

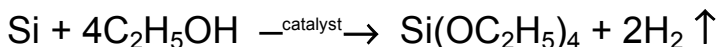
ETHYL SILICATE

Introduction

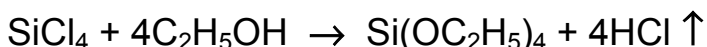
Ethyl silicate, the common name for tetra ethyl ortho silicate (TEOS), has found worldwide acceptance in applications when a liquid precursor of silica (SiO_2) is needed. When properly hydrolyzed, ethyl silicate produces very fine particles of silica which can act as a binder to adhere refractories into ceramic shapes or provide corrosion-resistant coatings in combination with zinc dust. When vaporized and thermally decomposed upon the surfaces of semiconductor chips ethyl silicate forms electrically insulating layers of silica glass which are necessary in the fabrication of integrated circuits. The chemical applications for ethyl silicate, including cross-linking of silicones, are numerous and new applications for this versatile chemical are constantly being developed. The information presented here is intended as an aid to tailoring ethyl silicate products to your own end use.

Manufacture

TEOS, $\text{Si}(\text{OC}_2\text{H}_5)_4$, is synthesized in one of two common ways: Firstly, directly from silicon metal and anhydrous ethyl alcohol:



Secondly, from silicon tetrachloride and anhydrous ethyl alcohol:



The silicon tetrachloride method is inherently prone to trace metal contamination and process variability. This is why Silbond produces their TEOS using the direct method. We have the longest continuously running direct process plant in the world and the knowledge to keep it running, producing the same high quality TEOS. We want our customers to enjoy the freedom of having it their way, without worry of extra trace ingredients, and completely chloride free. Our basic product, called Silbond[®] Condensed, is pure enough for most applications, however, we don't stop with "just pure enough". Want more? Consider Silbond[®] Pure, Silbond[®] EG or Silbond[®] UHPT.

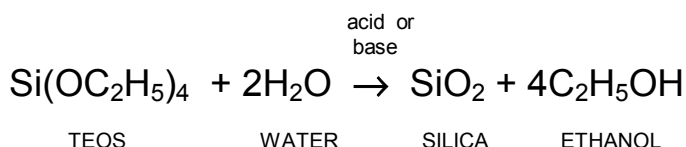
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Product	Assay
Silbond [®] Condensed	95%
Silbond [®] Pure	99.0%
Silbond [®] EG	99.5%
Silbond [®] UHPT	99.99%

Need more information about metal content? They are all low. See the individual product brochures to match the product to your own needs.

Hydrolysis

Complete hydrolysis of ethyl silicate will produce silica and ethyl alcohol.



From a practical perspective, partially hydrolyzed systems offer the user ready to use products with higher available silica content. 40% hydrolysis is the best compromise for pre-hydrolyzed systems providing physical properties that are easily managed for your individual processing needs and **consistent performance** to meet your individual specification targets. Silbond[®] 40 is a mixture of oligomers, with an average molecular weight of about 800. It has a broad distribution of individual species, ranging from monomer to more highly cross-linked polymer networks. Having **the right blend for dependability** is the key to producing successful binders. We have made them longer than anyone else.

The most common measure of performance of pre-hydrolyzed TEOS is the gel time. Gel time is a measure of the velocity of a blend of TEOS polymers to achieve sufficient molecular size to render a solution of TEOS non-flowing, i.e. gelled. Under this condition, a solution of TEOS polymers forms large enough networks to entrap the remaining solvent alcohol. This is one of the most **remarkable properties of Silbond[®] products**. The ability to produce useful gels in a variety of solvent combinations is the key to most applications. This gel tendency is very sensitive to pH conditions. At a pH of 2 to 4, the time to gel is measured in years. But adjust the pH to 6 to 8 and the fireworks begin. Now the gel time is measured in seconds. It is possible to go from a low viscosity liquid to a gelled mass with complete control. **Imagine the capability.** Depending on the solids content (amount of SiO₂ per liter), the characteristics of the gel

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change dramatically. At 20% solids, these gel masses are strong enough to walk on. Mix in some refractory and you can make a brick. Add some more solvent, and you make Jello. You have the **power and control**.

Here are some procedures and charts that illustrate some of the possibilities:

Starting formula for 100% hydrolyzed 20% silica solution:

Component	Weight %
Silbond [®] 40	50.00
Water	14.52
Ethanol	35.40
HCl (37%)	00.08

Table 1

The normal order of addition of these components is to mix the ethanol, Silbond[®] 40 and HCl and then add the water. This mixture is initially immiscible. However, the heat of reaction of the Silbond[®] 40 with the water (exothermic reaction) combined with the additional solvating power of the released alcohol of reaction, quickly produce a homogeneous solution that will remain liquid for over 1 year. Determination of gel time is a method of estimating the state of hydrolysis of an ethyl silicate binder.

To measure the gel time, we recommend the following procedure: An ammonium carbonate solution is used to adjust the pH of the pre-hydrolyzed binder.

Required Apparatus

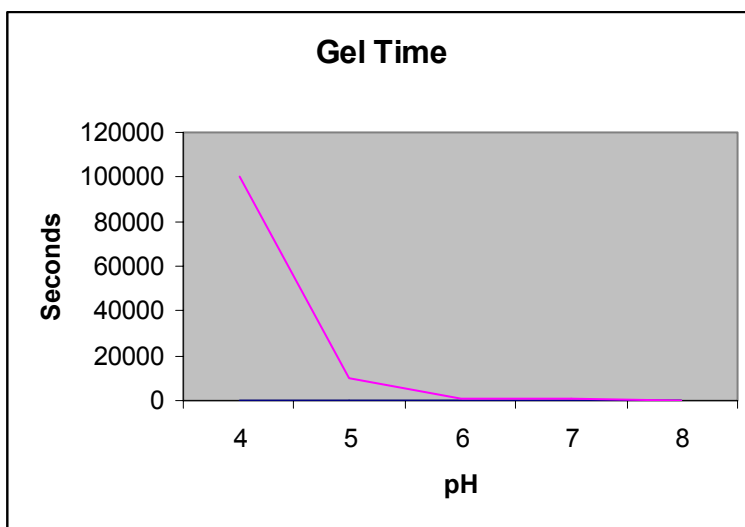
- Pipette - 2 ml
- Graduate Cylinder- 25 ml
- Disposable cups
- Stopwatch
- Constant temperature bath
- Stirring rod
- 2.5% ammonium carbonate solution

Gel Time Procedure

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1. Cool both binder sample (100 ml) and ammonium carbonate solution to 25° C.
2. Pipette 2 ml of the ammonium carbonate solution into the disposable cup.
3. Add 15 ml of the binder test solution to the beaker with stirring; start the stopwatch.
4. Swirl the beaker and let stand for 60 seconds.
5. Slowly twist the beaker, observing the contents. When gelation occurs, stop the watch and record the gel time.

If the solution in Table 1 is pH adjusted and the gel times plotted, the following curve is generated:



Pre-hydrolyzed Binders

For those customers who have the equipment to cool and control the hydrolysis reaction, Silbond® 40 is the most economical route to a useful binder. With further processing they can produce a usable binder, but take the responsibility for doing it right. Many customers want to shift the responsibility of doing the hydrolysis correctly to the experts at Silbond Corporation. We have years of experience doing it right. Silbond® H-4, H-5, H-6C and all other H-binders are pre-hydrolyzed to various degrees (percentages) of hydrolysis. These binders are essentially “ready-to-use”, and we back this claim. Most of the water for

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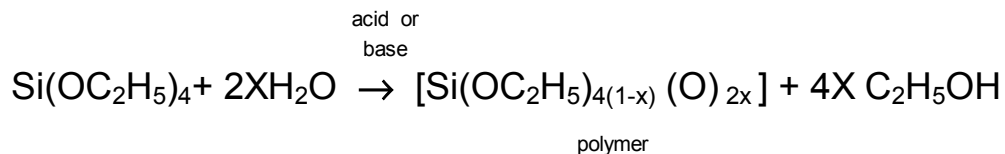
100% hydrolysis is present in these binders; a change in pH will push the reaction to completion.

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Partial Hydrolysis

The stoichiometric equation for partial hydrolysis is as follows:

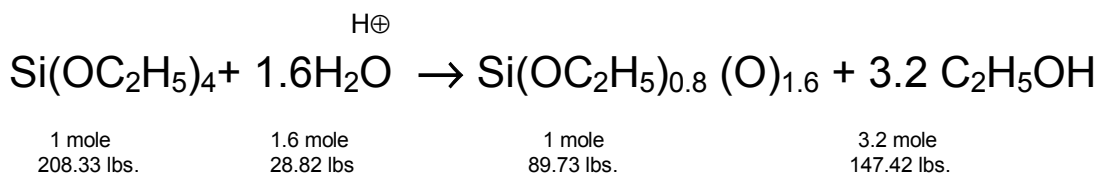


$$\text{Where } X = \frac{\text{degree (\%)} \text{ of hydrolysis}}{100}$$

For example, to produce a binder with 80% degree of hydrolysis,

$$X = \frac{80}{100} = 0.8$$

and the formula becomes:



The hydrolysis graph is shown below which follows the hydrolysis formula. Both forms of ethyl silicate, Silbond Condensed (monomer) and Silbond 40 (polymer), are represented. By choosing the desired degree of hydrolysis and referring to the chart, the proper ratio of water to ethyl silicate can be chosen.

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Making Binders

To make 100 pounds of binder, the following procedure should be followed:

1. Decide the percentage of silica desired in the finished binder. Use the following formulas to determine the amount of Silbond to use:

For Silbond 40:

$$X = \text{Amount of Silbond} = 100 \times \frac{S}{40}$$

Where S = Desired silica percent

For Silbond Condensed :

$$X = \text{Amount of Silbond} = 100 \times \frac{S}{28}$$

2. Choose the desired degree of hydrolysis. From the chart, pick the ratio of water to binder needed. Use this formula to determine the amount of water for the binder.

$$W = \text{Amount of water} = \left(\frac{\text{RATIO}}{100} \right) (X)$$

3. Subtract $W + X$ from 100. This is the amount of *anhydrous* ethanol (or other solvent) needed. If 190 proof ethanol is used, the amount of water (5%) contained in it must be included in W.

Example:

Prepare 100 lbs. of a 90% hydrolyzed binder from Silbond 40 which contains 19% silica.

1. Determine the amount of Silbond 40 required

$$X = 100 \times \frac{19}{40} = 47.5 \text{ lbs.}$$

2. For 90% hydrolysis, from the chart, the ratio is 12.0

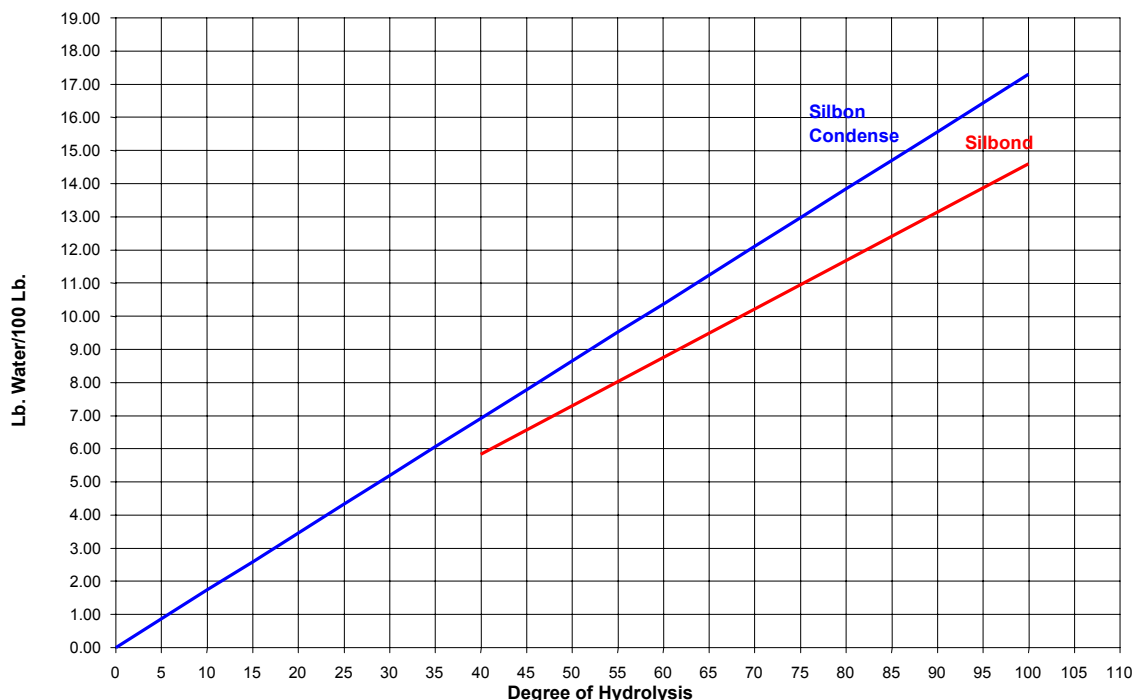
$$W = \frac{12.0}{100} \times 47.5 = 5.7 \text{ lbs.}$$

3. The amount of anhydrous ethanol is $100 - 47.5 - 5.7 = 46.8$ lbs. If 190 proof ethanol was used, 5% of this is water and must be accounted for. Water from ethanol = $0.05 \times 46.8 = 2.34$ lbs. Thus, the amount of free water added is now only $5.7 - 2.34 = 3.36$ lbs.

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The chart below shows the amounts of water in pounds to hydrolyze the two types of TEOS raw materials:

Degree of Hydrolysis with Various Water Additions to Ethyl

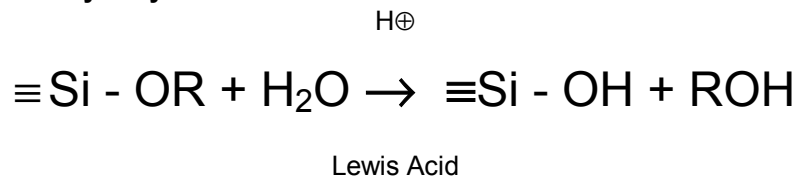


Important:

It's imperative that a small amount of acid or base be added to catalyze the hydrolysis. The following section outlines the reasons for this.

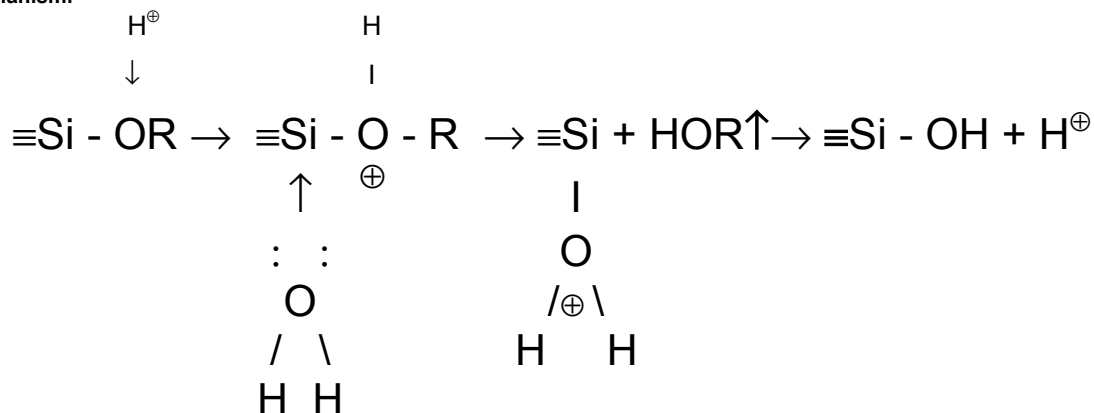
The mechanism of hydrolysis of ethyl (or other alkyl = R) silicate is as follows:

Acid Hydrolysis:



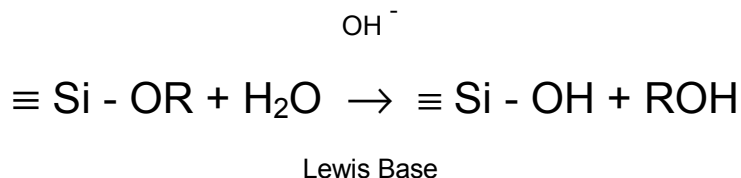
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Mechanism:

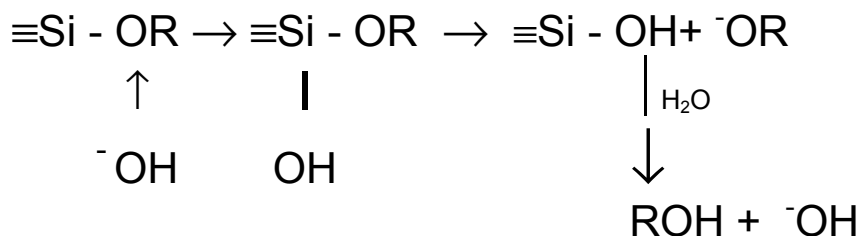


In this reaction, a silicic acid ester is generated, along with an alcohol, which leaves the reaction. A hydrogen (or Lewis acid) ion (H^+) is consumed and regenerated with no net gain or loss, thus perpetuating the reaction.

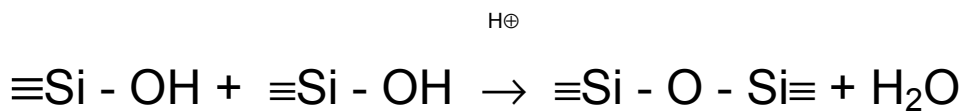
A similar reaction can take place with a base:



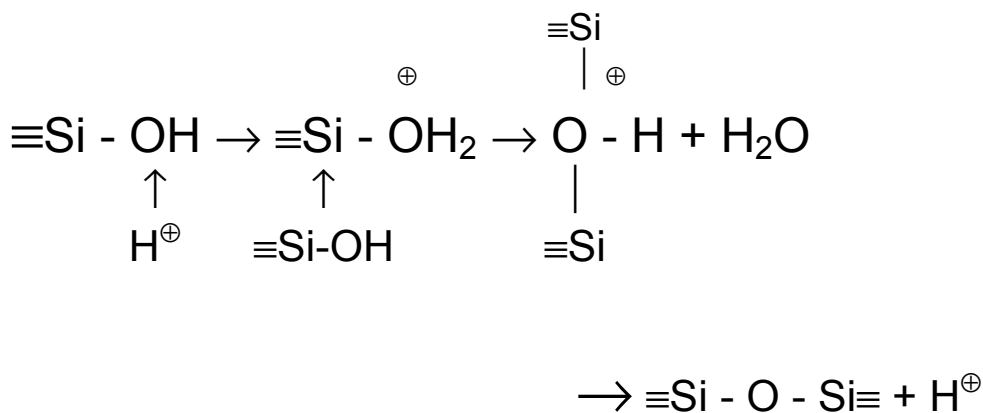
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Mechanism:


For alkyl silicate polymers to form, the following condensation reactions must occur:

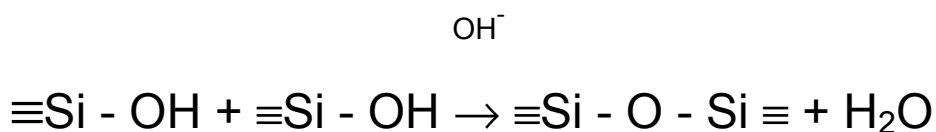
Acid Condensation:


Lewis Acid

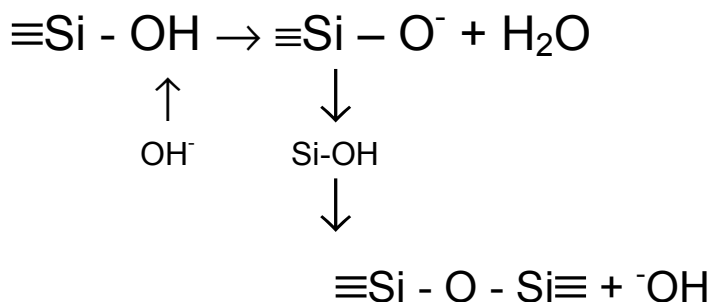
Mechanism:


In this reaction, two silicic acid esters react to form a dimer (or high polymer), generating H₂O, which continues the hydrolysis reaction. Again, there is no net loss or gain of the H⁺ ion.

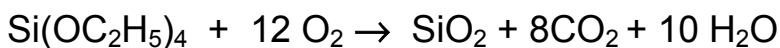
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Basic Condensation:


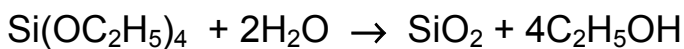
Lewis Base

Mechanism:

Production of Pure Silica

Silbond products are also a source of pure silica either by burning or by precipitation in water.



The burning process as shown above produces a product equivalent to fumed silica, a high surface area, nano-sized, particulate powder.



Complete hydrolysis produces colloidal silica particles up to several hundred nanometers in diameter.

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