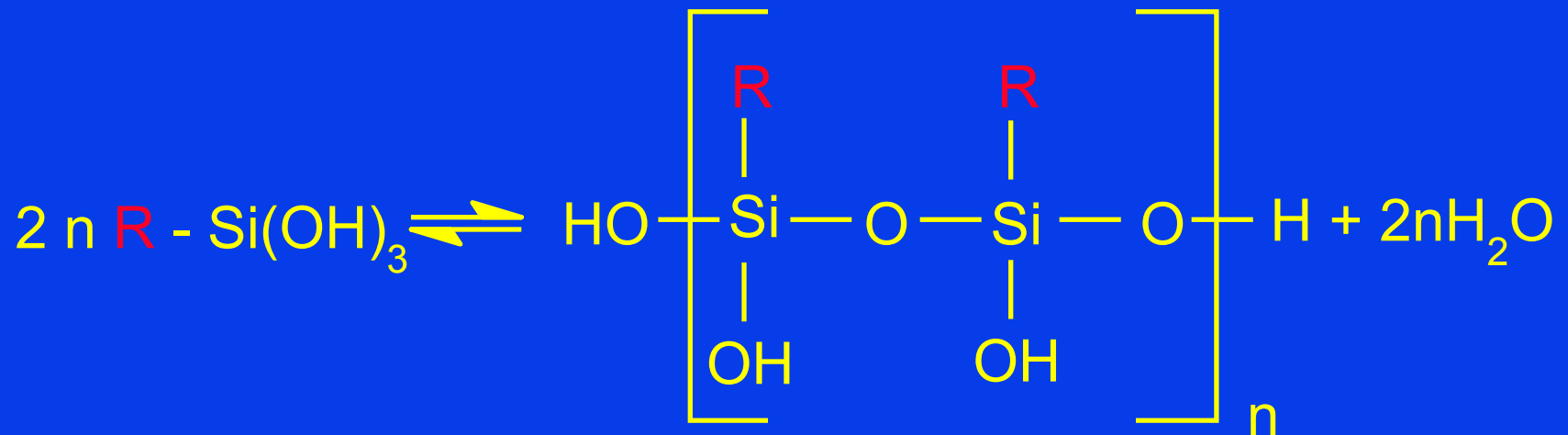
Organosilane coupling agents have been shown to dramatically improve the adhesion of polymeric resins to substrates such as glass, silica, alumina or active metals. The purpose of this paper is to review the basic principles of this technology, citing its preferred applications, limitations and application protocols. United Chemical Technologies (UCT) is a major manufacturer of these materials, and in many instances UCT catalog numbers will be introduced during discussion of individual reactions or in tabular data. In many chemical reactions the reacting groups are color coded for clarity.

Figure 1 illustrates a typical alkoxy silane coupling agent and also shows its hydrolysis reaction. Typically, the silane is functional at both ends and **R** is an active chemical group such as amino (NH<sub>2</sub>), mercapto (SH) or isocyanato (NCO) . This functionality can react with functional groups in an industrial resin or bio molecule such as peptides, oligonucleotides or DNA fragments. The other end consists of a halo (chloro most often) or alkoxy (most often methoxy or ethoxy) silane. This functionality is converted to active groups on hydrolysis called silanols . The silanols can further react with themselves, generating oligomeric variations. All silanol variations can react with active surfaces that themselves contain hydroxyl (OH) groups.

## Figure 1 Typical Alkoxy Silane and its Hydrolysis



Typical Alkoxysilane **R** = Reactive Group



Reactive Silanol Oligomer

Figure 2 shows the three main classes of silanes employed, chloro, methoxy and ethoxy silanes. Chlorosilanes are most reactive but evolve corrosive hydrogen chloride on hydrolysis. Methoxy silanes are of intermediate reactivity and evolve toxic methanol. Ethoxy silanes are least reactive but evolve non toxic ethanol. Only the scientist or technologist can decide based on his unique processing needs which classes he can use. Generally the reactivity differences between methoxy and ethoxy silanes are not a problem. At typical hydrolysis pH (acidic ~5, basic ~ 9), both versions hydrolyze in under 15 minutes at 2% silane concentrations.

Figure 2 Typical Silane Coupling Agents

**X - CH<sub>2</sub> - CH<sub>2</sub> - CH<sub>2</sub> - SiCl<sub>3</sub>**  
Most Reactive, Evolves Corrosive HCl

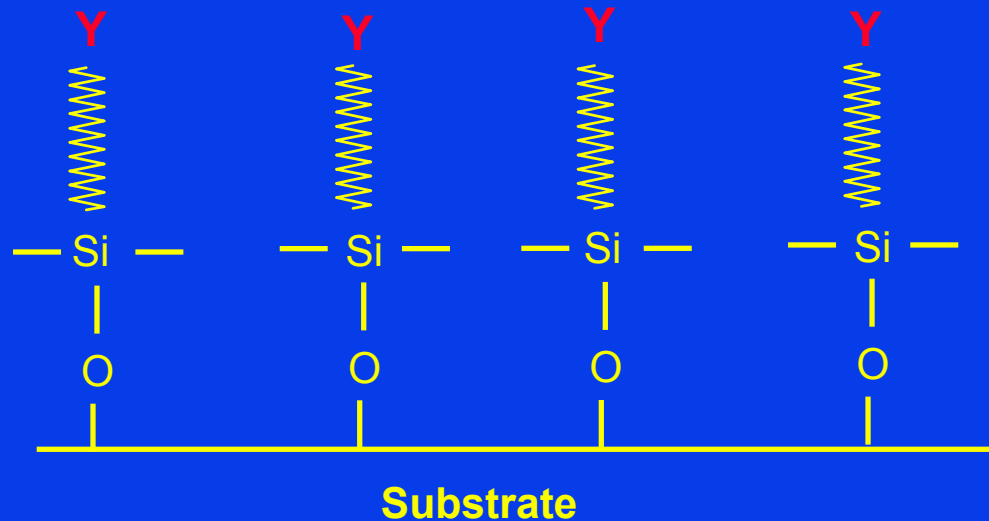
**X - CH<sub>2</sub> - CH<sub>2</sub> - CH<sub>2</sub> - Si (OCH<sub>3</sub>)<sub>3</sub>**  
Intermediate Reactivity, Evolves Toxic Methanol

**X - CH<sub>2</sub> - CH<sub>2</sub> - CH<sub>2</sub> - Si (OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>**  
Least Reactive, Evolves Non-toxic Ethanol

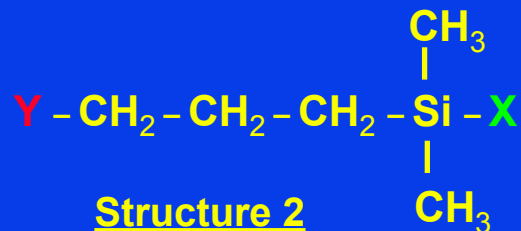


Figure 3 deals with the concept of monolayer vs multilayer deposition. A typical monolayer deposition is depicted. Monolayers are preferred in physical surface studies where the structure must be uniform, or in bio materials where a uniform surface structure is needed to promote specific interactions. However, monolayers suffer from one severe disadvantage. Cleavage of the bond is readily accomplished in high or low pH, resulting in adhesive failure. Monolayers are generated from monochloro or alkoxy silanes, see Figure 3, Structure 2. Conversely, trichloro or trialkoxy silanes can form network or “multilayer” structures at the surface from crosslinking of the silanetriols produced during hydrolysis (see Figure 2, Structure 1 and Figure 25). At a 2% silane concentration in aqueous alcohol typically 3-8 molecular layers are produced. While the multilayer structure is inherently less uniform, it possesses dramatically improved hydrolytic stability at the polymer/silane/substrate interface. The crosslinked network is not dissolved if one bond is broken, unlike the situation for monolayers, where a broken bond results in adhesive failure at that area of the surface. For those such as chromatography column manufacturers who require a monolayer, but also desire hydrolytic stability, United Chemical Technologies offers a line of Bis-isopropyl functional silanes, see structure 3. The bulky isopropyl groups sterically block attack by acidic or basic nucleophiles.

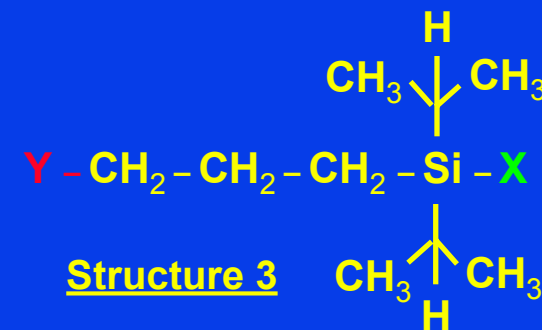
## Figure 3 Monolayer Vs Multilayer Deposition Monolayers



Crosslinks at surface, gives  
 3-10 layers at 2% concentration



Gives Monolayer,  
 but less hydrolytically stable



Gives Hydrolysis Resistant Monolayers

# Chromatographic Silanes

## **Sterically Hindered Silanes for Passivation or Functionalization of Chromatographic Stationary Phases**

UCT offers a line of functionalized bis-isopropyl modified silanes. These silanes react with polar substrates, generating monolayers of greatly enhanced hydrolytic stability. The steric bulk of the isopropyl groups retards the rate of nucleophilic cleavage of the silane in highly base or acidic media. In addition to the silanes below other chain lengths and functionalities are available on a custom basis.

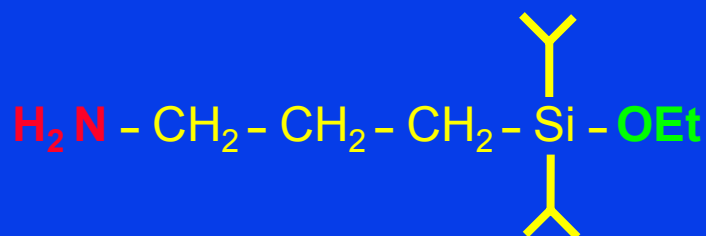
# Chromatographic Silanes

Catalog#

Name

A0745

3-Aminopropyldiisopropylethoxysilane

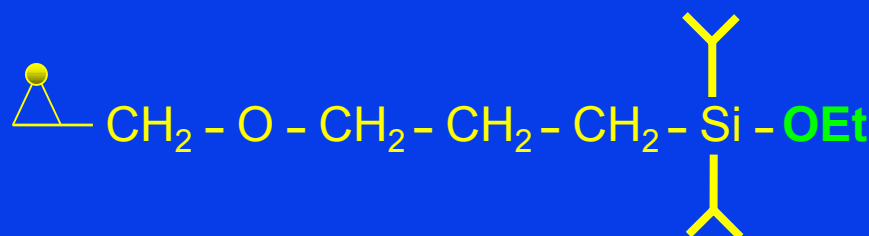


Catalog#

Name

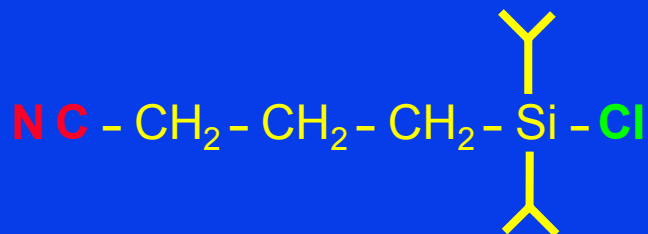
G6660

3-Glycidoxypropyldiisopropylethoxysilane



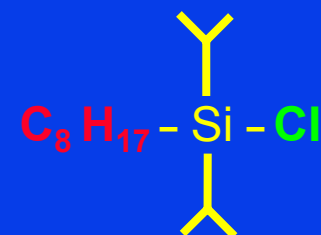
C3443

3-Cyanopropyldiisopropylchlorosilane



O9818.8

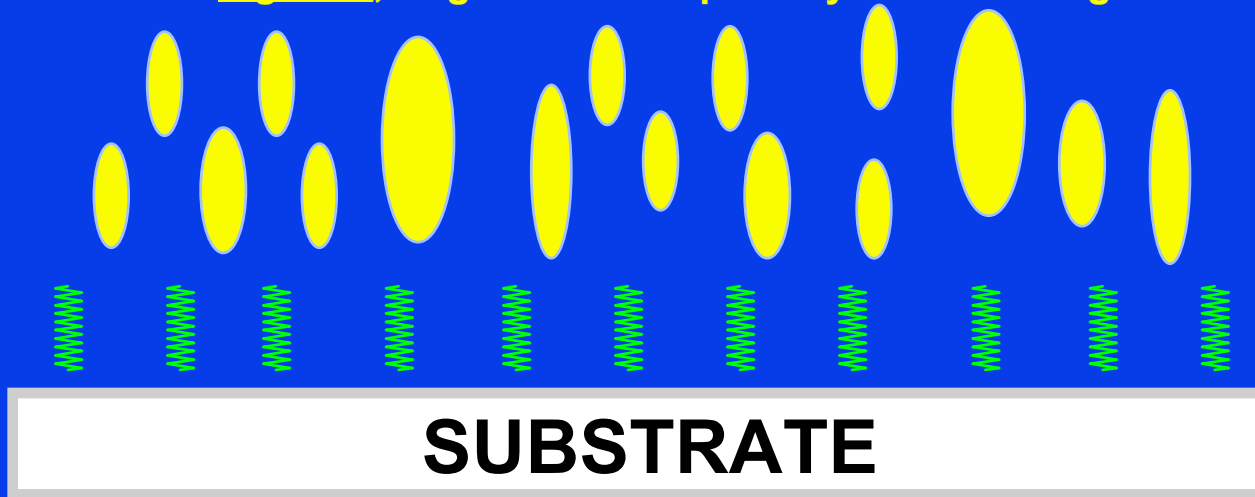
n-Octyldiisopropylchlorosilane



In addition to wide utility in enhancing resin or biomolecule adhesion, organosilanes have shown the ability to promote the alignment of nematic liquid crystals in orientations either parallel or perpendicular to the substrate surface. This orienting ability is critically important in liquid crystal (“LC”) display switching devices, where orientation in one direction is turbid to plane polarized light and the other direction is black.

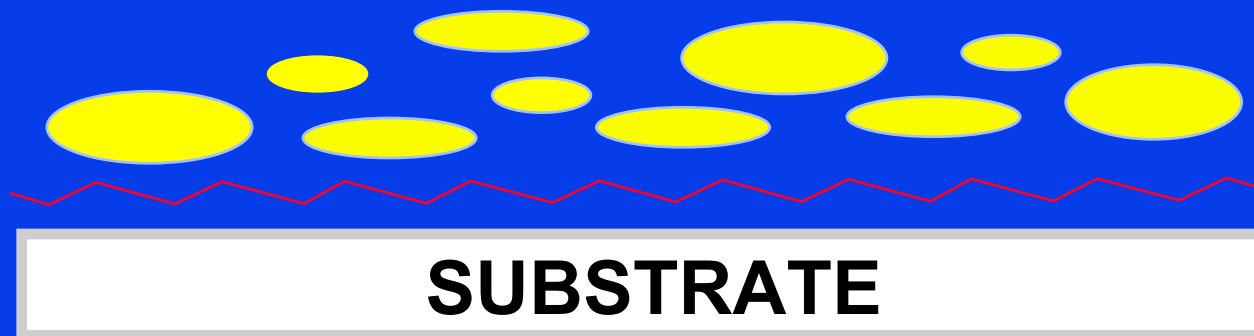
Figures 4 and 5 show examples of these orienting effects with specific United Chemical Technologies silanes. The interactions of the liquid crystal and the active group **X** on the silane are in these cases thought to be physical, that is, of the Van Der Waals, hydrogen bonding or IPN (interpenetrating network) types rather than through a chemical reaction.

Figure 4, Alignment of Liquid Crystals with Organosilanes



"DMOAP" = O9745

Orients nematic liquid crystals perpendicular to surface



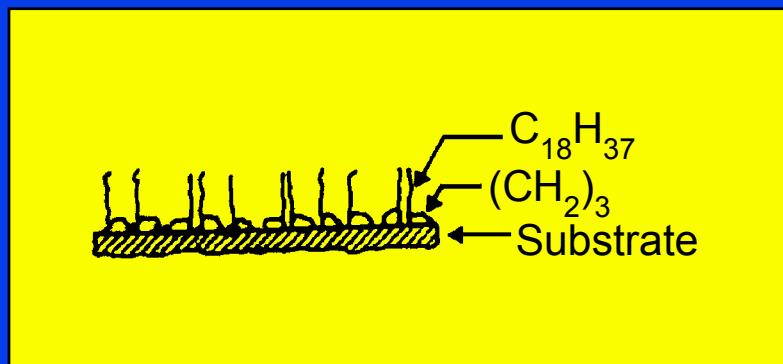
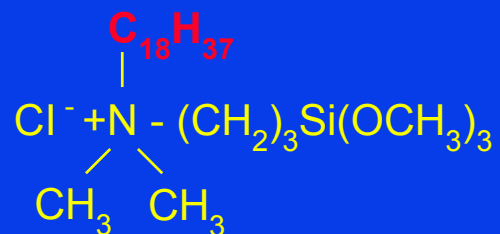
"MAP" = M8620

Orients nematic liquid crystals parallel to surface

**Figure 5, Examples of Liquid Crystal Orienting Silanes**

**N,N-dimethyl-N-octadecyl-  
3-aminopropyltrimethoxysilylchloride  
(DMOAP)**

**O9745**



**N-methyl-  
3-aminopropyltrimethoxysilane  
(MAP)**

**M8620**

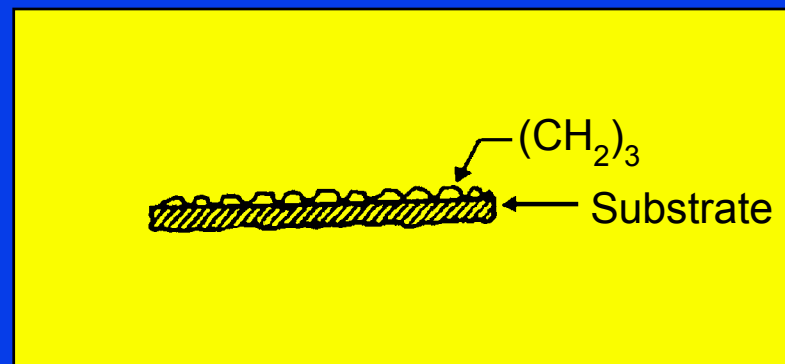
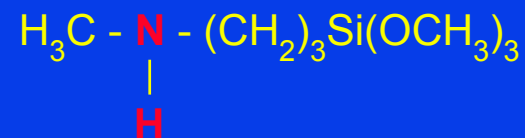
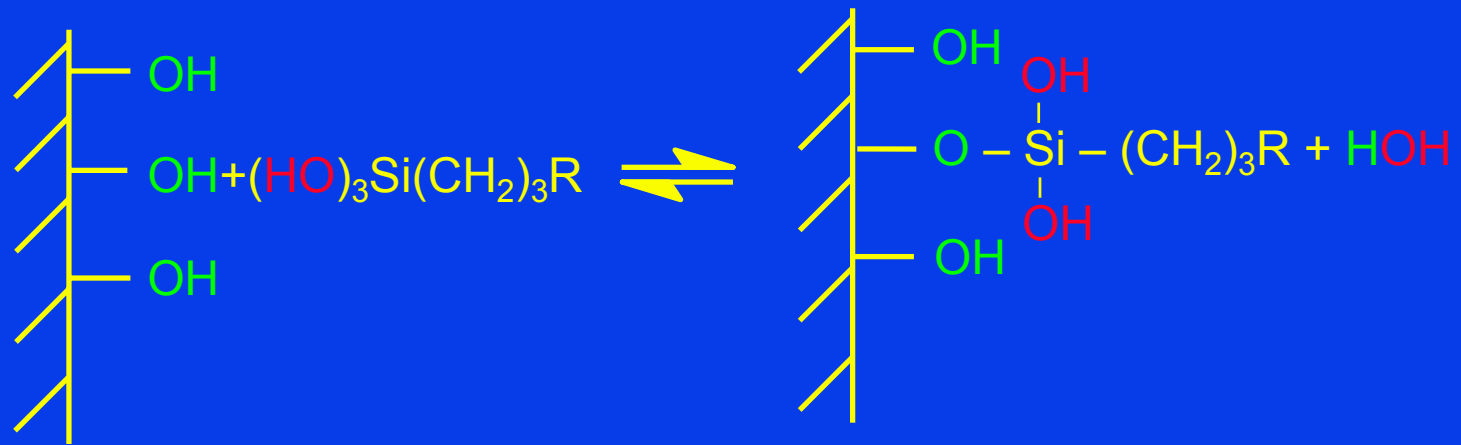


Figure 6 illustrates a substrate surface containing an active hydroxyl functionality, being approached by an active silanol intermediate. Covalent bonding occurs, generating a M-O-Si bond, where M is an active metal or activated polymer. This bond is very stable to hydrolytic cleavage when M is silicon or aluminum, less strong for transition metal elements and least for C-O-Si linkages. Corona or plasma treatments of organic polymer surfaces generate C-OH bonds. Thus silane depositions on these treated plastics are intrinsically less hydrolytically stable. Generation of multi layer surface networks via trifunctional silanes, or monolayer generation by use of the bis-isopropyl silanes previously discussed, are both good options if long term exposure of the interface to high or low pH is anticipated.



**Figure 6 Interaction of Active Surfaces with Silanols**



A basic mechanistic model for silane deposition on active substrates was described by Arkles (Ref 1). Figure 7 shows its main elements. The alkoxysilane is first hydrolyzed to generate active silanol intermediates. These intermediates partially oligomerize in solution. The illustrated model shows a partially oligomerized trimer approaching the substrate surface. Hydrogen bonding initially occurs, followed by elimination of water on thermal cure, generating a stable Si-O-Si covalent bond.

**Figure 7 Mechanism of Silane Deposition on an Active Substrate**

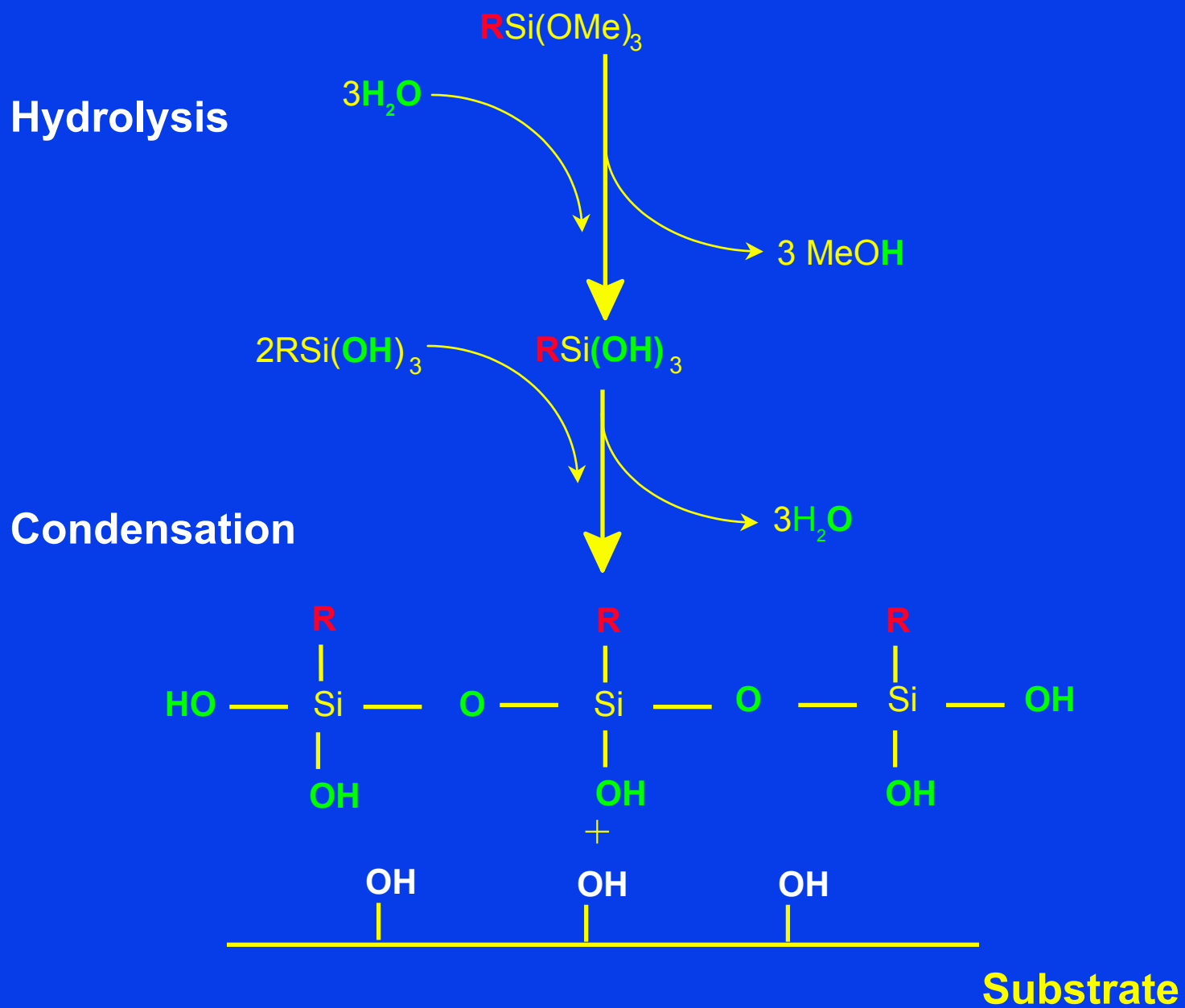
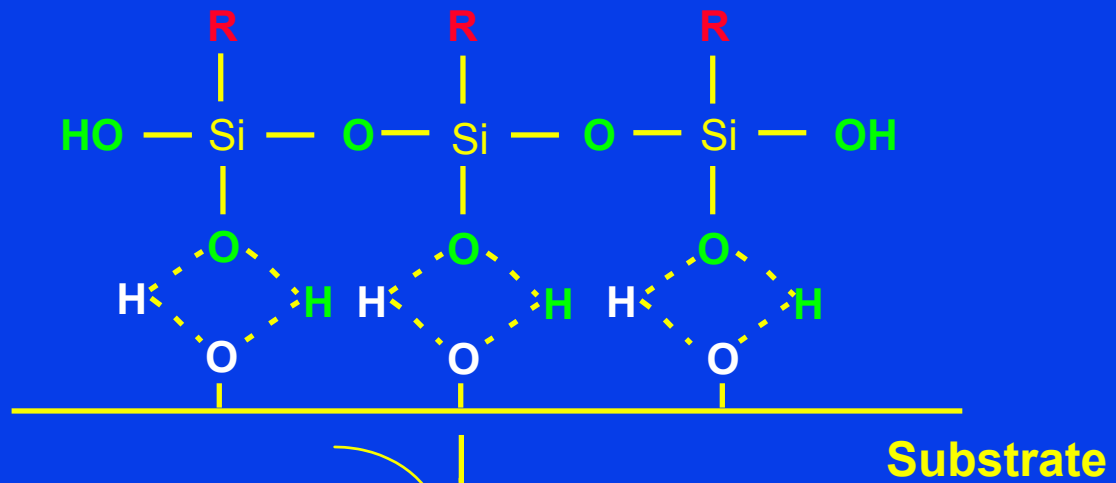


Figure 7 Continued

Hydrogen bonding



Bond Formation

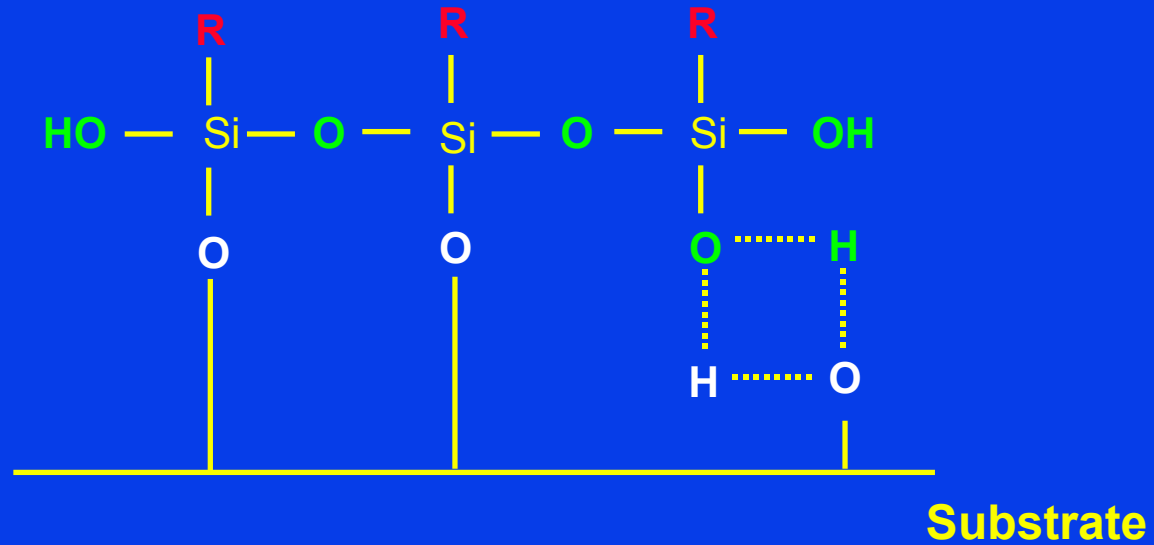
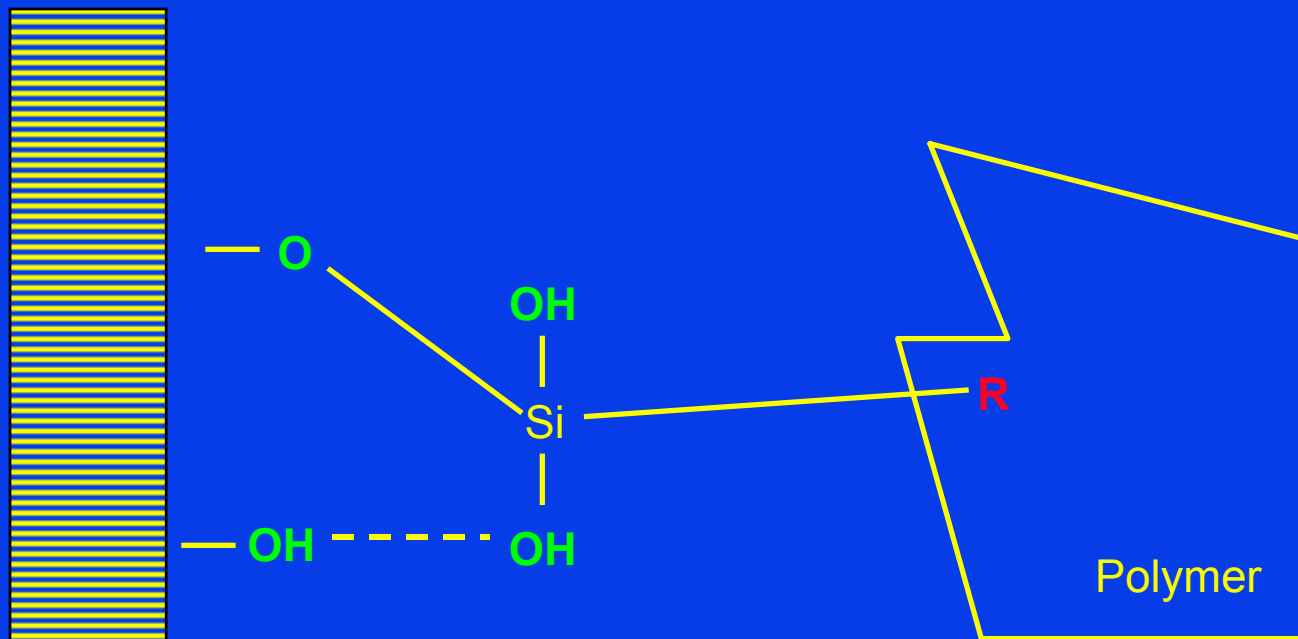
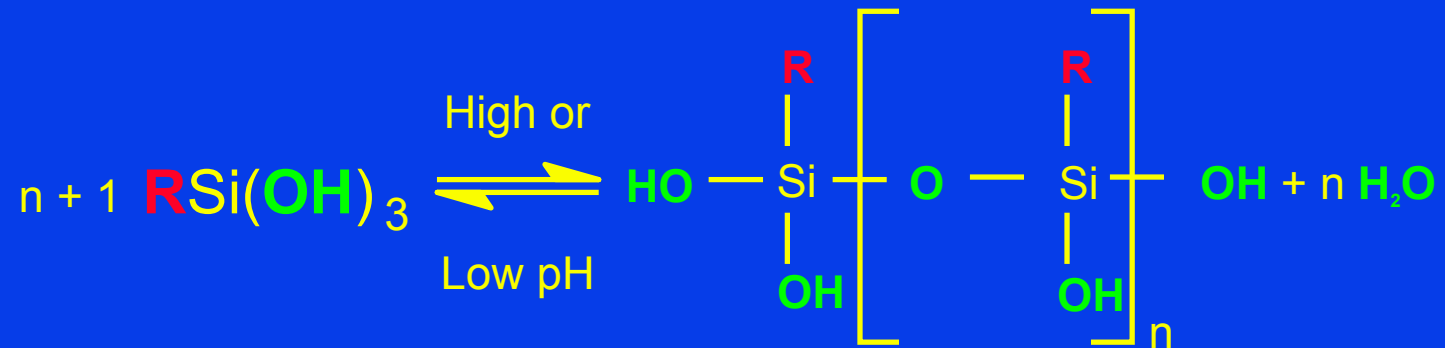


Figure 8 first shows the effect of high or low pH on the rate of silanol oligomerization. Rapid rates of oligomerization eventually result in gelation, as evidenced by turbidity or precipitated solids. Such solutions are ineffective as coupling reagents. The factors contributing to stability of silanols have been reviewed by Arkles et al (Ref 2). Silanols are stabilized by:

- a) Neutral conditions
- b) Limited condensation (high dilution)
- c) Presence of hydroxylic species (alcohols are stabilizers)
- d) Silanes forming stable zwitterions. Amino silanes form such species and are among the most stable water borne species. They readily dissolve in water on stirring and are most stable at pH 10-11.

Also illustrated in Figure 8 is the idealized coupling reaction of the silane with a polymer matrix. The group R may interact with the polymer through a purely physical entanglement (IPN = interpenetrating network), hydrogen bonding, Van Der Wals interactions or covalent chemical bonding. Of these covalent bonding is preferred for long term stability at the polymer/silane interface.

**Figure 8** Interaction of the Bound silane with a Polymer Matrix

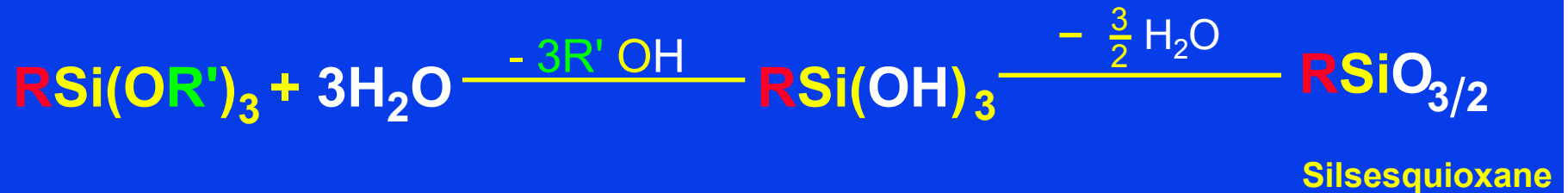


If a silanetriol is fully polymerized it forms a cage like structure known as a “Silsesquioxane” (see Figure 9). Such structures have found utility as high performance electronic coatings and refractory materials.

Once a silane is covalently bound to the substrate, a wide range of chemical reactions are available for binding to the polymer. Figure 9 through Figure 12 show the reactions available for vinyl, amino, epoxy and mercapto functionalized surfaces with functionalities readily achievable on a polymer or biopolymer.

## Figure 9 Reactivity of Vinyl Silane surface with Unsaturated Resins

Alkoxy groups of silane coupling agents react with water to form silanol groups which form siloxane bonds through a condensation reaction.



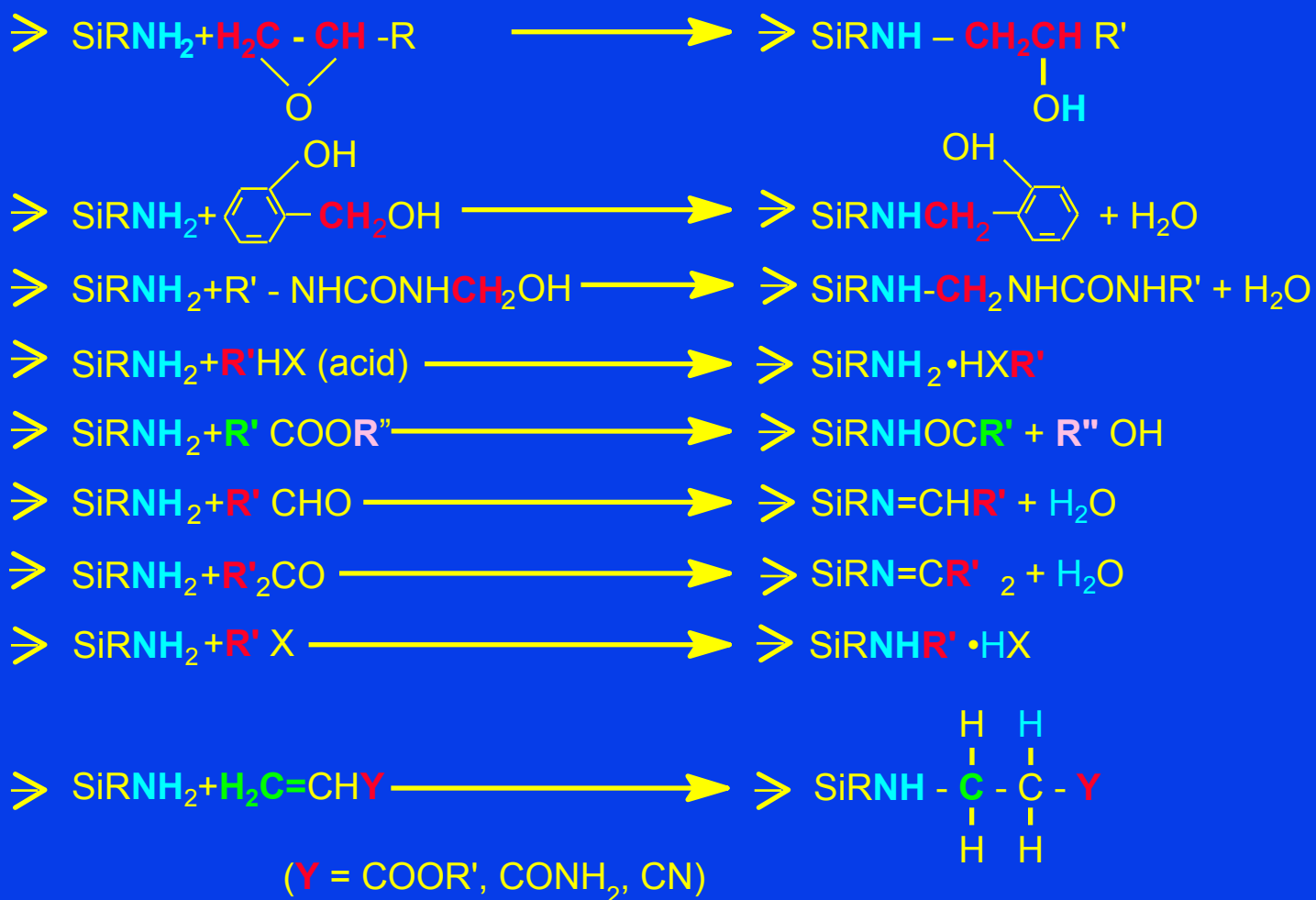
## Unsaturated silanes

Radicle Polymerization

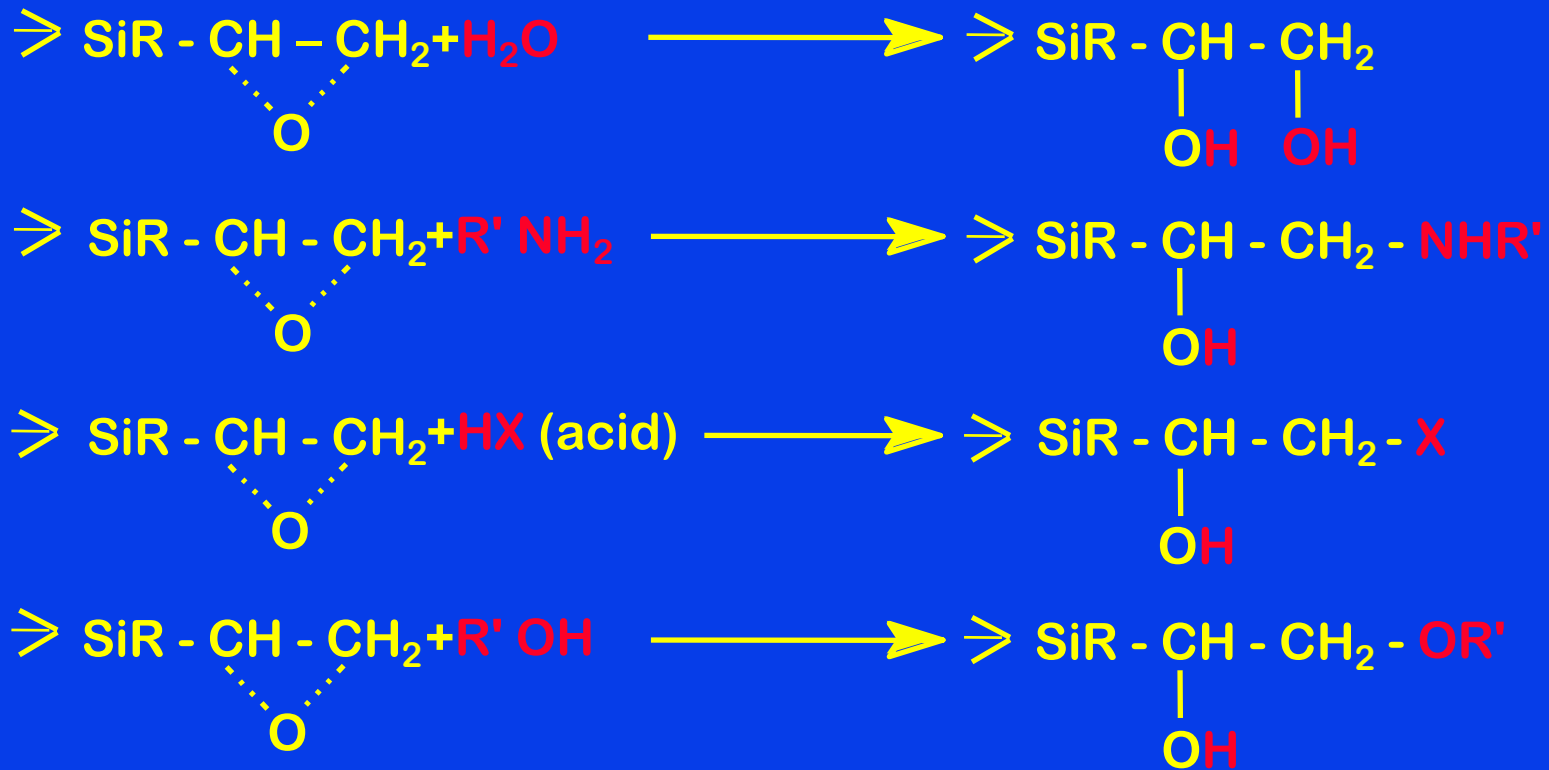




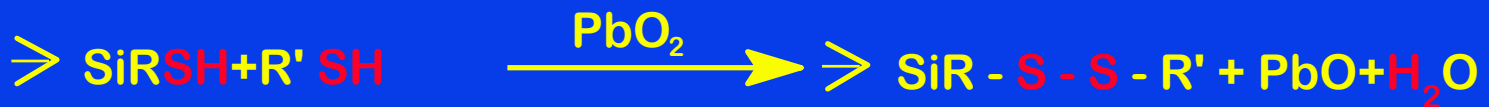
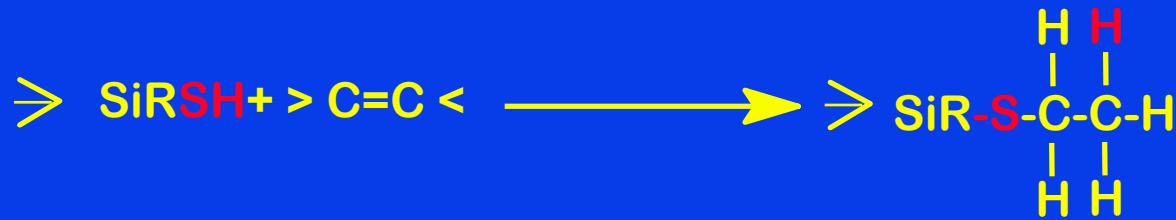
## Figure 10 Reaction of Amino functional Surfaces with Various Functionalities



## Figure 11 Reaction of Epoxy functional Surfaces with Various Functionalities

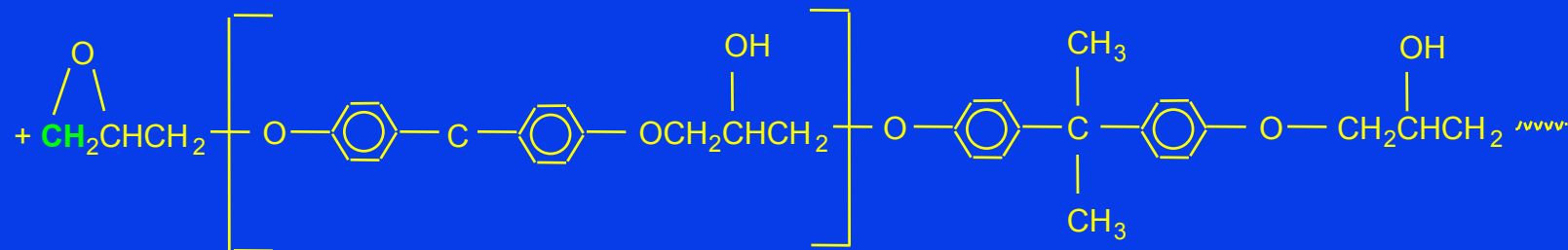


## Figure 12 Reaction of Mercapto Functional Surfaces with Various Functionalities

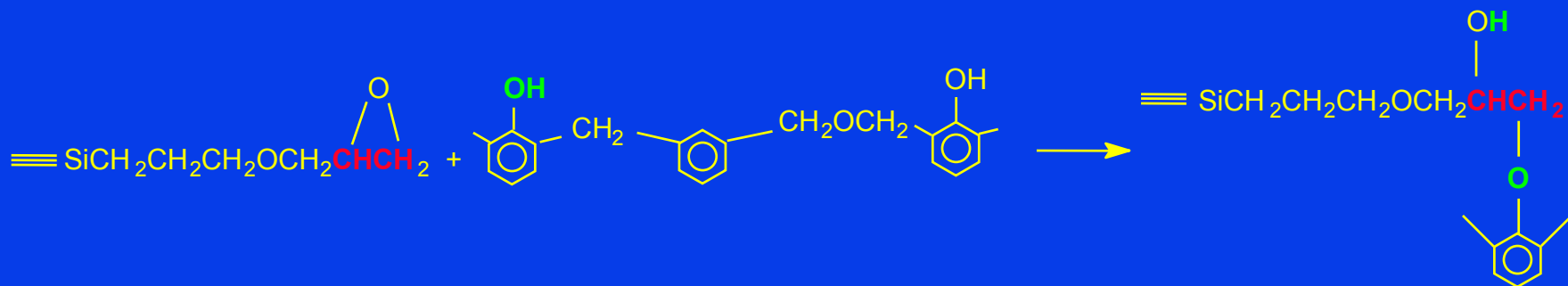
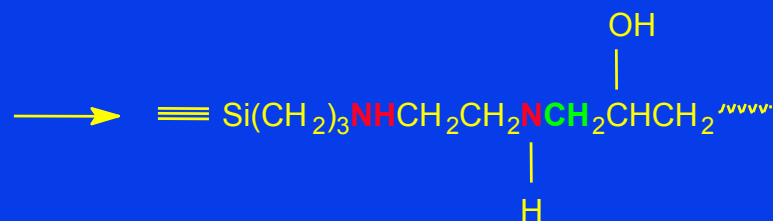


Industrial resins and adhesives manufacturers extensively employ silane coupling reagents to enhance adhesion to substrates such as glass, metals, and masonry materials. Figure 13 shows an amino functionalized surface binding with the epoxy functionality in a curing epoxy resin. Also illustrated is an epoxy functionalized surface reacting with free hydroxy groups in a curing phenolic system. In both instances the covalent bond produced anchors the polymer to the substrate. Figure 14 illustrates a methacryl functionalized surface reacting with the active vinyl groups in a styrene modified polyester resin system. Figure 15 illustrates a diol functionalized surface reacting with the active isocyanate groups in a curing urethane resin system

**Figure 13** Reaction of Amino Surface With Epoxy and Phenolic Resins

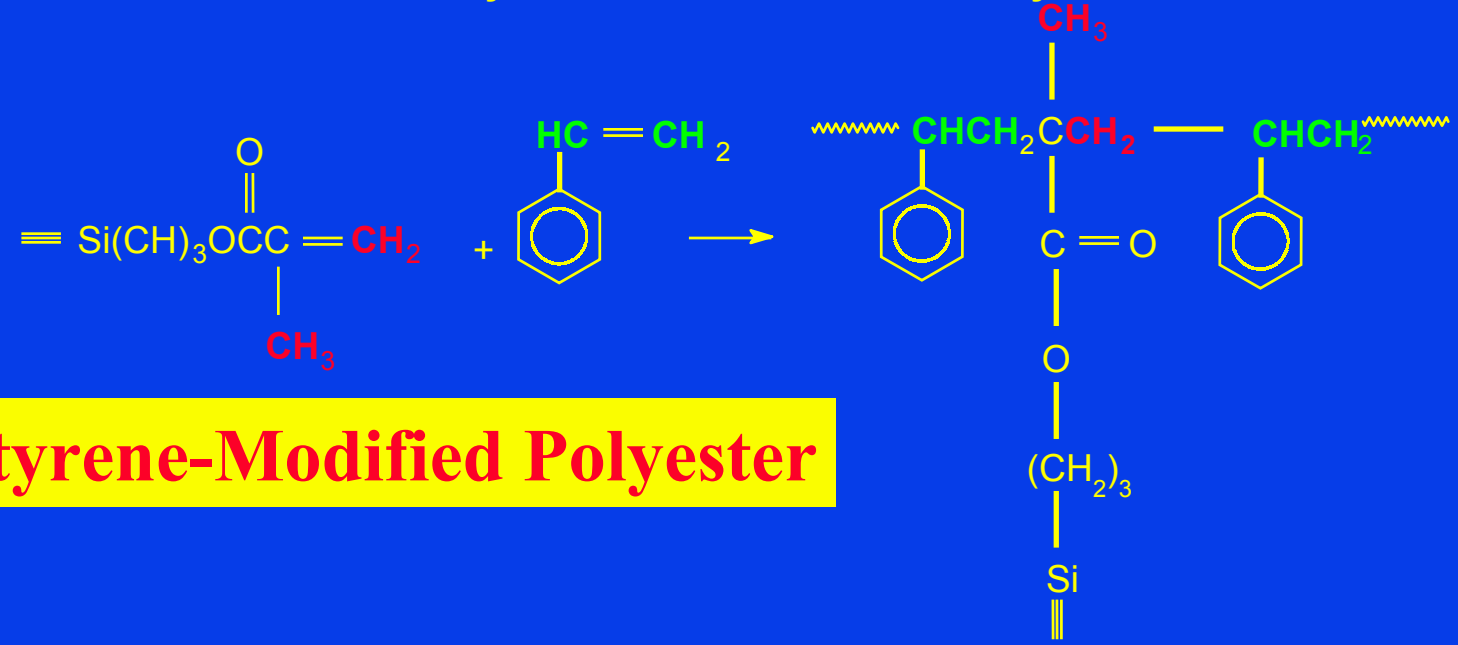


**EPOXY**



**PHENOLIC**

**Figure 14** Reaction of Methacryl Functional Surface with Styrene



**Figure 15** Reaction of Diol Functional Surface with Isocyanate

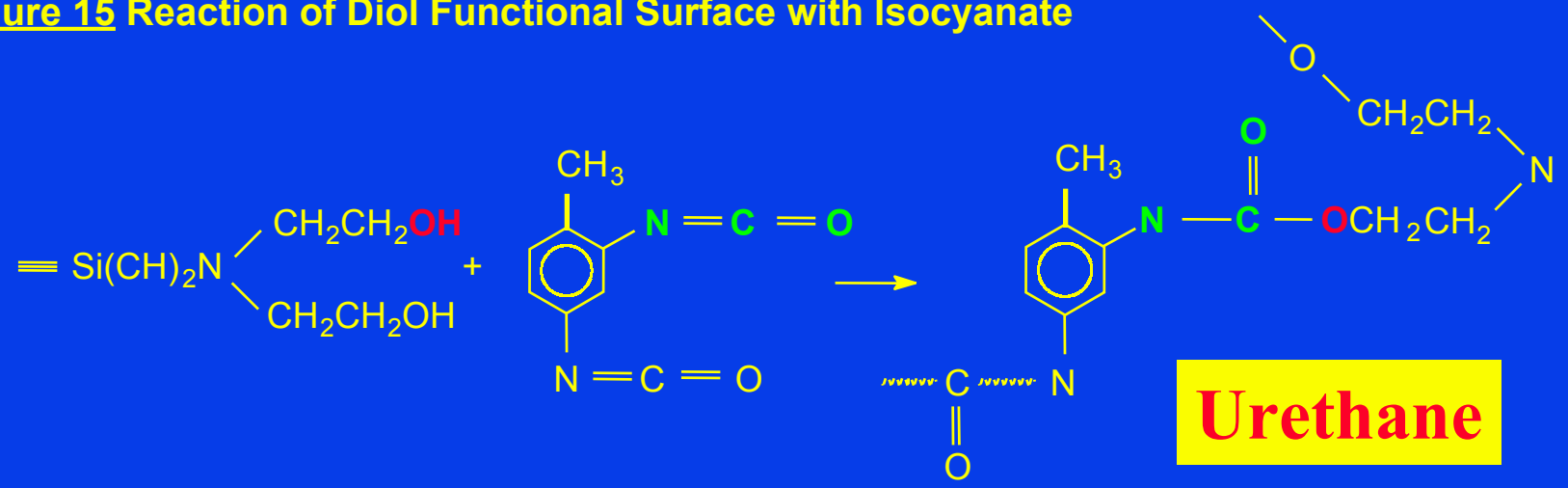
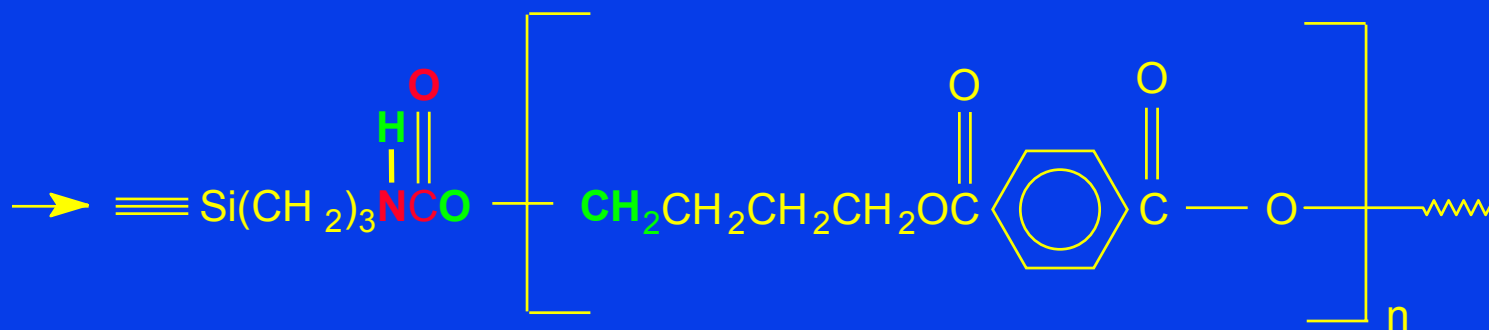
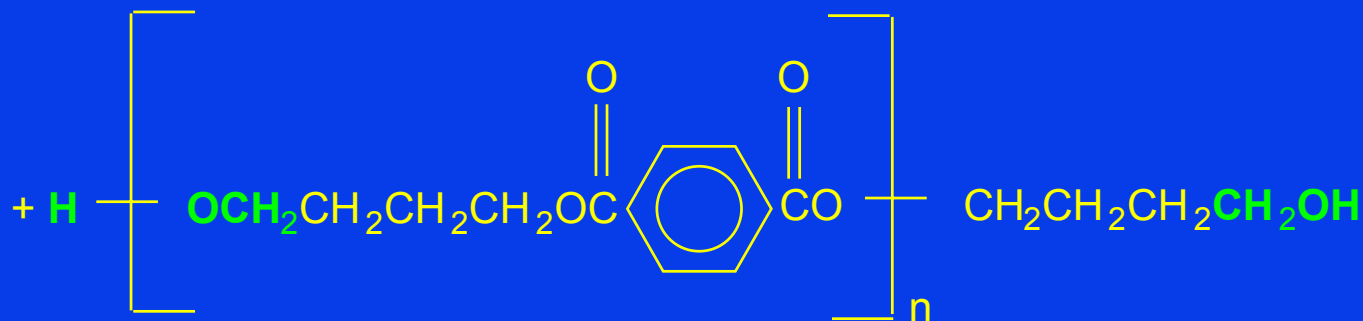


Figure 16 illustrates an isocyanate functional substrate reacting with the hydroxy groups in a polyester polyol and Figure 17 shows an amino functionalized surface reacting with the chlorine groups of polyvinyl chloride.

All of these examples employ classical organic chemical reactions known for decades. While of great utility industrially, they present certain limitations for anchoring peptides or oligonucleotides to substrates. Biochemists need specific binding of functional groups to surfaces to better predict surface orientation and sites for further reactivity of the bio molecule. Most of the functionalities presented above are non specific. For example, isocyanate functionality can react with hydroxyls, amines or mercaptans, all on the same peptide. Amino groups can react with acids, amides, phosphate esters etc. United Chemical Technologies has been active in developing a new class of aldehyde functional silane coupling reagents for specific binding of amino groups to polar substrates.

**Figure 16 Reaction of Isocyanate functional Surface with Polyester Polyol**

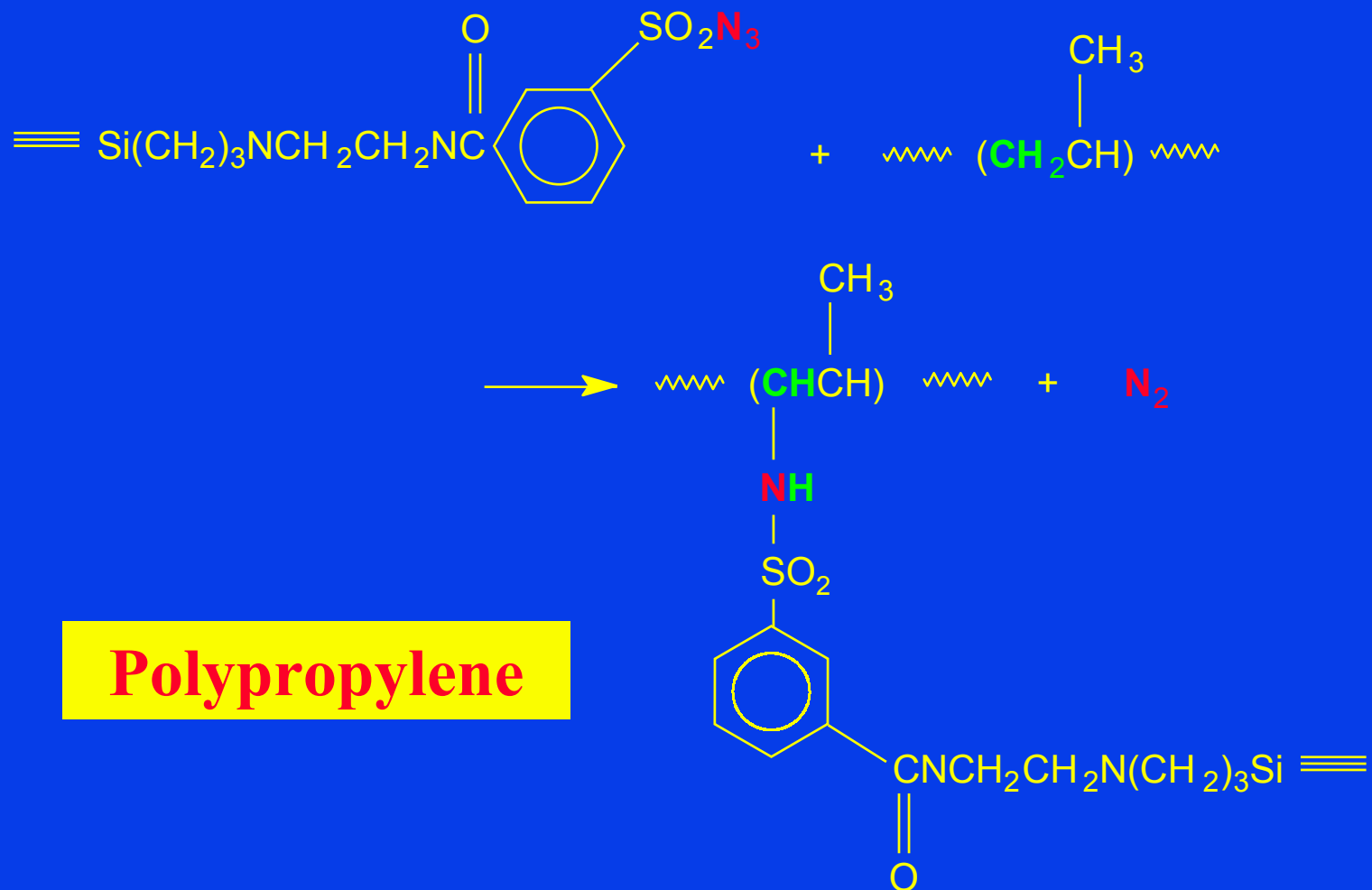


**Polybutylene Terphthalate**





**Figure 18** Insertion of Azido Functional Surface into Polypropylene Backbone



**Polypropylene**

**Figure 19 compares:**

**Method A, the classical APTES (aminopropyltriethoxysilane = UCT A0750) /glutaraldehyde method for specific binding of oligonucleotides with:**

**Method B, The aldehyde functional alkoxy silane route.**

**In method A the aminosilane is first coupled to the substrate by standard protocols. The amine functionalized surface is then reacted with glutaraldehyde, generating a Schiff base functional aldehyde intermediate. This intermediate is then further reacted with the amino groups of the oligonucleotide GOD , generating a bis Schiff base functional structure. This adduct is very hydrolytically labile, and often must be reduced with sodium cyanoborohydride to generate hydrolytically stable amines.**

**For method B the aldehyde silane is directly bonded to the substrate by standard protocols. Direct reaction with the oligonucleotide generates a mono imine functional Schiff base adduct, which is much more hydrolytically stable than bis imino adduct generated in method A described above.**

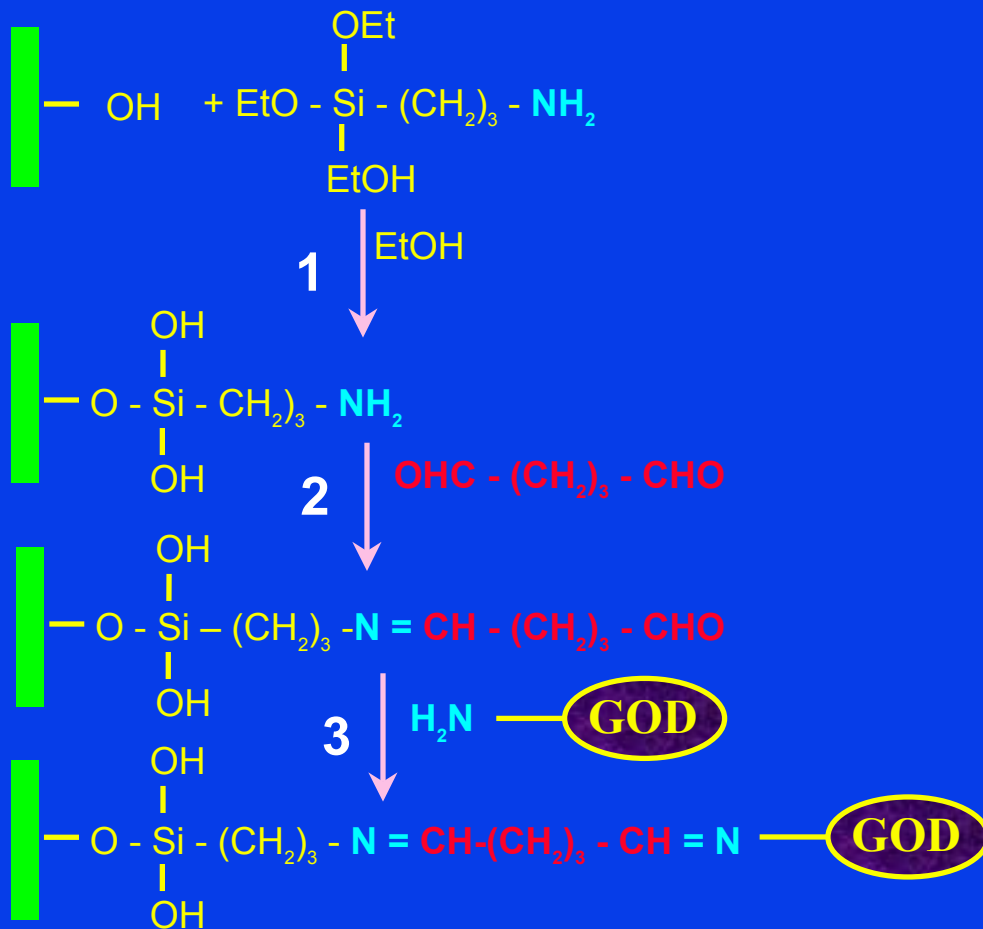
**Other advantages of the aldehyde silane route (method B) include:**

- 1) Avoidance of glutaraldehyde, an unstable reagent that generates undesirable side products. These products can be UV active and give background interferences.**
- 2) The mono imine functional Schiff base adduct may not need reduction of the imine to improve stability to hydrolysis. Bruning (Ref 3) has demonstrated increased enzymatic activity of substrates coated by this route as compared to those from method A.**

# Figure 19 Immobilization of an enzyme on a silica surface

## Method A

### APTES/glutaraldehyde



## Method B

### Aldehyde-functionalized silane

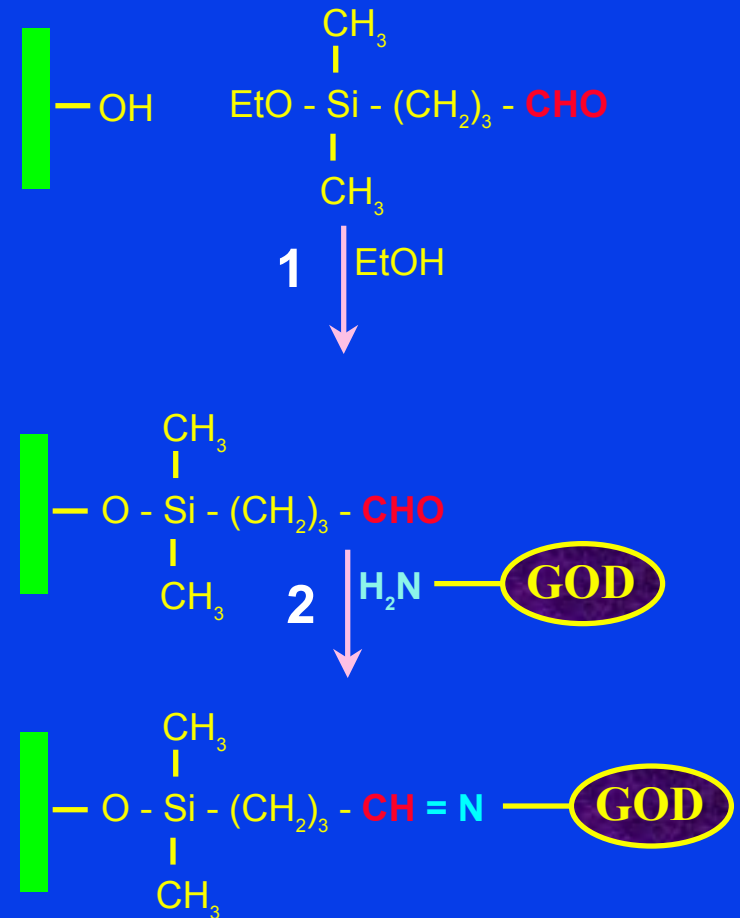
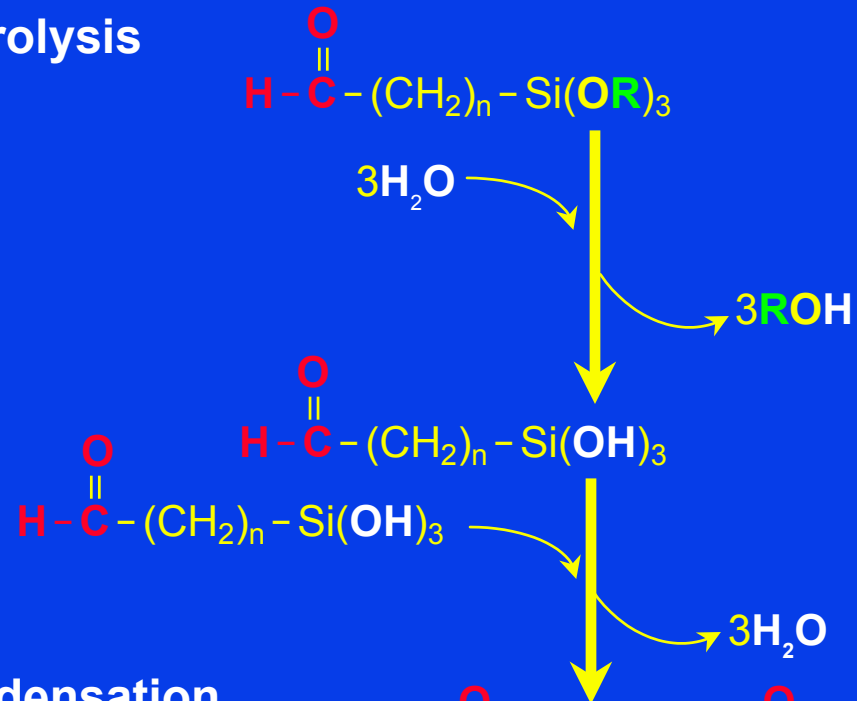


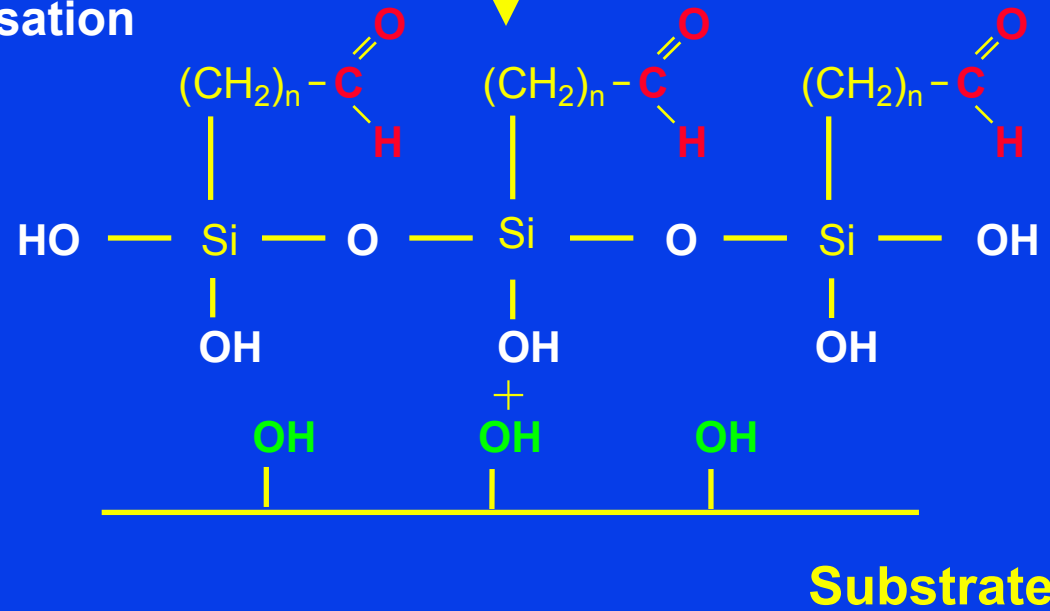
Figure 20 illustrates the mechanism for aldehyde silane deposition. It is entirely identical for the generic mechanism presented earlier. The best protocol for achieving this hydrolysis is deposition from aqueous alcohol (see Figure 27). The only complication over the standard silane deposition is the oxidative sensitivity of the aldehyde group. Solutions should be de-aired with nitrogen. Final cure and storage of treated plates also should be under a nitrogen atmosphere. Aldehyde silane treated silicas or other fillers can also be stored in deoxygenated buffer solutions.

**Figure 20**  
**Deposition**  
**of**  
**Aldehydic**  
**Silanes**

**Hydrolysis**

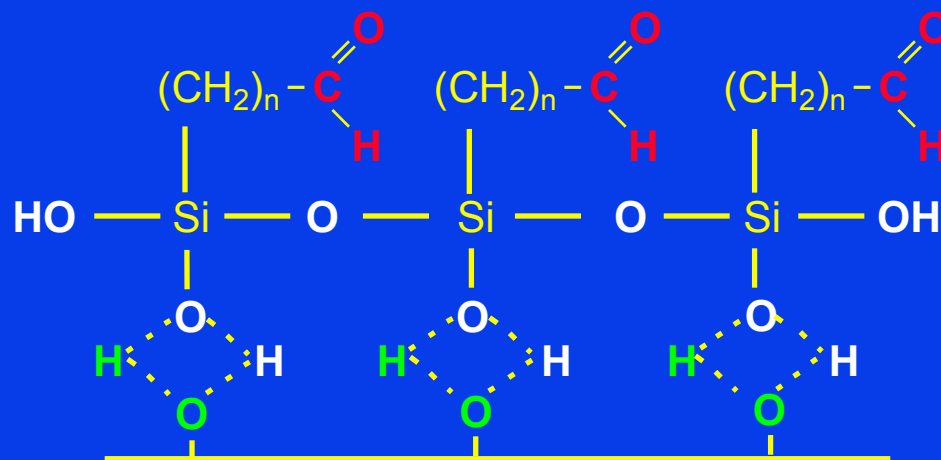


**Condensation**

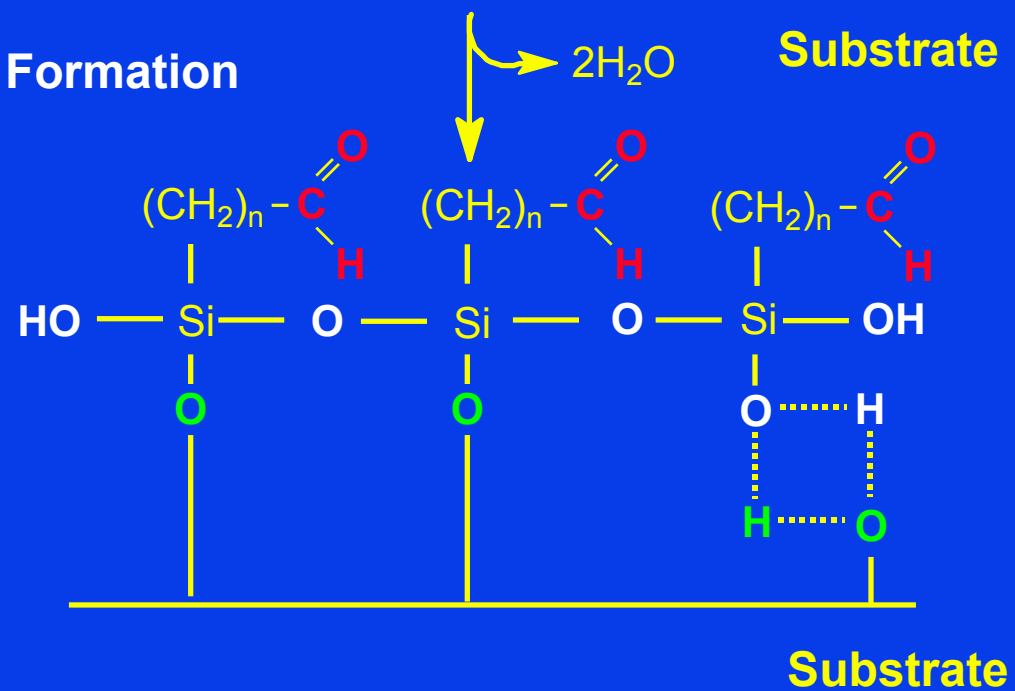


**Figure 20**  
**Deposition**  
**of**  
**Aldehydic**  
**Silanes**  
**(continued)**

Hydrogen bonding



Bond Formation

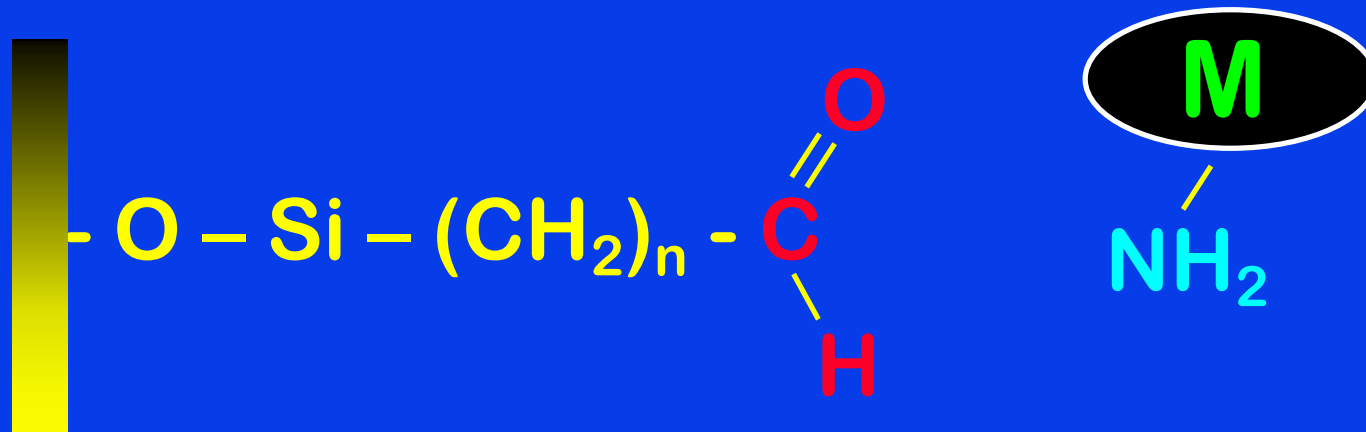


Figures 21 and 22 outline the advantages of the United Chemical Technologies BioConext® product line of aldehyde silanes for specific binding of amino functionalized oligonucleotides to coated substrates. Table 1 describes the current product offerings. Custom chain lengths are synthesizable if the precursors are commercially available. Contact United Chemical Technologies for more details.

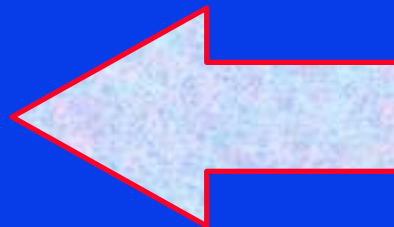


# Figure 21 BIO-CONEXT™

Derivatized Aldehydic Surface



**M** =



Antibodies  
Enzymes  
Amino-Modified Oligos (dT)  
Peptides  
Proteins  
Small Molecules

## Figure 22 Advantages of BIO-CONEXT™

- **Alkoxy silanes exhibit reactivity with most surfaces**

Will easily create a covalent linkage with most active glass, siliceous, metal and plastic surfaces.

- **A little bit goes a long way**

1 mole of silane will theoretically cover 7,500 m<sup>2</sup>. Approximately 1 gram of PSX1055 will cover 32 m<sup>2</sup> and 1 gram of PSX1050 will cover 39 m<sup>2</sup>.

- **Ultra high loading of aldehyde groups that provide remarkable binding capacity**

The aldehydic alkoxy silanes will typically form 3 to 8 molecular layers\* on the reacted surface. This creates a very dense population of aldehyde groups providing extremely high ligand binding and activity.

\* Based on a 2% solution.

## **Figure 22 Advantages of BIO-CONEXT™ (continued)**

- **Superior to classical techniques**

The classical procedure for ligand attachment requires reacting amine functional supports with glutaraldehyde. These techniques are more labor intensive, expensive and glutaraldehyde is unstable and difficult to purify. Additionally, the glutaraldehyde and primary amine form two Schiff bases, with only one formed with the aldehydic silanes coupling. As a result, there is greater stability and less denaturing over time with BIO-CONEXT™.

- **Total flexibility**

BIO-CONEXT™ silane chemistry provides you with a considerable number of choices for selecting coupling surfaces. Now you can bind your ligand to the support that meets your most demanding specifications with BIO-CONEXT™.

## Table 1 BIO-CONEXT™ Product Line

Package under nitrogen.

Protect from  
moisture and air.

Shelf life  
6 months from day  
of shipment.

Catalog Number	Quantity Grams	By-product of alkoxy reaction
PSX1050	1	Methanol
PSX1050	5	Methanol
PSX1050	10	Methanol
PSX1055	1	Ethanol
PSX1055	5	Ethanol
PSX1055	10	Ethanol

For all other quantities please call for pricing and availability.

**PSX1050** is more hydrolytically reactive than **PSX1055**.

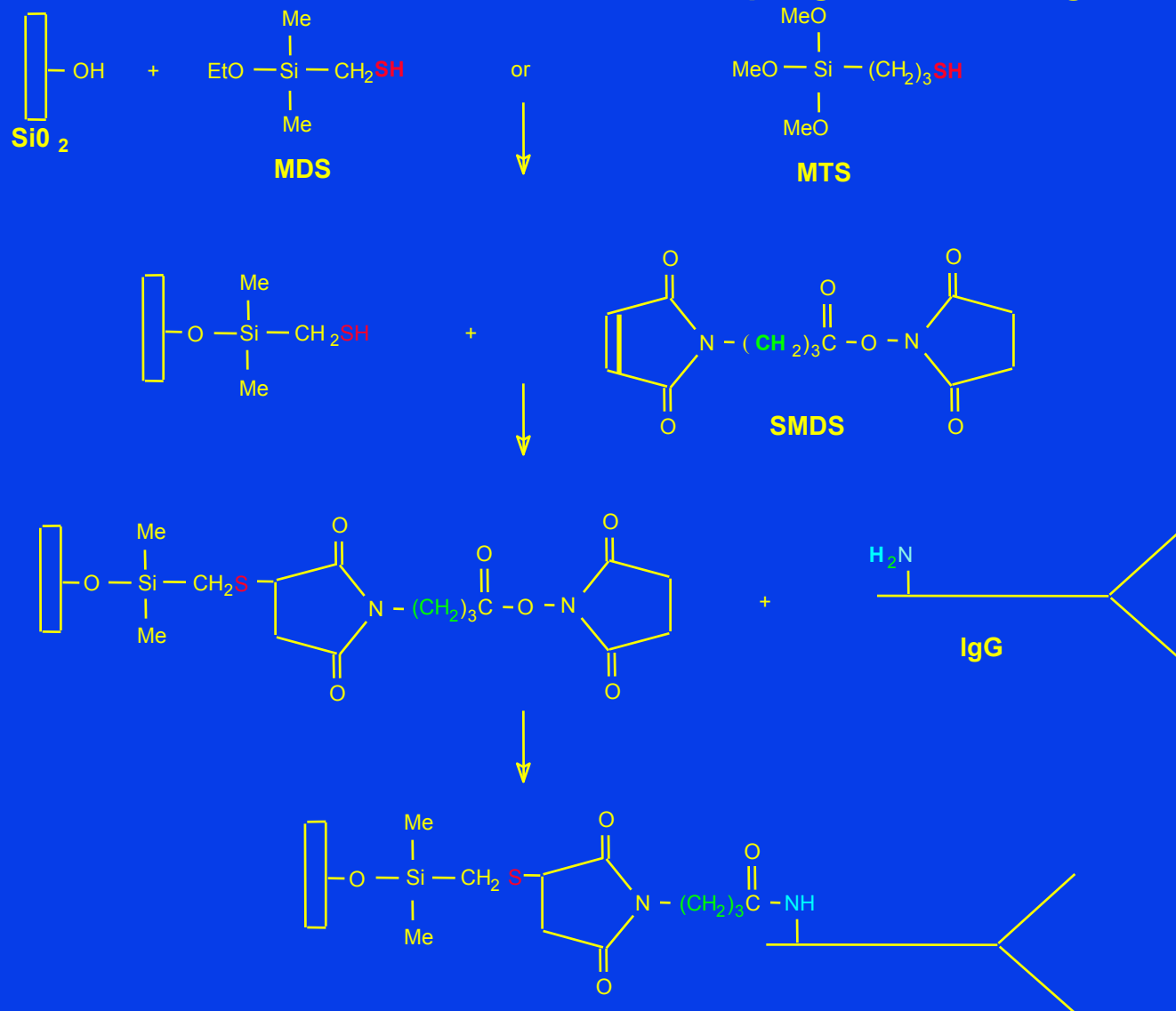
**FOR RESEARCH AND DEVELOPMENT PURPOSES ONLY**

**Aldehydic Alkoxy Silanes Available as Custom Syntheses**

United Chemical Technologies, Inc. can custom tailor an aldehydic alkoxy silane for specific chain lengths and / or surface loading. Please call our technical department at 800-541-0559 or write [techsupportPetrarch@unitedchem.com](mailto:techsupportPetrarch@unitedchem.com) for all inquiries on custom synthesis.

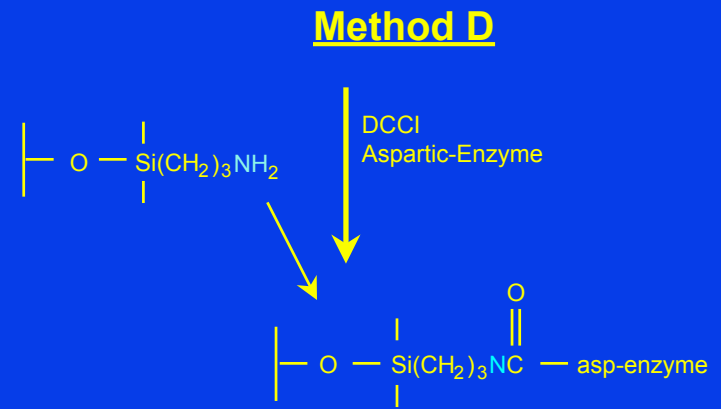
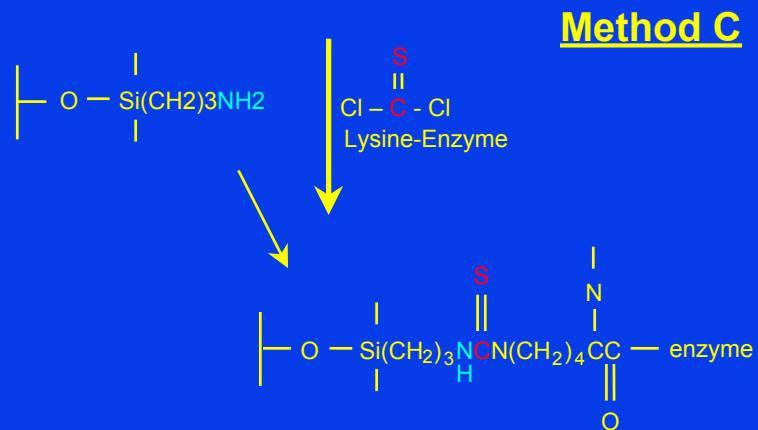
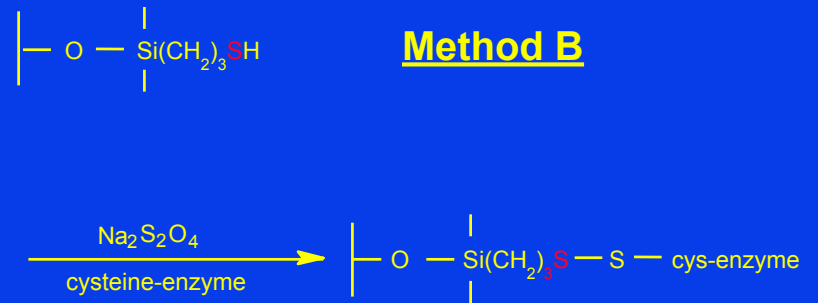
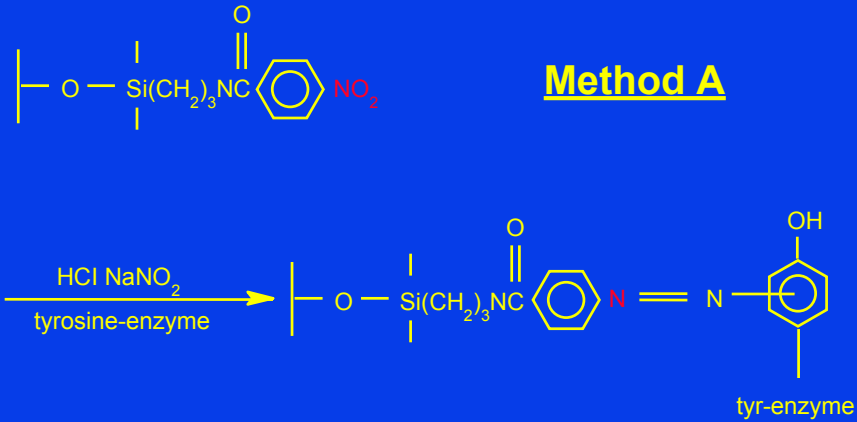
Figures 23 and 24 outline contrasting older methods to the aldehyde deposition. In Figure 23, a mercapto functional surface is reacted with a hetero bifunctional crosslinker, which in turn reacts by with the amino group of the oligonucleotide. This method suffers from the non availability commercially of the crosslinker and the presence of byproducts from the ester cleavage. Figure 23 lists four older methods. Method A involves a diazotization step which is critically temperature dependent and gives many byproducts. Method B requires oxidative coupling of mercaptan groups, also giving many byproducts. Method C requires thiophosgene, a very toxic and pungent reagent. Method D, involving coupling with DCCI, is the best of these four methods.

**Figure 23 Heterobifunctional Crosslinker Route for Coupling to Amino Oligonucleotide**



**Heterobifunctional Crosslinker**

**Figure 24 Other methods for Coupling Enzymes to Polar Substrates**



# Enzyme Immobilization

Figure 25 illustrates the various modes of silane complexation with a silica surface, depending on silane structure. Structure 1 shows a monolayer deposition from a monoalkoxy silane. Structure 2 illustrates a silane incorporated into the silica backbone by co-precipitation from a sol gel. Structure 3 shows a difunctional silane, partially crosslinked with its neighbor silane. Structure 4 illustrates the modes of crosslinking available at the surface for a fully hydrolyzed silanetriol. Structure 4 is capable of generating a multilayer structure, as described earlier (see Fig 3).





Table 2 lists the most industrially utilized of the wide variety of commercial silane coupling agents available from United Chemical Technologies. These and many others are available in bulk at competitive pricing. Contact our customer service department for quotations.

# Table 2 Silane Coupling Agents

Designation	Chemical Type	Chemical Name	Chemical Formula	Applications
A0700	Diamino	N-(2-Aminoethyl)-3-aminopropyltrimethoxy silane	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$	Epoxies, Phenolics, Melamines, Nylons, PVC's Acrylics, Urethanes, Nitrile Rubbers
M8550	Methacrylate	3-Methacryloxypropyl-trimethoxysilane	$\text{CH}_2 = \underset{\text{CH}_3}{\underset{ }{\text{C}}} - \overset{\text{O}}{\parallel} \text{C} - \text{O}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$	Unsaturated Polyesters, Acrylics
S1590	Styrylamine Cationic	N-(2-Vinylbenzylaminoethyl)-3-aminopropyl-trimethoxysilane	$\text{CH}_2 = \text{CH} - \text{C}_6\text{H}_4 - \text{CH}_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3 \cdot \text{HCl}$	Unsaturated Polyesters, Styrenics, Epoxies, PP, PE
G6720	Epoxy	3-Glycidoxypropyltrimethoxysilane	$\text{CH}_2 - \underset{\text{O}}{\underset{  \quad  }{\text{C} - \text{C}}} - \text{CH}_2\text{O}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$	Epoxies, Urethanes, Acrylics, PBT's Polysulfides
V4800	Vinyl	Vinyltriacetoxysilane	$\text{CH}_2 = \text{CHSi}(\text{OCCH}_3)_3$	Polyesters, Polyolefins, EPDM
C3300	Chloroalkyl	3-Chloropropyltrimethoxy silane	$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	Epoxies, Nylons, Urethanes
PSX1050	Aldehydic	4-Trimethoxysilylbutanal Mixture of isomers	$\text{H} - \overset{\text{O}}{\parallel} \text{C} - (\text{CH}_2)_3 - \text{Si}(\text{OCH}_3)_3$	Protein, Amino-modified Oligo Immobilization

# Inorganic – Si – R – Organic

The number of hydrolyzable X groups on the silane is another important parameter in controlling bond characteristics. The traditional silane coupling agents contain three hydrolyzable groups. They have maximum hydrolytic stability but tend to be hydroscopic. At the opposite end are the silanes with one hydrolyzable group. These yield the most hydrophobic interfaces but have the least long term hydrolytic stability. Silanes with two hydrolyzable groups form less rigid interfaces than silanes with three hydrolyzable groups. They are often used as coupling agents for elastomers and low modulus thermoplastics. Polymeric silanes with recurrent trialkoxy or dialkoxysilanes offer better film-forming and primer capabilities. For enhanced hydrolytic stability or economic benefit non-functional silanes such as short chain alkyltrialkoxysilanes or phenyltrialkoxysilanes can be combined in ratios up to 3:1 with functional silanes.

In more difficult bonding situations mixed silanes or silane network polymers may be employed. These include inorganic to inorganic and organic to organic. In these cases reaction of the silanes with themselves is critical.

## **Inorganic-O-Si-R-R-Si-O-Inorganic**

## **Organic-R-Si-O-Si-R-Organic**

An example of a mixed silane application is the use of mixtures of epoxy and amine functional silanes to bond glass plates together. A more general use is bonding organic to organic. Primers, prepared by prehydrolyzing silanes to resins in order to form bulk layers on metal substrates, are examples of the application of silanes as network polymers.

# Inorganic – Si – R – Organic

## Thermal Stability

Most silanes have moderate thermal stability making them suitable for plastics that process below 350°C or have continuous temperature exposures below 150°C. Silanes with an aromatic nucleus have higher thermal stability. A relative ranking where **Z** is the functional group is as follows:

<u>CLASS</u>	<u>EXAMPLE</u>	<u>THERMAL LIMIT</u>
<b>Z</b> CH <sub>2</sub> CH <sub>2</sub> SiX <sub>3</sub>	C3100	<150°C
<b>Z</b> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SiX <sub>3</sub>	A0700	390°
<b>Z</b> CH <sub>2</sub> aromaticCH <sub>2</sub> CH <sub>2</sub> SiX <sub>3</sub>	T2902	495°
Aromatic SiX <sub>3</sub>	P0320	550°

Table 3 is our guide for determining which classes of silanes are most effective for bonding a polymer substrate to a glass surface. It is also applicable for alumina, active metals such as aluminum, iron or nickel, and plasma or corona treated polymer surfaces. **It is not applicable for coupling two or more polymer surfaces devoid of active hydroxyl functionality**. Nor will it apply to bonding graphite or noble metals such as gold silver or platinum to polymer matrices. These substrates have no hydroxyl “handles”. Silane coupling agents are of utility for promoting better adhesion during chemical vapor deposition of these noble metals to glass or other hydroxy functionalized substrate. Mercapto (M8500, B2494) and phosphino (D6110) silanes are of particular utility.

To bond polymers unactivated by plasma, mixtures of two silane coupling agents can be employed. For example, to adhere a curing acrylate resin onto an epoxy surface, a methacryl silane (M8550) may be added to the resin while the epoxy resin surface is treated with an aminosilane (A0750). Coupling of the polymers occurs through an Organic-R-Si-O-Si-R-Organic bond.

In general, due to the wide variety of processing conditions and formulation variables, it cannot be predicted which class of a recommended group of silanes will prove most effective. For example, to bond polyester resin to glass, amino, methacryl, styryl and vinyl silanes have all proven effective. Usually it is recommended that the scientist or formulator screen one member of each functionality class. For example, in this case one would screen A0750, M8550, S1590 and V4917. Small trial quantities are available at nominal cost.

# Table 3 Coupling Agent Selection Guide Thermosets

<u>Polymer</u>	<u>Silane Class</u>	<u>Recommended Silanes</u>		
diallylphthalate	amine  styryl	A0698 A0750 S1590	A0700	A0710
epoxy	amine epoxy chloroalkyl mercapto	A0700 G6720 C3300	A0750 E6250  M8450	T2910  M8500
imide	chloromethylaromatic amine	T2902 A0698 A0750	A0700 T2910	
melamine	amine epoxy alkanolamine	A0700 G6720 B2408	A0750 E6250	T2910
paralene	chloromethylaromatic vinyl	T2902 V4800		

# Thermosets (contd)

<u>Polymer</u>	<u>Silane Class</u>	<u>Recommended Silanes</u>		
phenolic	amine chloroalkyl epoxy mercapto	A0700 C3300 G6720	A0750 E6250 M8450	T2910 M8500
photoresist, negative	silazane vinyl aromatic	H7300 D6208 P0320	D6208 V4800	V4900
photoresist, positive	silazane aromatic phosphine	H7300 P0320 D6110		
polyester	amine methacrylate styryl vinyl	A0700 M8550 S1590 V4917	A0750 V4800	T2910 V4910
urethane	amine alkanolamine epoxy isocyanate	A0700 B2408 G6710 I7840	A0750 G6720	T2910 E6250



# Thermoplastics (contd)

<u>Polymer</u>	<u>Silane Class</u>	<u>Recommended Silanes</u>		
cellulosics	amine isocyanate phosphate	A0700 I7840 D4520	A0750	T2910
polyacetal	thiuronium quaternary	T2921 T2909.7		
polyamide (nylon)	amine  ureido	A0700 A0742 T2507	A0750 PS076	T2910
protein	aldehyde	PSX1050	PSX1055	
polyamide-imide	chloromethylaromatic amine	A0700	T2902 A0750	A0800
polybutylene terephthalate	amine isocyanate	A0698 I7840	A0750	
polycarbonate	amine	A0700 T2910	A0750	

# Thermoplastics (contd)

<u>Polymer</u>	<u>Silane Class</u>	<u>Recommended Silanes</u>			
polyetherketone (ethylene-vinyl, acetate copolymer)	amine ureido	A0690 T2507	A0750	A0800	
polyethylene	amine vinyl vinyl-peroxy styryl	A0700 V4910 V4950 S1590	A0742 V4917	A0750	
polyphenylene oxide	amine aromatic	A0700 P0320	A0750	T2910	
polyphenylene sulfide	amine  mercapto chloromethyl- aromatic	A0698 T2910  T2902	A0700  M8450	A0750  M8500	B2494

# Thermoplastics (contd)

<u>Polymer</u>	<u>Silane Class</u>	<u>Recommended Silanes</u>		
polypropylene	vinyl-peroxy aromatic styryl	V4950 P0320 S1590	P0330	
polystyrene	aromatic epoxy vinyl	P0320 G6720 V4910	P0330 E6250 V4917	
polysulfone	amine	A0700	A0750	T2910
polyvinyl butyral	amine	A0700	A0742	A0750
polyvinyl chloride	amine alkanolamine	A0700 B2408	A0750	T2910

# Sealants

<u>Polymer</u>	<u>Silane Class</u>	<u>Recommended Silanes</u>		
acrylic	acrylic	A0380	M8550	
	styryl	S1590		
	epoxy	G6710	G6720	E6250
polysulfides	mercapto amine	B2494	M8500	M8450
		A0699	A0700	A0742
		A0750	T2910	

# Rubbers

<u>Polymer</u>	<u>Silane Class</u>	<u>Recommended Silanes</u>		
butyl	epoxide	G6710	G6720	E6250
neoprene	mercapto	M8450	M8500	PS078.5
isoprene	mercapto	M8450	M8500	PS078.5
fluorocarbon	amine styryl	A0698 S1590		
epichlorohydrin	amine  mercapto	A0699 A0750 M8450	A0700  M8500	A0742
silicone	amine (CONDENSATION CURE) allyl (ADDITION CURE) vinyl (ADDITION CURE)	A0700 A0567 V5050	A0750	A0728

# Water Soluble and Hydrophilic Polymers

<u>Polymer</u>	<u>Silane Class</u>	<u>Recommended Silanes</u>	
cellulosic	epoxy phosphate isocyanate	G6710 D4520 I7840	G6720
heparin	amine epoxy isocyanate	A0800 G6710 I7840	PS076 G6720
polyethylene oxide	isocyanate	I7840	
polyhydroxyethylmethacrylate	epoxy isocyanate phosphate	G6710 I7840 D4520	G6720
polysaccharide	epoxy phosphate isocyanate	G6710 D4520 I7840	G6720
polyvinyl alcohol	epoxy isocyanate phosphate	G6710 I7840 D4520	G6720

# Water Soluble and Hydrophilic Polymers(contd)

<u>Polymer</u>	<u>Silane Class</u>	<u>Recommended Silanes</u>		
siliceous	all listed in Thermosets	A0700		
aluminum, zirconium, tin, titanium metals	all listed in Thermosets, epoxies, acrylates and quats preferred	S1590	M8540	T2909.7
copper, iron	polyamine phosphine vinyl	T2910 D6110 V5050	PS076	A0728
gold, precious metals	phosphine mercapto	D6110 B2494	M8500	
silicon	vinyl	D6208	V4800	V5050

Figures 26, 27, and 28 describe the common protocols for depositing silane coupling agents to glass and other active substrates. The method used must be decided by the processor. For practical reasons many industrial formulators prefer to add the silane directly to the resin. Usually 0.2 to 0.5 wt % is adequate. Glass processors and academic researchers generally prefer treating the surface to insure uniform coverage. For these solution protocols, washing off excess silane after treatment is strongly recommended, in order to prevent irregular depositions from concentration of unreacted silane in localized areas as solvent evaporates. Spotting or white haze is a common indicator of undesired crosslinking of unreacted silanes on a surface.



# **Figure 26 Applying a Silane Coupling Agent**

- ❖ **Deposition from aqueous alcohol**
- ❖ **Deposition from aqueous solutions**
- ❖ **Bulk deposition onto powders**
- ❖ **Integral blend methods**
- ❖ **Deposition as a primer**

# Figure 27 Protocols for Surface Modification

**Deposition from aqueous alcohol solutions** is the most facile method for preparing silylated surfaces. A 95% ethanol-5% water solution is adjusted to pH 4.5-5.5 with acetic acid. Silane is added with stirring to yield a 2% final concentration. Five minutes should be allowed for hydrolysis and silanol formation. Large objects, e.g. glass plates, are dipped into the solution, agitated gently, and removed after 1-2 minutes. They are rinsed free of excess materials by dipping briefly in ethanol. Particles, e.g. fillers and supports, are silylated by stirring them in solution for 2-3 minutes and then decanting the solution. The particles are usually rinsed twice briefly with ethanol. Cure of the silane layer is for 5-10 minutes at 110°C or for 24 hours at room temperature (<60% relative humidity).

For aminofunctional silanes such as A0700 and A0750 this procedure is modified by omitting the additional acetic acid. **The procedure is not acceptable for chlorosilanes as bulk polymerization with a violent reaction will occur.** Silane concentration of 2% is a starting point. It usually results in deposition of trialkoxysilanes in 3-8 molecular layers. Monoalkoxysilanes are always deposited in monolayers or incomplete monolayers. Caution must be exercised if oven curing. Exhausted, explosion-proof ovens should always be used.

# Figure 27 Protocols for Surface Modification continued

**Deposition from aqueous solutions** is employed for most commercial fiberglass systems. The alkoxysilane is dissolved at 0.5-2.0% concentration in water. For less soluble silanes, 0.1% of a non-ionic surfactant is added prior to the silane and an emulsion rather than a solution is prepared. If the silane does not contain an amine group the solution is adjusted to pH 5.5 with acetic acid. The solution is either sprayed onto the substrate or employed as a dip bath. Cure is at 110-120° C for 20-30 minutes.

**Stability of aqueous silane solutions** varies from hours for the simple alkyl silane to weeks for the aminosilanes. Poor solubility parameters limit the use of long chain alkyl and aromatic silanes by this method. Distilled water is not necessary, but water containing fluoride ions must be avoided.

# Figure 27 Protocols for Surface Modification continued

**Bulk deposition onto powders**, e.g. filler treatment, is usually accomplished by a spray-on method. It assumes that the total amount of silane necessary is known and that sufficient adsorbed moisture is present on the filler to cause hydrolysis of the silane. The silane is prepared as a 25% solution in alcohol. The powder is placed in a high intensity solid mixer, e.g. a twin cone mixer with intensifier. The solution is pumped into the agitated powder as a fine spray. In general this operation is completed within 20 minutes. Dynamic drying methods are most effective. If the filler is dried in trays, care must be taken to avoid wicking or skinning of the top layer of treated material by adjusting heat and air flow.

# Figure 27 Protocols for Surface Modification continued

**Integral blend methods** are used in composite formulations. In this method the silane is used as a simple additive. Composites can be prepared by the addition of alkoxysilanes or silazanes to dry-blends of polymer and filler prior to compounding. Generally 0.2 to 1.0 weight percent of silane (of the total mix) is dispersed by spraying the silane in an alcohol carrier onto a preblend. The addition of the silane to non-dispersed filler is not desirable in this technique since it can lead to agglomeration. The mix is dry-blended briefly and then melt compounded. Vacuum devolatilization of byproducts of silane reaction during melt compounding is necessary to achieve optimum properties. Properties are sometimes enhanced by adding 0.5-1.0% of tetrabutyl titanate or benzyldimethylamine to the silane prior to dispersal. Aminofunctional silanes are available in concentrate form for dry-blending with nylons and polyesters. Concentrates eliminate any need for solvent dispersion and devolatilization and reduce variability due to relative humidity and shelf-aging.

**Deposition as a primer** is employed where a bulk phase is required as a transition between a substrate and a final coating. The silane is dissolved at 50% concentration in alcohol. One to three molar equivalents of water are added. The mixture is allowed to equilibrate for 15-20 minutes and then diluted to 10% concentration with a higher boiling polar solvent. Materials to be coated with the primer are dipped or sprayed and then cured at 110-120°C for 30-45 minutes.

# Figure 28 Chlorosilanes and Silazanes Deposition Protocols

**Chlorosilanes** such as V4900 may be **deposited from alcohol solution**. Anhydrous alcohols, particularly ethanol or isopropanol, are preferred. The chlorosilane is added to the alcohol to yield a 2-5% solution. The chlorosilane reacts with the alcohol producing an alkoxysilane and HCl. Progression of the reaction is observed by the halt of HCl evolution. Mild warming of the solution (30-40°C) promotes completion of the reaction. Part of the HCl reacts with the alcohol to produce small quantities of alkyl halide and water. The water causes formation of silanols from alkoxy silanes. The silanols condense with those on the substrate. Treated substrates are cured for 5-10 minutes at 110°C or allowed to stand 24 hours at room temperature.

**Chlorosilanes** and **silylamines** may also be employed to treat substrates under **aprotic conditions**. Toluene, tetrahydrofuran or hydrocarbon solutions are prepared containing 5% silane. The mixture is refluxed for 12-24 hours with the substrate to be treated. It is washed with the solvent. The solvent is then removed by air or explosion-proof oven drying. No further cure is necessary. This reaction involves a direct nucleophilic displacement of the silane chlorines by the surface silanol. If monolayer deposition is desired, substrates should be predried at 150°C for 4 hours. Bulk deposition results if adsorbed water is present on the substrate. This method is cumbersome for large scale preparations and rigorous controls must be established to ensure reproducible results. More reproducible coverage is obtained with monochlorosilanes.

Common terms encountered in determining effectiveness of a silane deposition on a surface are wetting surface and contact angle. Common silanes for which wetting surface values are available are listed in Figure 28a. Many other wetting surface values are available in the UCT silanes catalog. The wetting surface is of utility in calculating the theoretical amount of silane necessary for deposition on a powdered filler (see Figure 30). A representative contact angle measurement is shown in Figure 29. High contact angles result from hydrophobic silane depositions and low angles from hydrophilic depositions. Qualitatively, a scientist can quickly determine if a silane deposition has been successful by placing a drop of water on a coated and uncoated slide side by side. Visual or microscopic examination should show a contact angle difference.

Other qualitative wet methods are possible to determine presence of active silane on a surface. They include:

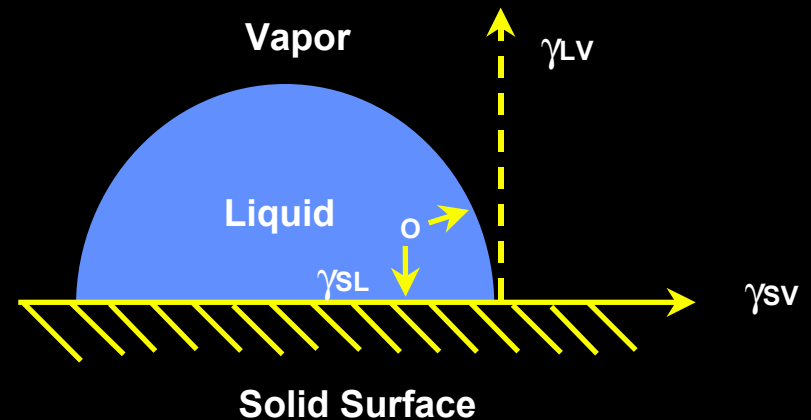
- 1) For substrates functionalized with vinyl or mercapto groups, putting down drop of bromine water (color fades) or aqueous potassium permanganate (surface turns brown).
- 2) For those substrates coated with amino silanes, treatment with Ninhydrin reagent (turns blue).
- 3) For aldehyde coated surfaces, treatment with Tollins reagent (forms silver mirror) or Fuchsin Aldehyde reagent (turns purple violet).

## Figure 28a Silane wetting surfaces

Silane	Specific wetting surface, m <sup>2</sup> /g
Vinyltrichlorosilane	480
Vinyltriethoxysilane	410
Vinyltris(methoxyethoxy)silane	280
Methacryloxypropyltrimethoxysilane	315
Glycidoxypropyltrimethoxysilane	330
Aminopropyltriethoxysilane	355
Trichlorosilane	240

The specific wetting surface of a silane is determined from the minimum amount of silane required to provide a uniform surface.

## Figure 29 Contact angle





# Figure 30 CALCULATIONS

Calculation of necessary silane to obtain minimum uniform multilayer coverage can be obtained knowing the values of the wetting surface of silane (ws) and the surface area of filler:

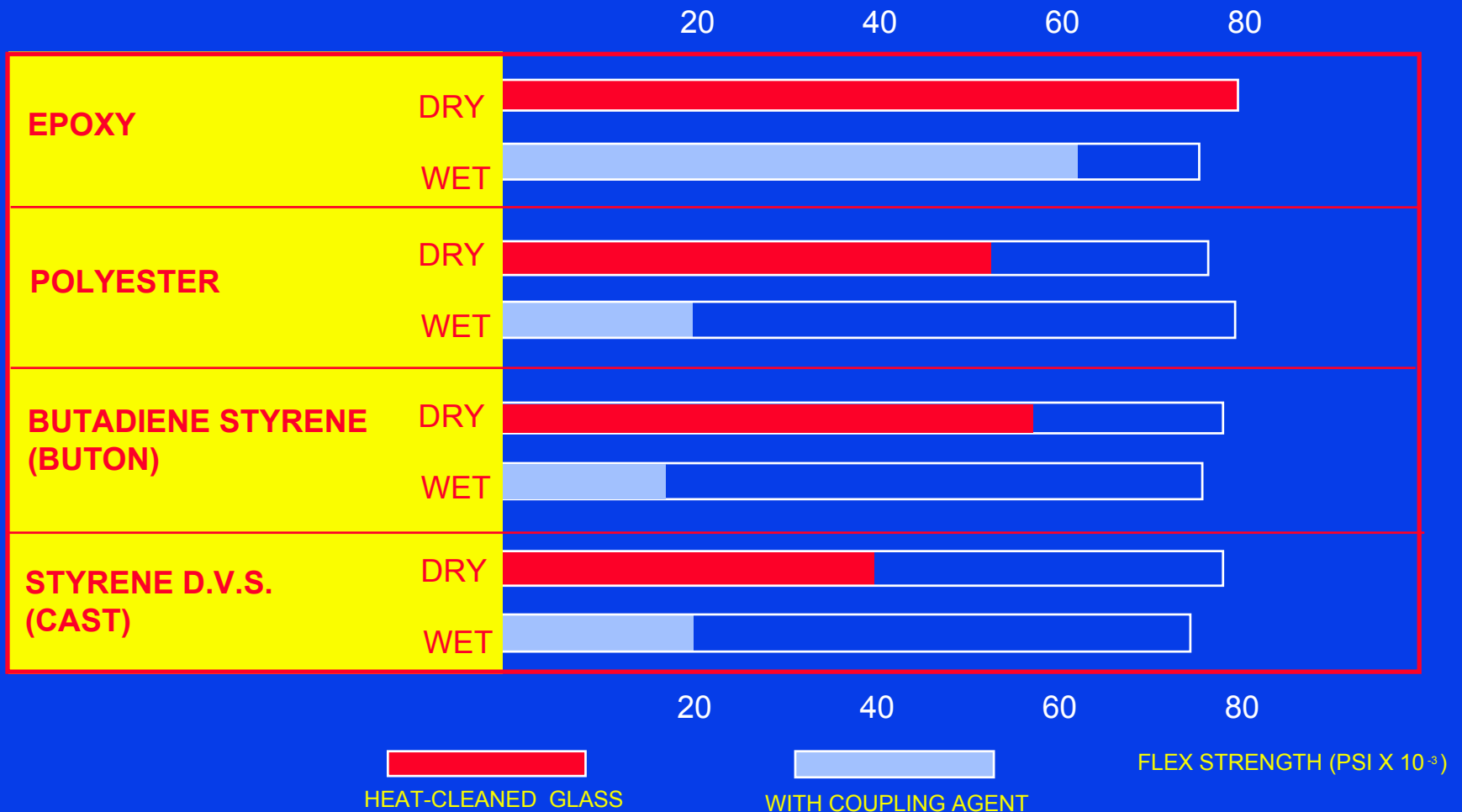
$$\text{amt. of silane (g)} = \frac{\text{amount of filler} \times \text{surface area of filler}}{\text{wetting surface (ws)}}$$

## Relative surface area of common fillers m<sup>2</sup>/g

E-Glass	0.1-0.12
Silica, ground	1-2
Kaolin	7
Clay	7
Talc	7
Si, diatomaceous	1-3.5
Calcium silicate	2.6
Silica, fumed	150-250

Silane coupling agents are extensively used in industry to enhance the performance of filler additives such as fiberglass or silica with industrial resin systems. Most fillers with the exceptions of graphite or noble metals have active sites, allowing the silanetriols to bond with the filler (see [Figure 6](#)). The silane additive is usually mixed in 0.2 to 0.5 wt % with the filled formulation in order to achieve optimal performance. [Tables 4 through 13](#) show dramatic improvements in polymer physical properties for both initial and wet aged composite formulations on addition of United Chemical Technologies silane coupling agents. The mechanism of the filler/polymer interaction is similar to that presented earlier for flat surfaces. The presence of water in the filler is beneficial in order to allow hydrolysis of the silane to active silanols (see [figure 7](#)).

# Figure 31 Typical performance of silane in glass fiber reinforced thermoset composites



# Table 4 Fiberglass-Reinforced Polyester Laminates

Fiberglass Finish	Flexural Strength, psi	
	Dry	Wet
None	58,900	42,700
0.2% M8550	78,800	78,000
0.2% S1590	89,000	78,300

# Table 5 Fiberglass-Reinforced Polyester Pultrusion Rods

Silane Ingredient in Size	Average Size Pickup wt. %	Flexural Strength, psi	
		Dry	Wet
None	1.4	104,000	49,600
M8550	1.4	118,000	77,000
S1590	1.4	124,000	84,400

# Table 6 Fiberglass-Reinforced Epoxy Laminates

Fiberglass Finish	Flexural Strength, psi		Compressive Strength, psi	
	Dry	Wet	Dry	Wet
NONE	88,000	65,000	55,000	23,600
0.2% G6720	94,400	85,400	62,000	61,000

# Table 7 Fiberglass-Reinforced Phenolic Laminate

Silane Percent	Flexural Strength, psi	
	Dry	Wet
None	64,600	43,200
1.4	89,200	77,800

# Table 8 Novacite - Reinforced Nylon 6/6

Strength Properties	Unfilled Nylon	35% (w/w) Novacite Reinforcement		
		Untreated	0.5% A0700	0.5% C3300
Flexural Strength, psi Dry Wet	16,100 10,400	16,000 10,000	21,100 31,900	21,400 NA
Flexural Modulus, 10 psi Dry Wet	3.87 1.67	6.60 2.67	6.39 3.07	6.25 NA
Tensile Strength, psi Dry Wet	11,500 9,200	8,700 6,300	12,200 9,800	11,900 NA



# Table 9 Mica - Reinforced Polypropylene

Strength Properties	Unfilled Resin	40% (w/w) Glass Bead Reinforcement	
		Untreated	0.5% S1590
Flexural Strength, psi	5,600	5,420	6,640
Flexural Modulus, 10 psi	2.55	7.77	10.8

# Table 10 Vinyl Ester Compound Containing Glass Bubbles and Silane Additives

Silane Additive	Paste Viscosity cps	Flexural Strength, psi	
		Dry	Wet
None	25,000	7,280	5,990
M8550	25,000	10,230	8,700
S1590	29,000	10,880	8,910

# Table 11 Mica - Reinforced Nylon 6

Strength Properties	Unfilled Nylon	35% (w/w) Mica Reinforcement		
		Untreated	0.5% A0700	0.5% C3300
Flexural Strength, psi Dry Wet	14,500 7,100	17,900 10,300	18,400 12,600	18,100 10,400
Flexural Modulus, 10 psi Dry Wet	3.20 1.24	14.1 5.34	14.3 7.35	14.0 6.75
Tensile Strength, psi Dry Wet	9,400 7,000	10,700 6,900	11,000 8,500	10,400 8,200

# Table 12 Glass Bead - Reinforced PBT

Strength Properties	Unfilled Resin	35% (w/w) Glass Bead Reinforcement	
		Untreated	0.25% G6720
Flexural Strength, psi			
Dry	12,900	10,800	14,900
Wet	13,000	10,100	14,400
Flexural Modulus, 10 psi			
Dry	3.14	5.83	6.07
Wet	3.00	4.04	5.38
Tensile Strength, psi			
Dry	7,300	5,600	8,000
Wet	7,300	4,800	7,900

# Table 13 Polyester Compound Containing Silanes-Treated Silicate Microspheres

0.75% Silane Treatment	Paste Viscosity cps	Flexural Strength, psi	
		Dry	Wet
None	8,000	7,570	5,940
S1590	6,750	7,920	7,690

In summary, this article has attempted to show the extensive utility of silane coupling agents in promoting the adhesion of polymer substrates, including bio polymers, to commercial substrates. United Chemical Technologies is a major manufacturer of high quality organosilanes for these applications. For further review, the reader may refer to the excellent text by Plueddemann ([Ref 4](#)).

## References

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