



A Subsidiary of PETRONAS Chemicals Group

Silanes for Coatings and Adhesives

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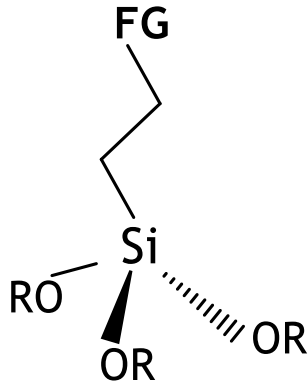
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Topics :

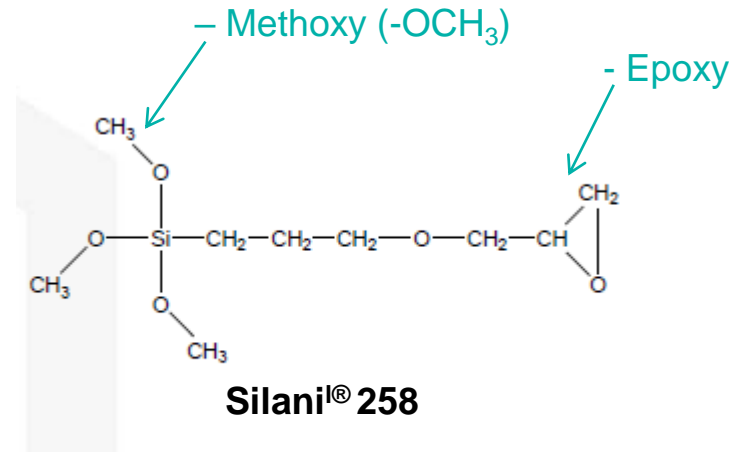
- Chemistry of Silanes
- Silanes for Coatings
 - > Primer
 - > Polymerization
 - > Post Addition
- Silanes for Adhesives and Sealants
- Factors of Silane Reaction

Silane Structure

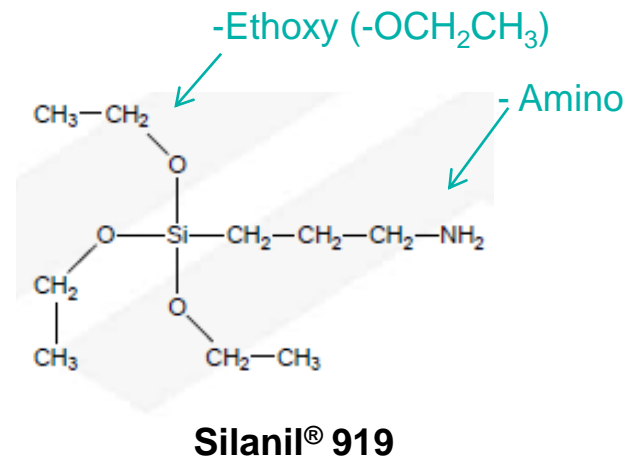
FG = Functional Group (Oragno Type)
e.g. -Vinyl, -Glycidoxy (Epoxy),
-Amino, -Methacryloxy, -AkyI ,etc.



e.g.



OR = Alkoxy, Acetoxy, Oxime
e.g. - Methoxy (-OCH₃) ,
-Ethoxy (-OCH₂CH₃) ,etc.

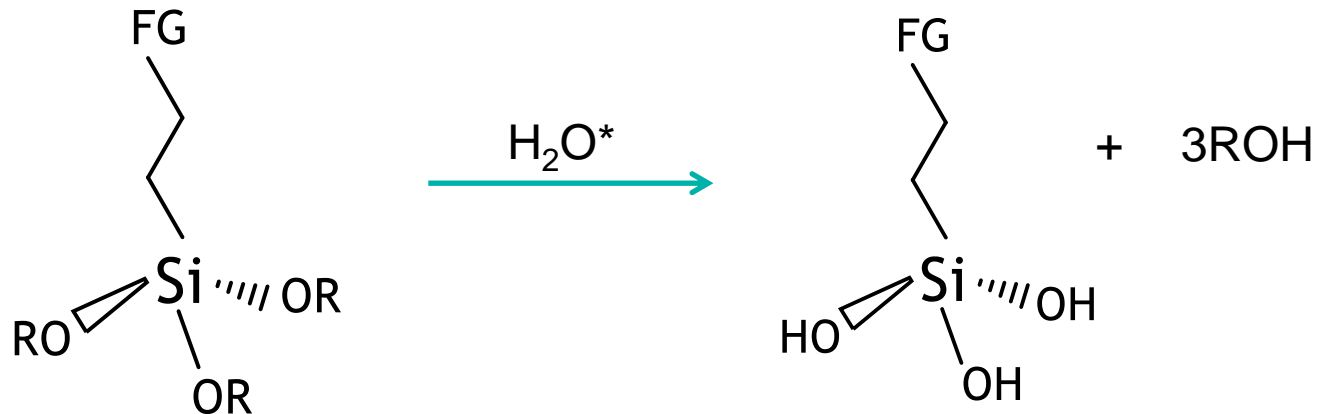


How Silanes work

Silanes are 2 step Reaction Chemical which most of them are monomer. When store under inert gas (N₂), Silanes will be non-reactive monomer in form of FG-Si-OR which -R or Akyl is non-reactive group .

However, **Silanes can be hydrolyzed by moisture** which -Si-OR will be changed to -Si- OH called “**Silanol**” group and be ready to react or bond to the substrates or the fillers .

The change of -Si-OR to -Si-OH is called “Hydrolysis” which is the 1st step of silane reaction .



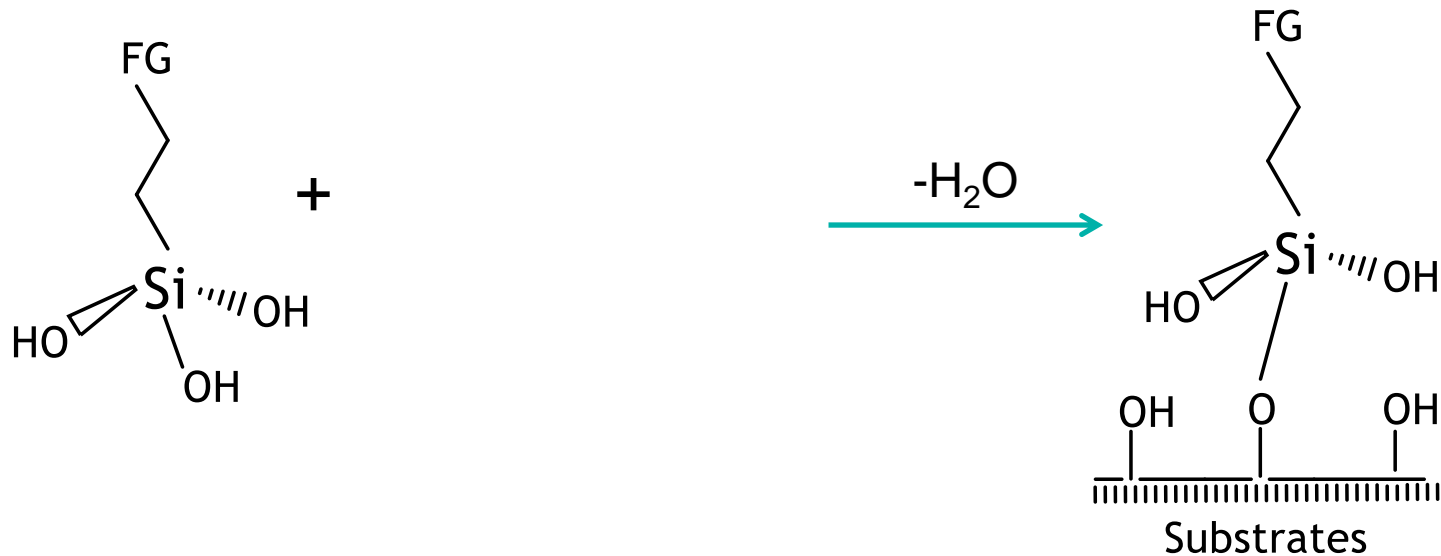
**1st Step Reaction-
Hydrolysis**

* H₂O can come from atmosphere/air.

How Silanes work

2nd step of the reaction is “**Condensation**”. After Hydrolysis , Silane contains “Silanol” group or Si-OH which is very reactive and ready to bond to substrates or fillers.

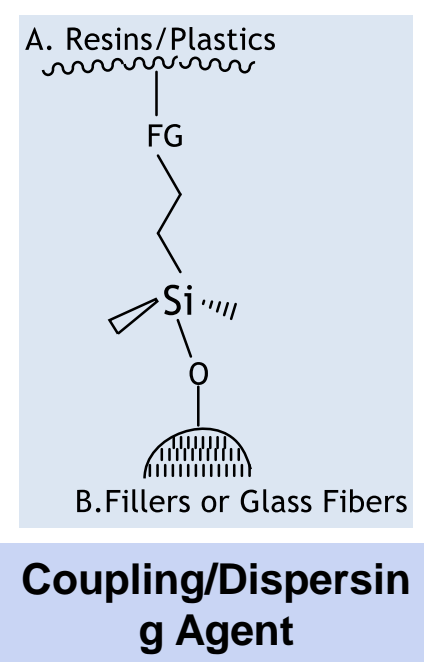
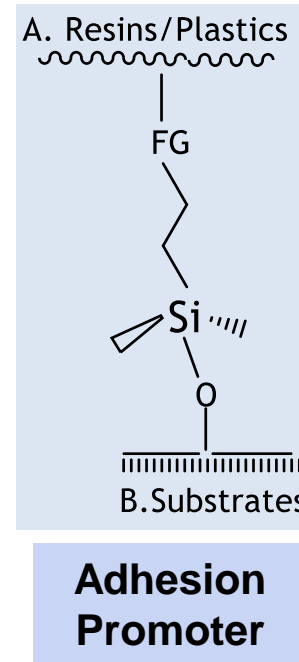
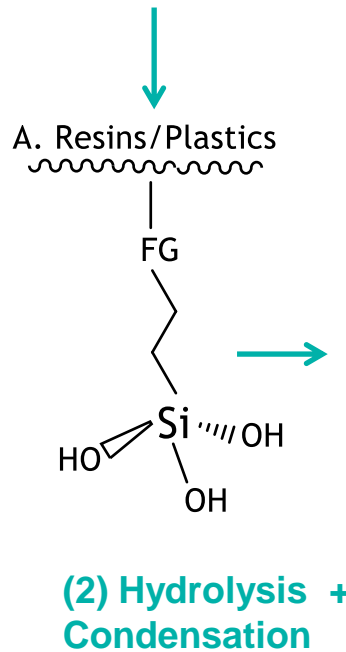
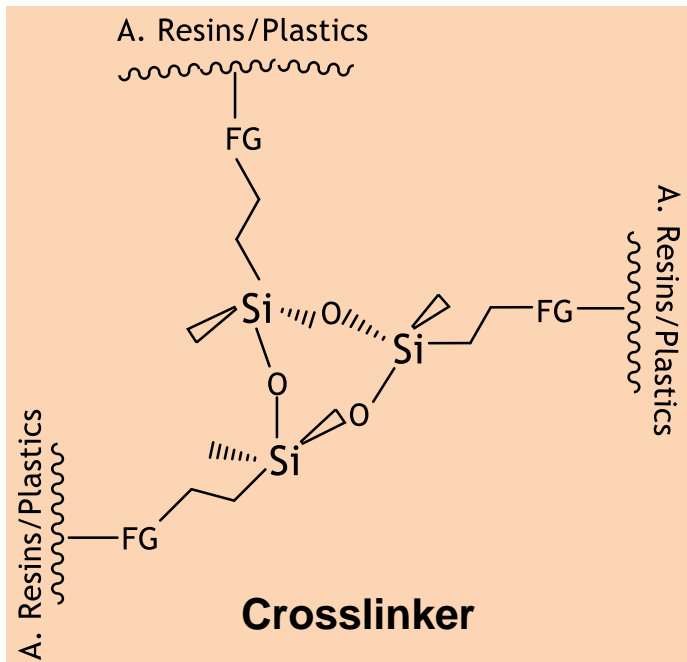
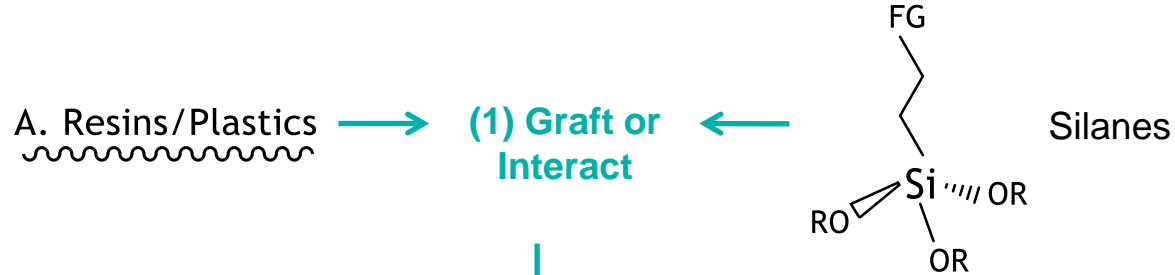
This bonding step is called “**Condensation**” which is function of adhesion promoter to the substrates or coupling/dispersing agent to the fillers



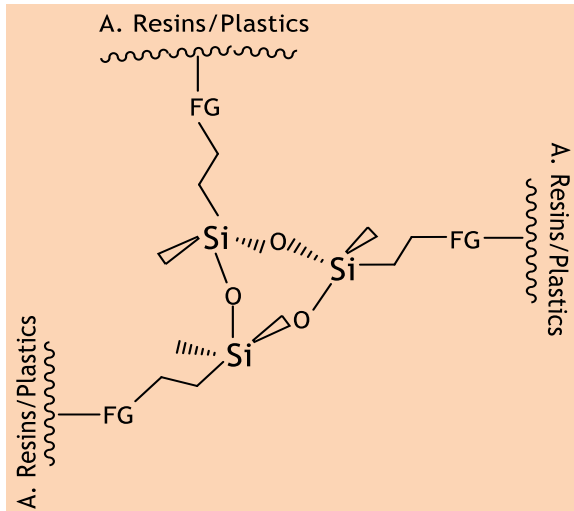
2nd Step Reaction-Condensation

* e.g. Application of Glass Fiber Surface Treatment

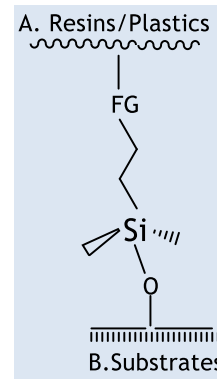
Benefits of Silanes in each function



Benefits of Silanes in each function

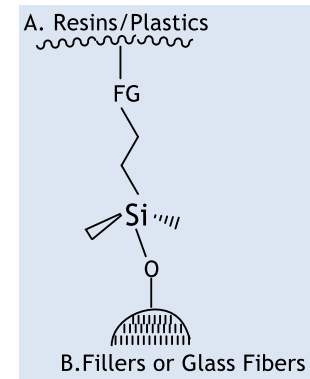


- Create net work structure in Polymer
- Increase strength and hardness
- Longer service life of product
- Higher temperature resistance
- Higher scrub/scratch resistance



Adhesion Promoter

- Enhance adhesion performance btw resins and substrates
- Improve corrosion resistance and prevent corrosion's spreading from crack line .



Coupling/Dispersion Agent

- Link btw resins and fillers, stay together as one system
- Optimize strength of composites
- Able to add higher filler loading
- Improve filler's dispersion in resins

Silanes for Coatings



Benefits of Silanes in Paint and Coatings

- Increase Adhesion Performance to Substrate
- Increase Crosslinking Density of Resin which affected to
 - > Increase hardness
 - > Increase mar resistance*
 - > Improve solvent, acid, alkaline resistance
 - > Improve water resistance
 - > Increase abrasion resistance or scrub resistance
- Change Resin Properties
 - > Thermoplastics to near Thermosets
- Disperse Pigments/Fillers
 - > Improve consistency of viscosity and able to have lower viscosity
 - > Benefit to lower loading of pigments in the formulation
- Bind Pigments/Fillers
 - > Act as coupling agent to pigments/fillers to improve scrub ability

* The mar resistance is surface coating's ability to withstand scratching and scuffing actions which tend to mar (change) the surface appearance of coating .

Typical Ingredients of Organic Coating

- **Resins** - Be also called binder, usually major non-volatile component, made up of a polymer
- **Solvents** - Dissolve the resin, soften the coating, allow good flow, viscosity control, drying behavior, and reduce cost
- **Surfactants** – Stabilize resin particles in WB coatings
- **Pigments/Fillers** – Provide color, opacity, special effect and cheapen coating
- **Thickeners** – Control and adjust viscosity
- **Stabilizers** - Provide longer service term e.g. Hindered Amine Light Stabilizers (HALS)
- **Neutralizers** - Adjust pH e.g. volatile amines
- **Additives** – **Silane is one of coating additives for adhesion promoter, crosslinker, and coupling agent.**
Other additives e.g. Flow, Slip, Anti-Foam ,etc.

Application in Paint and Coatings

Primer

2-5% Silani[®] 919
+
4-5% DI Water
Solvent (Alcohol/Toluene)

↓
Cold
Blend



Silane as Adhesion Promoter

Polymerization

Monomers to
produce Resin

+ →

Silanes
e.g. Silani[®]
276,250
(0.5-2% in WB,
Up to 10% in SB)



↓ Polymerization



Silane as Crosslinker

Post Addition

Resin+ Silane (e.g.Silani[®]
919,258 at 0.2-2% wt.of
Resin Solid)



↓ Induction time at
least overnight

Other Additives/
Fillers added
+ Mill-base added

↓
Paint

**Silane as Crosslinker, Coupling
Agent, Adhesion Promoter**

Application: Primer



Typical Formulation of Primer

Components

Amino silanes 2-6%

+

Mixed Solution :

Alcohol e.g. IPA

Distilled water

Toluene

n-Butanol

Butyl Cellosolve

- Dissolve 2-6 % wt. silane in a compatible volatile solvent (or mixture of solvents) .
- Amino silanes e.g. Silanil® 919, 138 and 176 are recommended.
- Alcohols are most commonly used, for water compatibility.
- Water at equal part of silane may be added to pre-hydrolyze silane if water is compatible with the solvent.
- Apply to grease-free surface by wiping, spraying, brushing, or dipping.
- Film thickness < 0.1 mil .
- Leave the surface dry to remove solvent around 15- 30 mins. Apply the top coat within 24 hrs to protect surface from contamination .

Application: Polymerization

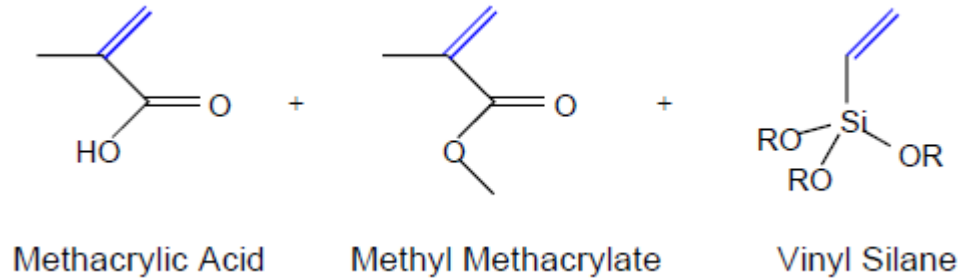


Silanes for Polymer Modification

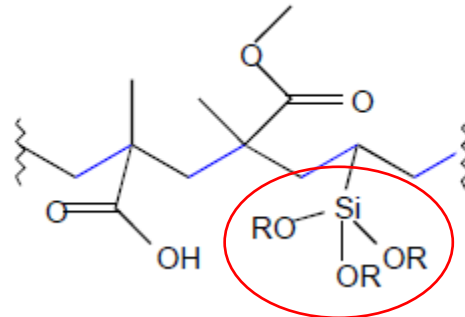
Silaniil® 276, 780 and 250 are widely used to modify polymer structure especially in surface coating resin for both of WB and SB such as Acrylic Latex which is commonly added in polymerization step.

Silane as Crosslinker in Emulsion Polymerization :

Typical Monomers for Acrylic Latex



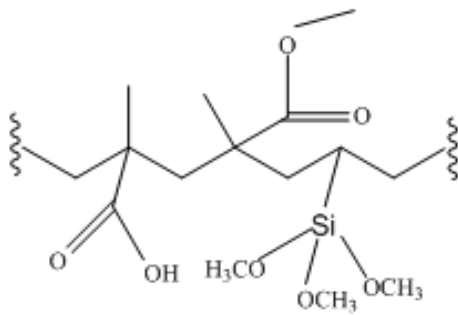
Emulsion Polymerization



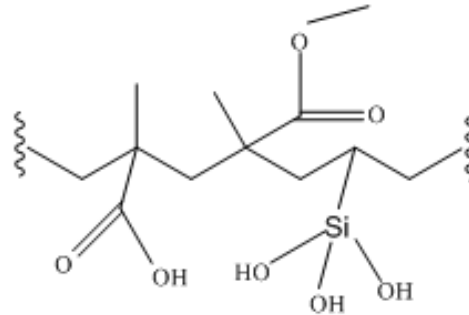
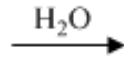
Silane Modified Structure e.g. R is -CH₃

Silanes for Polymer Modification

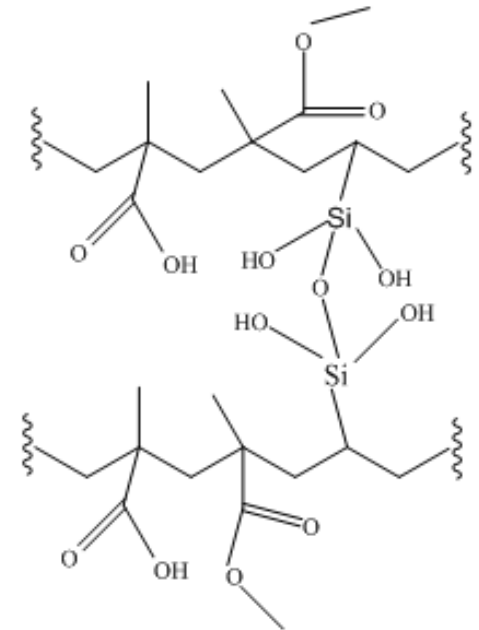
Silane as Crosslinker in Emulsion Polymerization :



Silane Modified Structure



Silane Modified Structure after Hydrolysis



**Silane as Crosslinker
or called “Silylated Acrylic”**

Silane Dosage in Polymerization

In Soventborne Resin : recommended silane dosage at 0.4-10.0% on total monomer wt.

In Waterborne Resin : recommended silane dosage at 0.1-2.0% on total monomer wt.
pH is recommended close to neutral or ≤ 8.5 pH for stability purpose.

For emulsion polymerization, it is recommended to add silane in the pre-emulsion stage.

In case of **none pre-emulsion stage**, it is recommended to add silane into the monomixture at the remaining of 10-15% monomers feeding time .

Typical Formula of Silylated Acrylic

Monomers :

- BA 20-30 Mole %
- MMA 65-75 Mole %
- MAA 2-3 Mole %
- Silane 1-3 Mole%



Typical Emulsion Recipe

Water	40-50 %
Monomers	40-50 %
Surfactants	2-5 %
Initiator	0.3-0.5 %
Others Additives	

General Specification of Emulsion

Tg	40-80
Acid Value	10-50
Solids	40-50%

Effect of Glass Transition (Tg) on Latex Properties

Latex properties

- Drying speed
- Gloss
- Heat resistance
- Resolubility
- Solvent tolerance
- Adhesion
- Film formation
- Flexibility
- Water resistance
- Pigment dispersion

Low Tg

High Tg

Low	→	High
Low	→	High
Low	→	High
High	←	Low
Low	→	High
High	←	Low
High	←	Low
High	←	Low
Low	→	High
High	←	Low

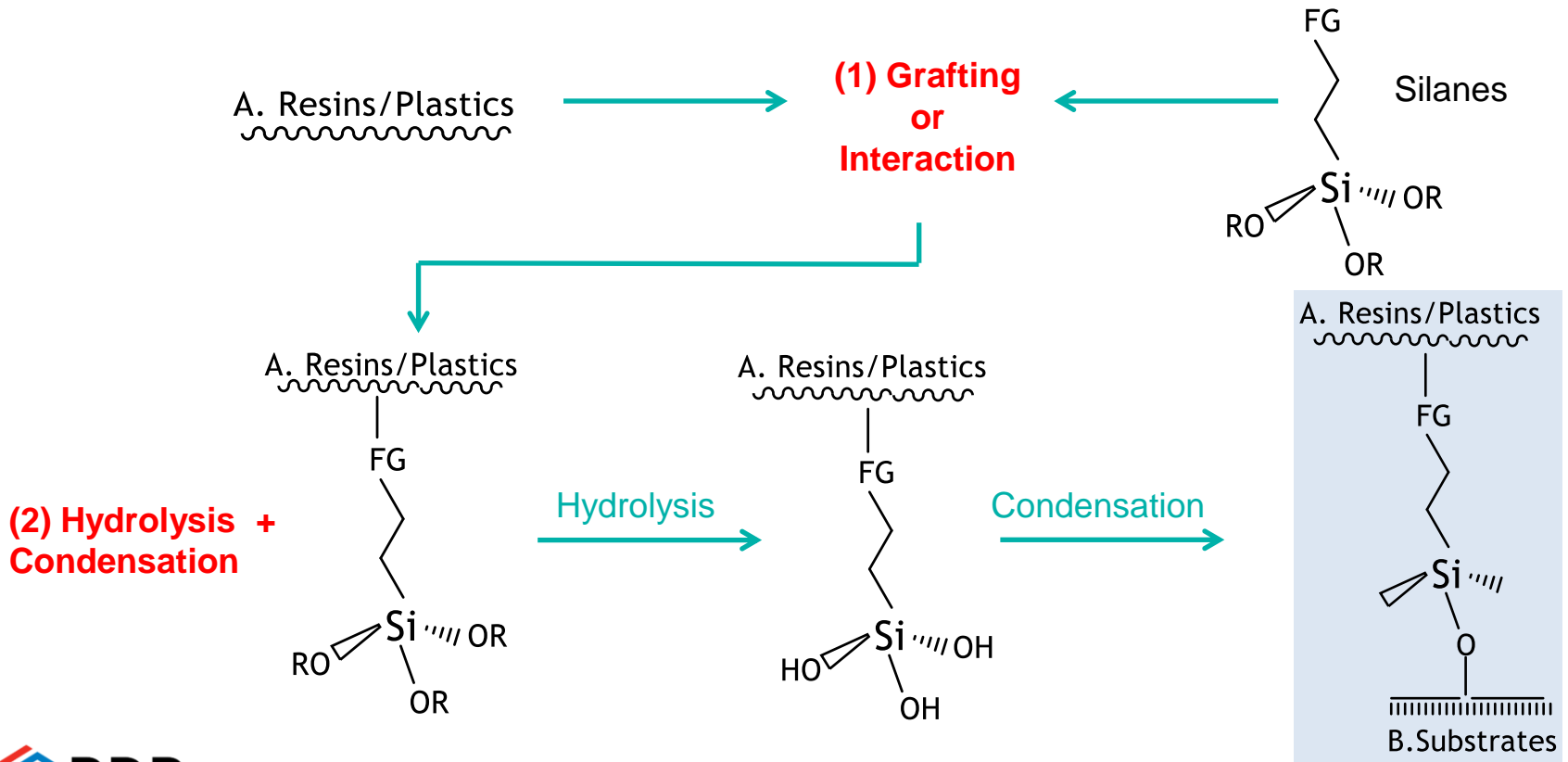
*** Silanes could increase the Tg value in Acrylic Latex .**

Application: Post Addition



Silanes for Post Addition

Post addition is the process to add chemicals or additives into polymer (resin) after the polymer is formed or after polymerization. Silanes in Post addition show 2 mechanisms 1) Grafting in part of functional group of silanes and 2) Hydrolysis and condensation in part of -OR which is changed to -ROH (Silanol Group) .



Manufacturing Process of Paint

Part 1 – Accurate measurement of ingredient

Part 2 – Mill-base preparation and pigment dispersion

Part 3 – Let-down

In a separate, larger, vat the rest of the paint (resin, solvent, additives **and also “Silanes”**) is combined and mixed. This is called the let-down. When the let-down and the mill-base are completed, the mill-base is added with stirring to the let-down. At this stage, if required by the formulation, any final additions are made and added in.

Part 4 – Finished product and in process laboratory testing

Part 5 – Canning

Application Guideline for Post Addition

First step
Silane + Resin



Second step
Addition of Solvent or Water + Other Additives
e.g. Matting Agent, Wetting Agent, Wax,
Pigments , Ammonia ,etc .

Guide Line for Post Addition : Silane Grafting on Resin

- Blend silane directly into resin . (without other additives or pigments)
- Prefer pH near to neutral or pH of resin should be < 8.5 before adding silane. (for water-based resin)
- Induction time is needed after adding silane into resin. pH may be increased during induction time comparing to resin without silane. Proper induction time is able to study by pH evolution curve VS time.
- The induction time is at the onset point which pH is started to increase dramatically. Typical induction time is 5-48 hrs.
High shear agitation is able to accelerate the induction time
- It is recommended to add additives and fillers after the induction period.
- If pH adjustment is required for final coating , it is recommended to adjust pH after the induction period.
- Aging test at high temperature (for product stability study) have to be done after induction period .

Silane Dosage in Post Addition

Epoxy and amino silanes e.g. Silanil[®] 258, Silanil[®] 289, Silanil[®] 919, and Silanil[®] 176 are popular to be used for “Post Addition” .

The effective silane dosage is varied up to type of polymers,
“ It is recommended at 0.2-2 %wt of silane based on resin solid content.”

However, ladder test is recommended with various silane dosages to study the optimum point which may show different results in each polymer.

Recommendation in Paint and Coatings

By Functional Group Matching

Acrylic	PU 1K	PU 2K	Epoxy	Alkyd	Polyamide	Phenolic	PBT	Polyester	PUD	Silicone	Melamine
Silanol 250	Silanol 258	Silanol 258	Silanol 258	Silanol 176	Silanol 176	Silanol 258	Silanol 258	Silanol 250	Silanol 258	Silanol 176	Silanol 176
Silanol 258	Silanol 260	Silanol 919	Silanol 919	Silanol 919	Silanol 919	Silanol 919	Silanol 919	Silanol 780	Silanol 289	Silanol 919	Silanol 919
Silanol 289		Silanol 176	Silanol 250		Silanol 1479	Silanol 307	Silanol 176	Silanol 276	Silanol 260	Silanol 1479	Silanol 260
Silanol 919		Silanol 138	Silanol 289			Silanol 176			Silanol 919		Silanol 258
Silanol 276		Silanol 1479									
Silanol 780											

By Functions

Crosslinker		Adhesion Promoter	Coupling Agent	Primer
Process: Polymerization	Process: Post Addition*	Process: Post Addition	Process: Post Addition	Process: Cold Blend
Silanol 250	Silanol258	Silanol 919	Silanol 919	Silanol 919
Silanol 276	Silanol289	Silanol 176	Silanol 176	Silanol 138
Silanol 780		Silanol 138	Silanol 138	Silanol 176
		Silanol 1479	Silanol 258	
		Silanol 258	Silanol 289	
		Silanol 289		

* Sequence of silane addition into formulation is affected to the function of silane .

Remark: Recommendation based on testing and historical experience data.

Silanes for Adhesives and Sealants



Application in Adhesives and Sealants

Applications are in the same direction as coatings :

- Primer > as adhesion promoter
- Polymerization > as crosslinker
- Post addition > as adhesion promoter, coupling agent, or crosslinker

Typical Ingredients of Sealants

Typical Ingredients :

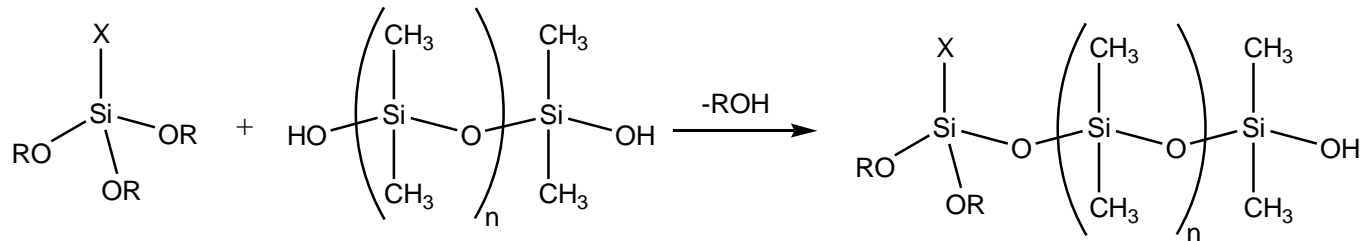
- Resins
- UV stabilizers
- Plasticizers
- **Moisture scavengers** > Silanil® 276
- Fillers (CaCO₃ ,etc.)
- Thixotropic agents
(Fumed silica or additives)
- Pigments/Colorants
- **Adhesion promoters*** > Silanil® 176, 138, 919, 1479, etc.
- Catalysts > BRB DBTDL, BRB DBTDA , etc.
- Other additives
- May be solvents
- Also **curing agents for silicone sealants**
> Silanil® MOS, VOS, MTAS, ETAS, PTAS, etc.



Planetary Mixer for
High Viscosity

* Dosage of silanes in range of 0.2-2% on resin solid wt.

Curing (Crosslinking) Type of RTV-1

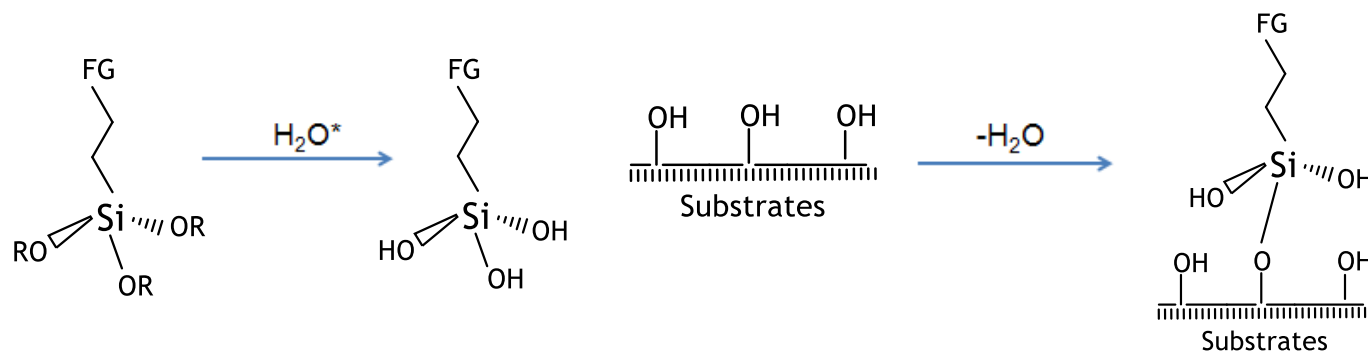


Curing Type	By product	Features
Oxime	Methylethylketoxime	<ul style="list-style-type: none"> ✓ Good adhesion on plastics ✓ Neutral cure, no acidic odor ✓ Low corrosive to metallic substrates ✓ Longer tack free time and cure time than acetoxy type
Acetoxy	Acetic acid	<ul style="list-style-type: none"> ✓ Fast cure and short tack free time ✓ Good adhesion on any substrates ✓ Good stability up to 300° C ✓ Vinegar odor from by product ✓ Corrosive to metallic substrates
Alkoxy	Alcohols i.e. Methanol or Ethanol	<ul style="list-style-type: none"> ✓ Neutral cure, non-acidic odor ✓ Non-corrosive to metallic substrates ✓ Good adhesion (< acetoxy type) ✓ Longer tack free time and cure time than acetoxy type ✓ Stability up to 220° C

Silanes as RTV-1 Crosslinkers

Curing Type	BRB Silane	Chemical Name	CAS no.
Oxime	Silanil MOS	Methyltris(methylethylketoxime)silane	22984-54-9
	Silanil VOS	Vinyltris(methylethylketoxime)silane	2224-33-1
	Silanil POS	Phenyltris(methylethylketoxime)silane	34036-80-1
Acetoxy	Silanil MTAS	Methyl(triacetoxy)silane	4253-34-3
	Silanil ETAS	Ethyl(triacetoxy)silane	17689-77-9
	Silanil PTAS	Propyl(triacetoxy)silane	17865-07-5
	Silanil MTAS/ ETAS Blend	Methyl(triacetoxy)silane/ Ethyl(triacetoxy)silane	4253-34-3/ 17689-77-9
	Silanil MTAS/ PTAS Blend	Methyl(triacetoxy)silane/ Propyl(triacetoxy)silane	4253-34-3/ 17865-07-5
	Silanil 118	Methyltrimethoxysilane	1185-55-3
Alkoxy	Silanil 203	Methyltriethoxysilane	2031-67-6

Silanes as RTV-1 Adhesion Promoters



Functional Group	BRB Silane	Chemical Name	CAS no.
Amino	Silanil 919	3-aminopropyltriethoxysilane	919-30-2
	Silanil 138	3-aminopropyltrimethoxysilane	13822-56-5
	Silanil 176	N-(2-aminoethyl)-3-aminopropyl-trimethoxysilane	1760-24-3
	New product Silanil 1479	Diamino alkyl silane co-oligomer	-
Epoxy	Silanil 258	3-glycidoxypropyltrimethoxysilane	2530-83-8
	Silanil 289	3-glycidoxypropylmethyldiethoxysilane	2897-60-1
	Silanil 260	3-glycidoxypropyltriethoxysilane	2602-34-8
Methacryloxy	Silanil 250	3-methacryloxypropyltrimethoxysilane	2530-85-0

Adhesion Promoter: Silanil[®] 1479

New product

Diamino Alkyl Silane Co-oligomer

The benefits over regular amino silanes:

Lower VOC, less by products, resulting in lower odor during application

Less yellowing to resins

Higher hydrophobicity than diamino silane monomer, resulting in good wet adhesion

High elasticity with lower modulus of cured adhesives

Good adhesion performance between organic resins and inorganic substrates.

Product Package for RTV-1 Sealants

1. Acetoxy sealants
2. Alkoxy Sealants
3. Oxime Sealants
4. MS Polymer Sealants

1. Acetoxy sealants

A: 100% Silicone Sealant General Purpose

- BRB OH Fluid 80,000 cSt → 60-80%
- BRB Silicone Oil 1,000 cSt → 10 – 20%
- BRB Silanil[®] MTAS → 5 – 10%
- BRB DBTDL → 0.2 -1%
- Third party fumed Silica → 10%

*Optional adhesion promoters: BRB Silanil[®] 176, Silanil[®] 919, Silanil[®] 138, Silanil[®] 1479, etc.

1. Acetoxy sealants

B: Extended Silicone Sealant General Purpose

- BRB OH Fluid 80,000 cSt → 40-60%
- Third party solvent plasticizer → 20 – 40%
- BRB Silanil[®] MTAS → 5 – 10%
- BRB DBTDL → 0.2 -1%
- Third party fumed Silica → 10%

*Optional adhesion promoters: BRB Silanil[®] 176, Silanil[®] 919, Silanil[®] 138, Silanil[®] 1479, etc.

Catalyst for Fast Cure: DBTDA

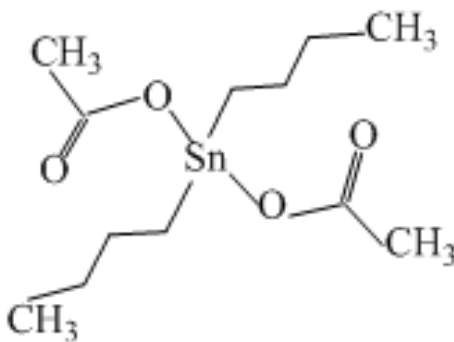
New product

Dibutyltin diacetate (Diacetoxybutyltin)

Faster speed of catalysis performance – faster gelation, tack-free time, and cure time – than DBTDL.

Suitable for acetoxy sealants. (The mixture of DBTDA : DBTDL can be used to design cure time such as ratio of 1.9 : 2.8.)

Soluble in the common solvents i.e. toluene, xylene, benzene, acetone, ethanol, ethyl acetate, chloroform, and other petroleum ethers.



CAS# 1067-33-0

2. Alkoxy sealants

- BRB OH Fluid 20,000 cSt and 80,000 cSt
- BRB Silicone Oil 500 cSt
- Third party coated calcium carbonate
- BRB Silanil[®] 118

*Optional adhesion promoters: BRB Silanil[®] 176, Silanil[®] 919, Silanil[®] 138, Silanil[®] 1479, etc.

3. Oxime Sealants

Neutral Cure All Weather Purpose

- BRB OH Fluid 80,000 cSt → 30 -40%
- BRB Silicone Oil 100 cSt → 5-10%
- Third party coated calcium carbonate → 40-50%
- BRB Silanil[®] MOS and VOS → 3-4%
- BRB DBTDL → 0.2 – 1.0%

*Optional adhesion promoters: BRB Silanil[®] 176, Silanil[®] 919, Silanil[®] 138, Silanil[®] 1479, etc.

4. MS-Polymer

Crosslinker and adhesion promoter for MS-Polymer

- BRB Silanil[®] 118

*Optional adhesion promoters: BRB Silanil[®] 176, Silanil[®] 919, Silanil[®] 138, Silanil[®] 1479, etc.

What BRB offers

1. Full range of siloxane, silanes, and tin catalyst products
2. Formulation help
3. Only raw material supplier, not competing with sealants in the market
4. Flexible supply from regional warehouse
5. Competitive prices for continuous sustainable growth

Recommendation in Adhesives and Sealants

By Functional Group Matching

Acrylic	Polyurethane 1K	Poyurethane 2K	Epoxy	Silicone	Polysulfide	MS Polymers
Silanil 250	Silanil 258	Silanil 258	Silanil 258	Silanil 176	Silanil 258	Silanil 176
Silanil 258	Silanil 260	Silanil 919	Silanil 919	Silanil 919	Silanil 442	Silanil 919
Silanil 289		Silanil 176	Silanil 176	Silanil 780	Silanil 919	Silanil 1479
Silanil 919		Silanil 138	Silanil 289	Silanil 1479		Silanil 118
Silanil 276		Silanil 1479				
Silanil 780						

By Functions

Adhesion Promoter	Coupling Agent	Moisture Scavenger	Primer	Curing Agent for RTV
Silanil 919	Silanil 919	Silanil 276	Silanil 919	Silanil MOS (Oxime)
Silanil 176	Silanil 176		Silanil 138	Silanil VOS (Oxime)
Silanil 138	Silanil 138		Silanil 176	Silanil MTAS (Acetoxy)
Silanil 307	Silanil 307			Silanil ETAS (Acetoxy)
Silanil 258	Silanil 258			Silanil 118 (Alkoxy)
Silanil 289	Silanil 289			Silanil 203 (Alkoxy)
Silanil 442	Silanil 442			Silanil MES (Ester)
Silanil 1479				Silanil VES (Ester)

* Sequence of silane addition into formulation is affected to the function of silane .

Remark: Recommendation based on testing and historical experience data.

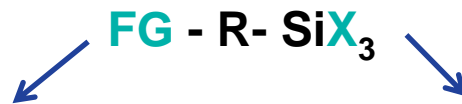
Factors of Silane Reaction



Factors affecting performance of Silanes

The performance of Silane is influenced by many parameters including:

- Silane Structure
- Dosage of Silane
: Too high dosage may affect poorer property e.g. too rigid, poor stability.
- pH of Resin or Coating
: pH can catalyze rate of Hydrolysis and Condensation per next page .
- Unknown Chemicals may catalyze Silane
: Mineral Acids, Alkoxide Salts, Tin Compound, Titanate Ester, Zirconium Salts, Phosphorous Compound, and Amines are catalysts for Silanes.
- Temperature of System
: Molecule can be moved faster and met each other at higher temperature.



> FG (functional group) matches to the resin chemistry to let silane graft well on the resin chains.

> X group affects to reactivity rate .

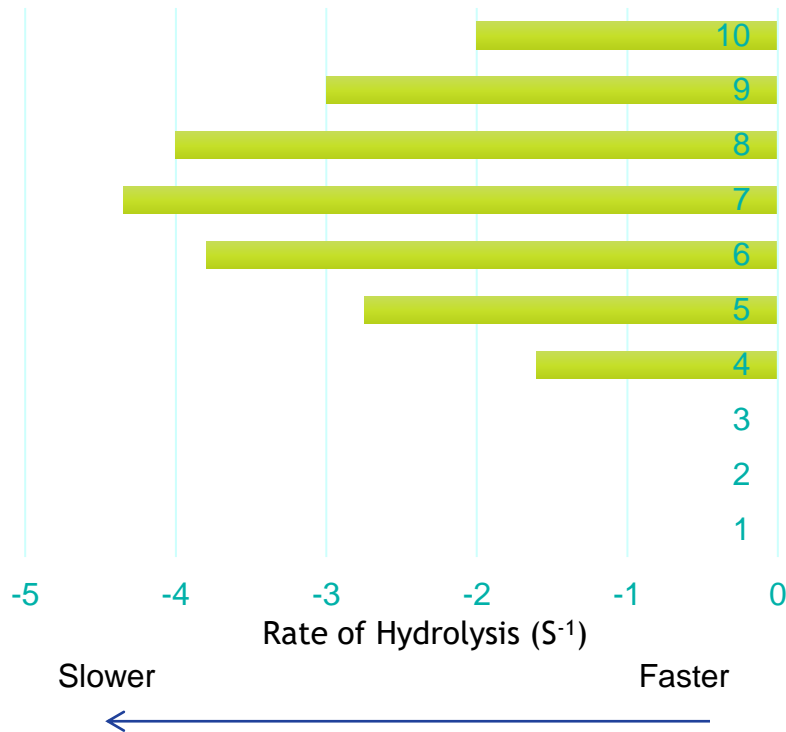
> Bulkier group gives slower reactivity .

Methoxy is faster than Ethoxy .

Hydrolysis Rate of Silanes

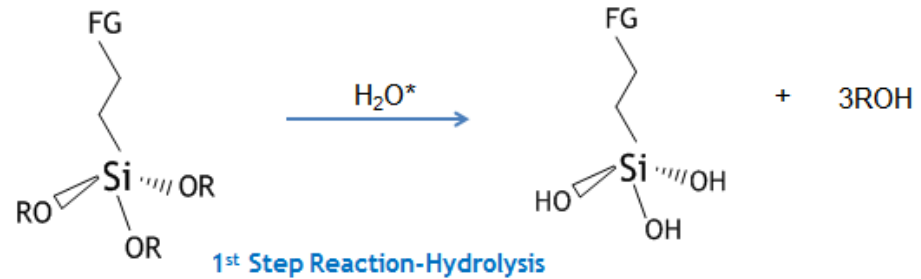
Time for hydrolysis is dependent on solution's pH.

Rate of Hydrolysis*



* Study of Epoxy Silane Hydrolysis

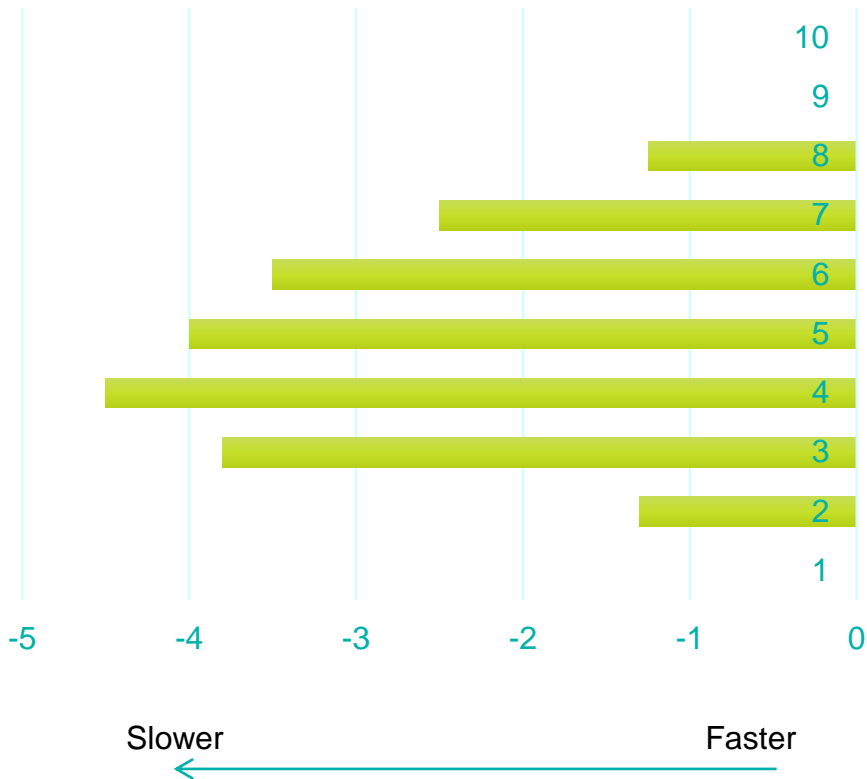
Ref: Pohl, E.R. and F.D. Osterholtz. 1985. Kinetics and mechanism of aqueous hydrolysis and condensation of alkyltrialkoxysilanes. *Polym. Sci. Technol.* 27:157-170.



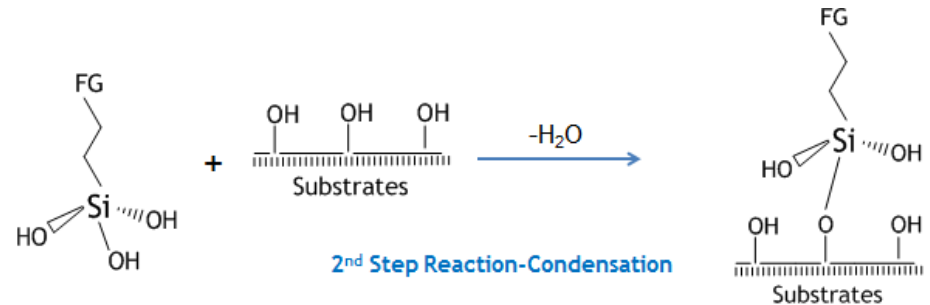
- Prefer pH near to neutral (pH 7) for storage stability purpose in adhesion promoter function .
- For WB, pH is not recommended at > 8.5 which may affect to shelf life of Paints&Coatings .
- -Si-OH (silanol groups) can also react each other or so-called self-crosslink which is not required.

Condensation Rate of Silanes (After Hydrolysis)

Rate of Condensation*



*Study of Epoxy Silane Condensation



- At pH 7, condensation rate is medium in which condensation is the reaction happening after hydrolysis of silane.
- During application, the environment which is contained moisture in the air and unstable pH, hydrolysis and condensation can happen and let silane react to substrate.

Ref: Pohl, E.R. and F.D. Osterholtz. 1985. Kinetics and mechanism of aqueous hydrolysis and condensation of alkyltrialkoxysilanes. *Polym. Sci. Technol.* 27:157-170.

Hydrolysis Tips for WB and SB

Waterborne (WB)

- Hydrolysis is slowest around pH 7, this is good for storage purpose.
- Acid pH and alkaline pH can catalyze rate of hydrolysis.
- Bigger substituents (hydrocarbon) on silicon retard hydrolysis e.g. Ethoxy is slower hydrolysis rate than methoxy.

Solventborne (SB)

- Hydrolysis of the first alkoxy group is slow.
- Alcohols can retard hydrolysis rate.
- Silanetriol species are unstable and able to condense in SB.

Signs of Unexpected Hydrolysis + Condensation of Silane

Trouble signs in Resins or Coatings

- Gel formation
- Seeding
- Viscosity buildup
- White precipitate
- Loss of performance over time

e.g. The first test shows good adhesion performance but after a few weeks, the second test shows poor adhesion on the same sample.

**These signs mean silanes may self-crosslink.
The worst case is entire gel.**



BRB

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