



Practical Considerations for

Making Low-VOC Silicon-based **WATER REPELLENTS**

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Among ways to protect concrete, natural stone, and masonry structures from degradation, the use of water repellents has proven to enhance durability significantly, due largely to the fact that water is the most damaging environmental assailant to structures made from these materials.

Of course, in order to provide long-term protection against the damaging effects of water, the protective treatment itself has to have good durability. Silicon-based products cover a variety of chemistries, but the main feature of most silicon-based products is their ability to resist degradation from oxidation, UV exposure, and—in many cases—pH extremes. In the more specific case of silicon-based water repellents, the ability to penetrate below the surface of the treated substrate also enhances durability, because the treatment will not wear away from friction or abrasion.

Another important aspect to long-wear and excellent performance of any treatment is the ability to bond to a substrate. In the case of silicon-based water repellents, an actual chemical bond is created when the silicon-species reacts with and forms a covalent bond to the substrate.

Specific silicon chemistries used for water repellency are chosen for their ability to orient in the substrate and at the substrate-air interface and produce a highly hydrophobic surface.

In short, silicon-based water repellents have the ability to penetrate a substrate, form covalent bonds to the substrate, and impart excellent hydrophobicity to the substrate. In addition, these properties are long-lasting because silicon-based water repellents have proven resistance to degradation from environmental effects.

The properties make silicon-based water repellents a nearly ideal protective treatment, but the chemistry which allows the best silicon-based water repellents to react and cure to the substrate has been shown to be a source of volatile organic compounds (VOCs). Even though the protective benefits of these treatments in many ways outweigh the VOC contribution, regulation on VOCs is continuing to tighten, and so, as technologists, we are faced with the reality that the VOC contribution from any protective treatment must be minimized. This article presents the basics of the chemistry involved, and also examines options for minimizing the VOC contribution of a treatment.

CHEMISTRY OVERVIEW

There is often confusion as to what is meant by the terms silicon, silica, silicate, siliconate, silicone, siloxane, silane/siloxane formulations, and organic chemistries. *Table 1* is a quick reference point to explain the differences, but some additional detail may also be helpful.

Silicon

Silicon is our starting point. While silicon is an element (atomic number 14) and extremely plentiful, it does not exist in nature in a pure form, but is most frequently found in silica, or quartz, which has a chemical formula of SiO_2 . For commercial purposes, silicon is therefore derived from quartz in a process involving heat and reduction with carbon, and the result is silicon metal. Silicon metal is a semi-conductor, and in highly purified form is widely used to make integrated circuits and chips, which has enabled most modern electronics. Like carbon, silicon can accept four bonds; but unlike carbon, the nature and strength of the bonds is quite different.

Silica

Silica commonly occurs as natural quartz, but there are also a number of ways that silica can be manufactured or refined to yield a wide variety of forms, for a wide variety of uses. It can exist as an amorphous silica structure, or as a crystal-line structure. One of the main uses of silica is as

Table 1—Terminology

Silicon (Si) — An element. Second most abundant element on earth.

Silica (SiO_2) — Naturally occurs as sand (quartz). Present in natural stone and concrete.

Silane — A functional monomeric Si-compound with four chemical attachments.

Siliconate — A functional monomeric Si-compound reacted to a metal counter ion, making it water-dispersible.

Siloxane — Linear Si-O-Si polymer or pre-polymer. (i.e., silicone or PDMS).

Formulated Silane/Siloxane — A product formulated from one or more of the above, to meet a variety of applications.

Silicate — A compound containing silicon, oxygen, and one or more metals. Commonly used as densifying treatments for concrete, but not hydrophobic.

Organic — Compounds of C-C (generally derived from petroleum); acrylics, urethanes, epoxies, methacrylates, and paraffin waxes are most common. Usually from visible coatings or films.

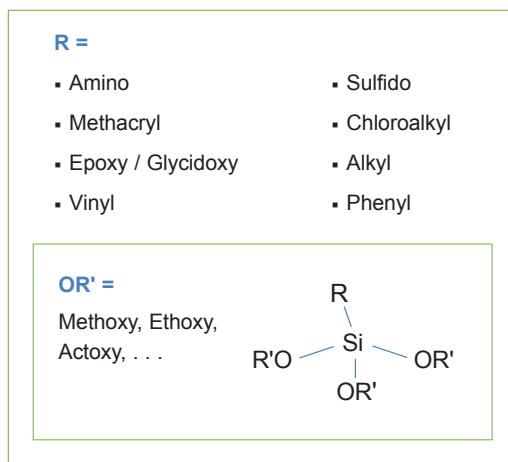


Figure 1—Silanes basic structure and key chemistries.

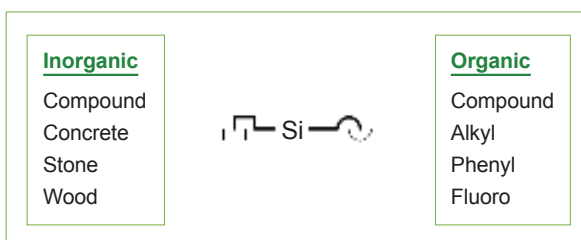


Figure 2—Different attachments to a silicon.

a filler; as such, silica can be either a reinforcing filler, or a simple extending filler, depending on purity, structure, and size of the silica particles.

Silane

Silanes are the monomers of silicon, and have some very interesting and useful characteristics. Because silicon can accept four chemical bonds, and because of the unique nature of the bonds, silicon can have four distinctly different chemical entities attached. Most useful for this discussion is a group of silanes known as alkoxy-silanes—named for the alkyl (organic) and oxygen structure of one or more of the attachments (see *Figure 1*).

One of the most useful properties of silanes is the ability to act as a bridge, or coupler, between organic and inorganic chemical compounds. *Figure 2* illustrates how the different attachments to a silicon can couple one type of chemistry to another:

Alkoxy-silanes represent an important set of aptly named “coupling agents,” and in the case shown in *Figure 2*, the inorganic bonding group would be an alkoxy group, and the organic group would normally be an alkyl (organic carbon-hydrogen) group. Alkoxy-silane chemistry is very important to water repellents, and this will be discussed more thoroughly in upcoming sections.

Silicate

Silicates are next on the list of silicon-based chemistries. Since silicates are not technically wa-

ter repellents, they will not be discussed in detail for the purposes of this article, but silicates are important products used in the hardening and densification of concrete. Basically, a silicate is a silicon compound where at least one attachment to the silicon is oxygen and at least one other is a metal. Silicates are found naturally in many forms, but the most useful to the cement and masonry industry are synthetic silicates such as sodium, potassium, and lithium silicates. These harden concrete by reacting with calcium hydroxide to form calcium-silicate-hydrate (CSH), which is the same chemical “glue” that is formed by reacting Portland cement with water. For further information, look up cement chemistry or calcium-silicate-hydrate (commonly referred to as “CSH”) online or other references.

Siliconate

Siliconates are closely related to silanes, and are similar in some respects to silicates, but have a different structure and use. Siliconates can be thought of as “silane salts,” where a metal replaces one or more of the alkyl groups attached to oxygen. Siliconates are supplied as aqueous, alkaline solutions, and are diluted to lower levels for use. Like silanes, siliconates are used widely for water repellents, and will be discussed more thoroughly.

Silicone

Silicone is a term that typically indicates a polymer structure where a silicon atom is attached to two oxygen atoms and two organic (usually methyl or CH_3) groups. These are commonly referred to siloxane units, and these units are joined together through the oxygen to form siloxane molecules (Figure 3).

Silicone polymers tend to be quite hydrophobic, and are useful in supplementing water-repellent properties. Silicones have a breadth of chemistry much broader than described here—they can be linear, branched, organic substituted, or very low or very high molecular weight. Almost limitless variations are possible.

Formulated Silane/Siloxane

Formulated silane/siloxane water repellents are usually complex mixtures, containing one or more alkoxy silanes, siloxane polymers, and

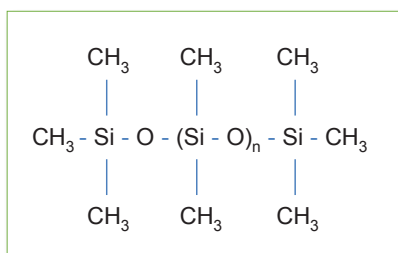


Figure 3—Siloxane molecules.

typically enabling additives to deliver these ingredients in a convenient or more effective form for the intended application. Most of these formulated products are for general-purpose applications and performance.

Organic

Organic refers to the chemistry involving carbon and hydrogen—and is by far the chemistry most used for commercial purposes. Everyday substances like plastics (polypropylene, polyethylene, etc.), adhesives, and coatings (urethanes, epoxies, acrylics) are all derived from organic chemistry. With few exceptions, organic-based treatments for masonry, concrete, and stone are in the form of coatings. These coatings can be inexpensive and temporary, or can be engineered for high durability. The most common coatings in use for masonry and concrete are specialty paints. An advantage of coatings is that they can enhance the appearance of a surface, but a disadvantage is that coatings can be subject to wear, and organic components may need to be protected against degradation from UV and heat.

SILANES AND SILICONES AS WATER REPELLENTS

Silanes

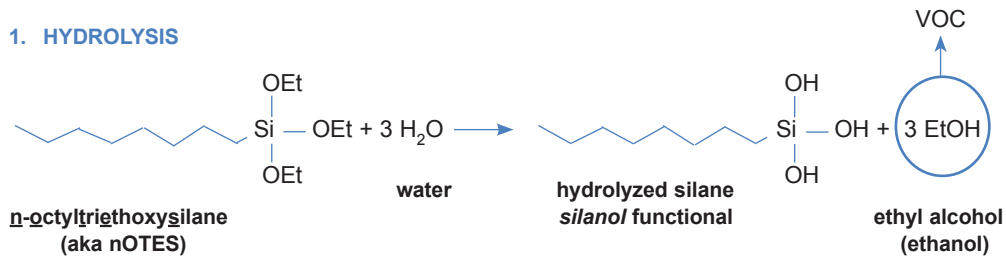
The main reason silanes work so well as water repellents is because they start out as a very low viscosity, low molecular weight fluid. Add to that, silanes have a very low surface tension, and it is easy to see why silanes can penetrate so well into concrete, masonry, and stone surfaces.

Beyond penetration, durable water repellency is achieved through being able to anchor to the substrate, and silanes do this by first reacting with water (from the atmosphere) and then chemically bonding to the substrate. Silica is commonly found in most natural stone, cement, and masonry, and is a prime candidate for this attachment. Silica is composed of silicon and oxygen in a regular arrangement of SiO_2 , but at the surface silica particles have a structure known as a silanol—chemically Si-OH . Figure 4 depicts how a silane first hydrolyzes with water, forming silanols on the silane. These silanols condense (inter-react and release water) with other silanols both in the silane and with the silica in the substrate to form a three-dimensional siloxane resin network at and below the surface.

Some points to consider about the way silanes react and build a network: when silanes have a longer hydrophobic alkyl tail—such as a butyl (4 carbon) or octyl (8 carbon) group—they tend to orient themselves such that this tail is pointed

The chemical processes of hydrolysis and condensation:

1. HYDROLYSIS



Factors Affecting Hydrolysis:

- pH
- Temperature
- Availability of water

2. SILANE CONDENSATION—WITH THE SUBSTRATE ... OR ITSELF

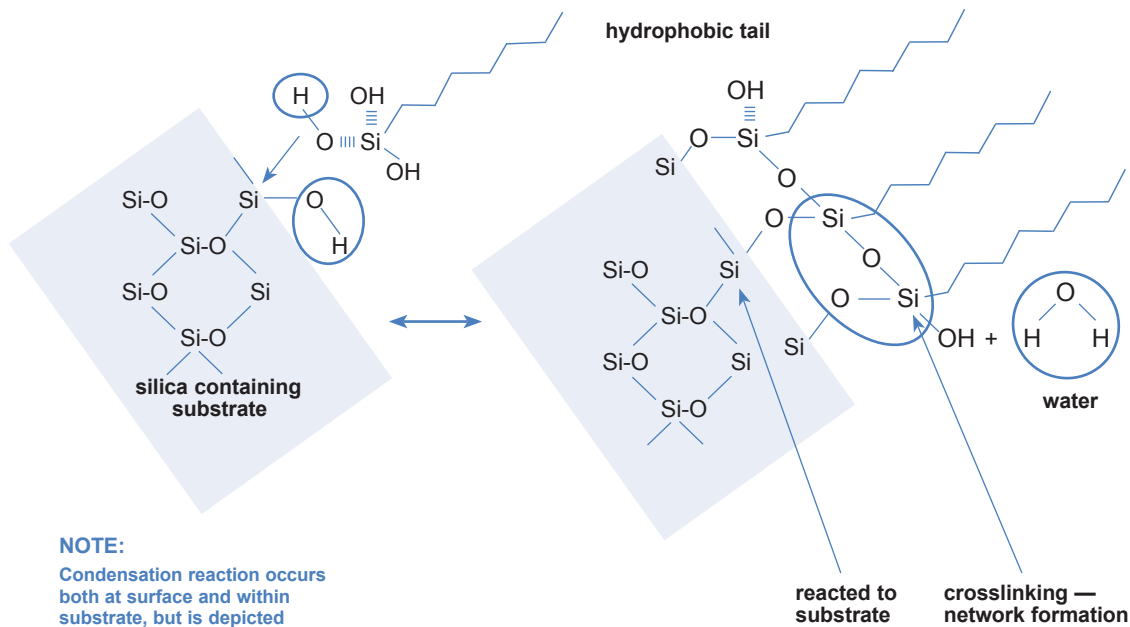


Figure 4—How silanes work.

out towards the air. The effect is to impart a low surface energy to the substrate. Water, of course, has high surface energy (surface tension). The difference between these energies causes water to be more attracted to itself than to the substrate, and so the water has a tendency to stay in a spherical droplet shape. This is why water “beads” on a hydrophobic surface. Water beading is not an absolute measure of the ability to keep out water, but because the water does not “wet-out” on a surface, the tendency for water to find and flow into small cracks in the surface is substantially reduced (Figure 5).

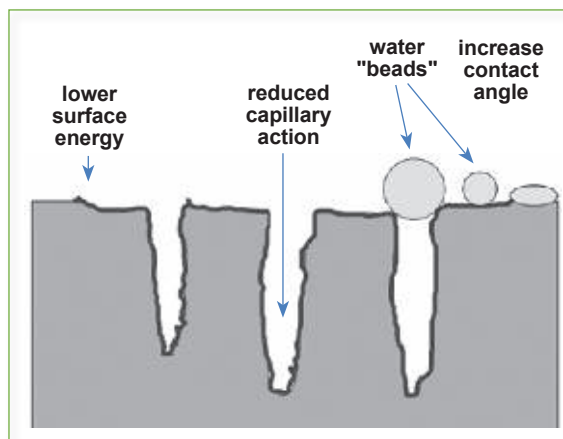


Figure 5—Hydrophobing, repelling water.

Bond Energies	
Silicon-to-oxygen	443 kJ/mol
Carbon-to-carbon	356 kJ/mol

Figure 6—Bond energies.

Silicones

Silicones, also known as siloxanes, have some very interesting properties that are also useful in formulating water repellents. Linear siloxane polymers are extremely flexible, but the chemical bonds are very strong. In fact, both of these properties are exemplified by the fact that while polydimethylsiloxane (PDMS) has a very low glass transition temperature ($T_g = -127^\circ\text{C}$) among polymers, it is also not degraded by the most common wavelengths of ultraviolet light. There are two basic reasons for this. First, the siloxane (silicon-oxygen) bond is comparatively long and flexible. This accounts for the excellent low-temperature properties, and the tendency for siloxanes to exhibit small viscosity change over a wide temperature range. Secondly, the bond energy of the siloxane bond (Figure 6) is relatively high, and requires more energy to break than the energy imparted by normal UV radiation from sunlight.

While these properties explain the durability of siloxane networks and silicones, equally important are the seemingly competing tendencies for siloxanes to be both very hydrophobic *and* also water-vapor permeable. This seems to be a unique property set among silanes and silicones, and is again due to the fact that the siloxane bond is quite long (on an atomic scale), so the spaces between the silicone and attached oxygen are actually larger than the size of individual water molecules. This allows water vapor to pass through the polymer or network. At the same time, the methyl groups (most commonly) attached to the silicon are quite hydrophobic, so liquid water is repelled.

Like silanes, siloxane polymers—especially linear forms—impart a low surface energy to a surface. Because they have such a low surface tension, the polymers tend to flow and coat sur-

faces very well. These properties all make silicone polymers excellent water repellents, *but*, because they are essentially inert, they do not react or anchor to a substrate. Siloxanes can be functionalized with reactive groups, the most common being silanol (Si-OH) groups, and these can add reactivity to siloxanes, but because they are larger molecules than silanes, they do not tend to penetrate very deeply.

Silicone Resins

Silanes *and* siloxanes can be formulated together to produce general purpose water repellents that take advantage of the properties of both types of structures. An additional component which can also be considered is silicone resins. These resins are more three dimensional in structure, as opposed to the monomeric structure of silanes or the linear structure of most siloxanes. Silicone resins are either formed from silanes that have been pre-reacted, or siloxanes which have had functional groups added and reacted to make three-dimensional molecules. Because silicone resins have a bulkier structure, they do not generally penetrate like silanes, and they do not tend to spread as easily as linear siloxanes. However, they can be very hydrophobic, and they can also help block pores, micro-cracks, and spaces between particles in treated substrates. By combining the effects of these three silicon chemistries, you can get very good and even complementary properties. In basic terms, you can get depth of penetration and high reactivity from silanes; spreading and enhanced water beading from siloxanes; and controlled penetration and pore blocking from resins.

Siliconates

Siliconates are one of the oldest forms of silicon-based water repellents. They can impart good water resistance to substrates such as brick, but they are not used as much on concrete and stone. The advantages to siliconates are that they are relatively low-cost, and are considered as near-commodities. In addition, siliconates tend to be low or even zero VOC, depending on the level of purity. Siliconates are made from silanes—either chlorosilanes (the most basic silane building block) or alkoxy silanes—and the most common form is usually a sodium (Na) or potassium (K) methyl siliconate. This means that one or more of the alkoxy groups has been replaced with a metallic species, and that the alkyl group is a methyl group. The structure and reaction of potassium methyl siliconates is illustrated in Figure 7.

Unfortunately, the disadvantages of siliconates limit their use as long-term protection on most substrates. Siliconate treatments depend more on

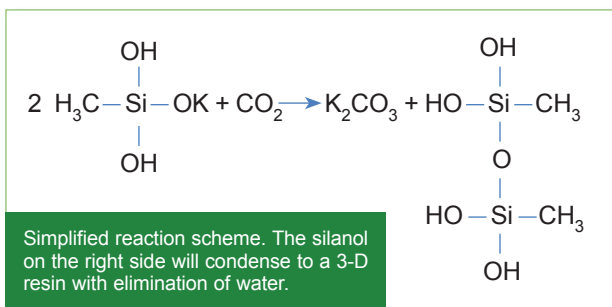


Figure 7—Siliconate reaction.

network formation than do silanes because the alkyl group is normally a methyl (single carbon) and this does not lower the surface energy as much as higher alkyl groups used on alkoxysilanes. Siliconates can only be used in very low concentrations on a substrate. This is because of the formation of carbonate salts as shown. Above levels of ~4%, the presence of these salts can become visible on the substrate. Once they are evident, the salts can be difficult to remove. These salts can also diminish any hydrophobic properties, allowing the substrates to be wetted more easily, which can overshadow the water-resistant properties created by the network formation. So this is a case where more is not necessarily better. Lastly, siliconates are applied as low actives, aqueous, high pH solutions—typically at pH>12. The pH makes them caustic enough to require considerable care on how they are stored and used, and being water-borne, their penetration can be limited.

UNDERSTANDING VOLATILE ORGANIC COMPOUNDS

Volatile organic compounds, by the most general definition, are *any [volatile] compound of carbon which participates in atmospheric photo-chemical reactions*. As used in most coatings and treatments, a VOC is typically an ingredient in a formulation that will evaporate (volatilize) under normal use. Probably the simplest example of a VOC would be a solvent or drying aid. Common examples would be alcohols (like IPA), mineral spirits, kerosene, toluene, and xylene, etc.

If formulating low-VOC silicone water repellents was as easy as removing carrier solvents, this would be a short subject, as water-based emulsion technology allows us to formulate practically any type of silicone into a water-deliverable form. However, the “gold” standard for protecting concrete especially is using alkoxysilanes—and alkoxysilanes generate VOCs as they cure. The next approach might be to make a water-based product where the reactive materials are a small percentage of the total formulation. In the case of emulsions, that would mean adding more water. Unfortunately, the way VOC regulations are written, a product that is 5% silane and 95% water has almost the same VOC content as a product that is 95% silane and 5% water because the VOC content is based on the active component(s). See *Table 2*.

There are some exceptions to the rules. For instance, a low-solids VOC coating calculation can be used for some coatings, but unfortunately these are not universally applied. So the definition of a qualifying low-solids formula in Southern California may not be the same as the definition applied by the EPA. So to truly conform to all of the current

Table 2—VOC content, using the methods in EPA Reference Method 24 for determination of volatile matter content and the formula per EPA 40 CFR part 59 for calculating VOC in architectural coatings is typically expressed as follows:

Grams of VOC per liter of coating, less water and less exempt compounds, is the weight of VOC per combined volume of VOC and coating solids:

$$\text{VOC (grams/liter)} = \frac{Ws - Ww - Wes}{Vm - Vw - Ves}$$

Where:

Ws = weight of volatile compounds in grams
 Ww = weight of water in grams
 Wes = weight of exempt compounds in grams*
 Vm = volume of material in liters
 Vw = volume of water in liters
 Ves = volume of exempt compounds in liters

**This calculation excludes or factors out water and other exempt compounds in calculating VOC content.*

regulations, and to plan for near-certain tightening of regulations around VOC, we need to continue to find ways to lower the overall VOC contribution from reactive treatments.

A note about VOC terminology: the term “VOC” is quite often used in referring to VOC content, and so when the “VOC” of a product is mentioned here, this is the intended meaning.

WATER REPELLENT TYPES AND TESTING

Adequately describing all of the various testing methods used for water repellents could fill a fair sized book, but there are some standard methods that are thought of as benchmarks, and some technologies tend to work better for some applications than they do for others.

Reinforced Concrete

Silanes are recognized as one of the best treatments for reinforced concrete. In 1981, the National Cooperative Highway Research Program (NCHRP) conducted a study on usage of “Concrete Sealers for Protection of Bridge Structures” and developed testing protocols for determining a treatments ability to prevent waterborne salts from attacking the steel-reinforcing bar (re-bar) imbedded in reinforced concrete. These test methods are still widely used today to screen or validate performance of treatments in preventing re-bar corrosion. Now, as then, alkoxysilanes are among the best performing treatments—typically excluding >95% chloride as compared to untreated controls. Some formulated products can do reasonably well in these tests, and it is possible to formulate

water-based silane treatments that perform well. However, the performance tends to be dependent on a minimum level (typically 40%) of alkoxysilane, and a certain coverage rate, regardless of the carrier. For this reason, many highway departments and Departments of Transportation stipulate that a treatment used for this purpose must contain a certain level of alkoxysilane, and they require suppliers to certify to this level—and they may also perform an audit to confirm.

Additionally, because of the durability aspects achieved due to penetration, some specifications also stipulate that a certain depth-of-penetration be demonstrated. This can cause issues for water-based treatments because water as a carrier does not typically allow the same level of penetration as a pure silane or a solvent-diluted silane. Use of co-solvents can help this, but these typically increase the level of VOC. Use of surfactants can help lower the surface tension of the water phase, but surfactants usually are counterproductive to the effects of a water repellent.

There are several other methods used for determining performance specifically on reinforced concrete, most common are AASHTO (American Association of State Highway and Transportation Officials, www.transportation.org) and Alberta (Ministry of Transportation, www.transportation.alberta.ca) test methods, and these can be found by consulting any number of online references, especially those for testing service providers.

Vertical (Non-Reinforced Concrete and Masonry)

For vertical structures, there are other methods typically used. One of the more common methods

cited is ASTM E514, which measures the resistance of wall structures to wind-driven rain. Other protection sought for concrete block, stone, or masonry walls is the ability to resist damage from freeze/thaw cycling, and damage and aesthetic problems caused by efflorescence. Efflorescence is the appearance of salts on the surface of substrates, caused by water getting into the substrates, and then transporting the salts to the surface, as the water evaporates. For these applications, formulated products such as silane/siloxane blends can provide excellent performance for the price. While general purpose treatments can perform very well on many surfaces, for more difficult applications such as split-face concrete block, or a rough natural stone, a treatment that has more pore-blocking ability might be more useful.

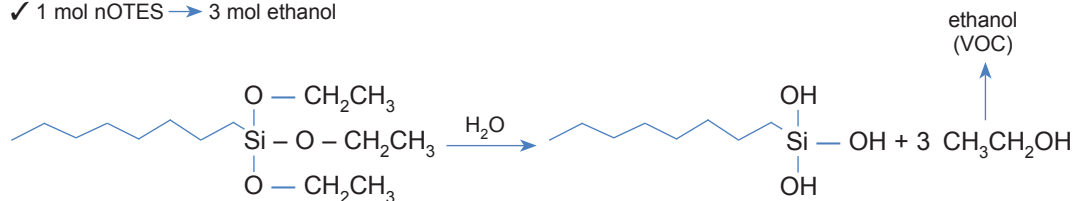
General Requirements

For waterproofing, there are several other test methods and practices used, but the common theme for penetrating water-repellent treatments on all substrates and all methods is that the treatment must be able to exclude water in a measurable way from penetrating the substrate, and it must not be able to be easily removed by normal weathering or washing. These are the basics of performance—the rest is really just specifics intended to standardize the testing.

Requirements for the treatments can vary depending on where they are going to be used, by whom, and for what purpose. Silane treatments have traditionally been sprayed on with a low pressure (garden) sprayer, and they are expected to cure enough to withstand weather and traffic within 24 hours. Coverage rates are around 100–

Ex: n-octyltriethoxysilane "nOTES" (CAS RN 3069-40-7)

✓ 1 mol nOTES → 3 mol ethanol



✓ MW nOTES = 234 g/mol

✓ MW EtOH = 46 g/mol so 3 mol = 132 g

✓ $(132 \text{ g} / 234 \text{ g}) * 100 = 60\%$ (by weight)

✓ Thus, the theoretical VOC of nOTES is 60%

✓ Using a density of about 0.873, the theoretical VOC works out to about 524 g/L.

Figure 8—Chemistry of silanes.

200 square feet per gallon for diluted silanes, and can be as much as 200–300 square feet per gallon for pure silanes.

For general purpose use, solventborne water repellents are beginning to vanish from the North American market. As VOC regulations go, the Federal VOC limit is still around 600 g/L for many architectural coatings, but the more common limits are trending down. Solvent-based water repellent formulations can still comply with many of these regulations, but time is growing shorter. Water-based treatments are also much improved, so the extra precautions needed, and expense of carrying more than one line, is starting to have an effect. Of course, the main reason for more water-based treatments is that the application aspects are considered more user-friendly, and there is more on-site formulation flexibility. Water is usually available at the point-of-use, where a carrier solvent is not likely to be. A growing trend in the “green” movement, over and above the reduction of VOCs and emissions, is the idea of shipping less bulk, and over shorter distances. So, the more concentrated the material, the better, and the more dilute it can be used . . . also better.

REGULATORY CONSIDERATIONS

There is little doubt among silicone technologists that the main performer in any silicone water repellent is still the alkoxy silane. Granted, the ability to formulate with siloxane polymers and resins gives some flexibility, but the fact remains that the workhorse is the silane. Especially in reinforced concrete applications, the penetration and reactivity of a silane is not really matched by any other chemistry. Here is the problem though: when you look more specifically at the chemistry of silanes, there does not seem to be a way out of VOC generation. We learn why in *Figure 8*.

In this example, about 60% of the silane is going to be converted to ethanol after the silane reacts with atmospheric water. So, theoretically, by weight, you would get about 600 g/L of VOC. In practice, and through experimentation and analysis, we know that this does not really occur to quite this extent.

One main reason is that the alkoxy groups do not all hydrolyze (react) with water. The first group hydrolyzes fairly easily, but the second and third alkoxy groups become increasingly harder for the water to find. The second factor is that as the silane starts to build a resinous structure, the solubility of the molecule with water gets much lower and that further affects the ability of the silane to react and form the alcohol. Because this reaction is faster in acidic or basic media, the relatively

Composition

n-octyltriethoxysilane (nOTES)	$\text{CH}_3(\text{CH}_2)_7\text{Si}(\text{OEt})_3$
n-octyltrimethoxysilane (nOTMS)	$\text{CH}_3(\text{CH}_2)_7\text{Si}(\text{OMe})_3$
isobutyltrimethoxysilane (iBTMS)	$\text{CH}_3\text{CH}(\text{CH}_3)\text{Si}(\text{OMe})_3$
isobutyltriethoxysilane (iBTES)	$\text{CH}_3\text{CH}(\text{CH}_3)\text{Si}(\text{OEt})_3$

Product	nOTMS	nOTES	iBTMS	iBTES
Color	Clear	Clear	Clear	Clear
VOC* g/L	243	329	343	423

*VOC—expressed in g/L refers to grams per liter (weight/volume) and is a common means of expressing the volatile organic compound content.

Figure 9—Composition of silanes.

alkaline environment of concrete and related substrates accelerates this process.

Fortunately, this characteristic of silanes is recognized by the industry, ASTM, and regulating bodies. For this reason, a specific volatile content method (ASTM D5095) which catalyzes the silane reaction is used to determine the volatile content of a silane when it is used as a penetrating water repellent. With this method, the VOC content of this same silane, as determined by measurement, is considerably lower, at 329 g/L. Other silanes can be determined similarly (*Figure 9*).

To get away from VOCs, an obvious question might be: why not start with the hydrolyzed version of the silane, remove the alcohol, and just have the silanols which are formed? The answer is that this is a fine way to make silicone resins—in other words, the chemistry does not stand still. Once the alkoxy groups hydrolyze, the formed silanols will start to self-condense, forming higher molecular weight species, usually in a three-dimensional manner. If the alkoxy groups are gone, the attributes important in a silane—low molecular weight, low surface tension, and reactivity—are immediately lost, and long before the material ever gets applied.

If the engine that drives performance is an alkoxy silane, and the silane is the main source of VOC, what are the permissible options? First a quick review of some of the regulations.

As of July 2006, the only rules that really excluded, by regulation, the use of pure silanes were those of the South Coast Air Quality Management District (SCAQMD) and at 100 g/L or less for these products, these are still the most stringent regulations in the U.S. (See Rule 1113.)

Recently, the California Air Resources Board (CARB) enacted a new set of suggested control measures (SCMs) that regulate the VOC of

"Concrete/Masonry Sealers" to 100 g/L or less. (SCMs are model rules that serve as the minimum requirements with which local air districts in California are expected to comply.) Currently, there is a separate category in these SCMs (Reactive Penetrating Sealer) that allows silanes with a VOC up to 350 g/L to be used for protecting concrete in the near-term.

The Ozone Transport Commission, an organization of 13 central and northeastern states, currently limits "Waterproofing Sealers" to a level of 250 g/L per the MODEL RULE 2002 Architectural, Industrial and Maintenance Coatings (AIM).

The U.S. EPA listing for definition and VOC limits (Title 40(CFR), part 59) currently shows the VOC limit for "Waterproofing Sealers and Treatments" to be at 600 g/L.

Federal regulations are superseded by local regulations where the local (state, county, air district, etc.) are more stringent.

Clearly, this sampling shows that making, formulating, or using water repellents in different areas requires knowledge of the most restrictive regulation for that area. It also necessitates choosing a product that conforms, based not only on performance, but also on regulation.

FORMULATION CONSIDERATIONS

If allowed, pure alkoxysilanes will give excellent performance for protecting against chloride ion attack on re-bar in concrete. Diluting alkoxysilanes in solvent (like isopropyl alcohol) will nearly always increase the VOC level, but can still be done within some of the higher VOC limits. This is usually done to either help control costs, or to speed up or slow down drying time after application. As a rule, larger alkyl groups on a silane will have lower VOC, and a higher alkoxy group will have lower VOC. For this reason, an ethoxy functional silane (such as octyltriethoxysilane) will have higher VOC than the corresponding methoxysilane (octyltrimethoxysilane); but an octyl silane will have a lower VOC than the corresponding butyl silane (octyltriethoxysilane versus butyltriethoxysilane). If the most stringent VOC limit for the area is 600 g/L, then most common alkoxysilanes could be used. However, if the limit is 400 g/L, isobutyltriethoxysilane (iBTES, 429 g/L) will be out of the running. At a limit of 350 g/L, n-octyltriethoxysilane (nOTES, 329 g/L) and isobutyltrimethoxysilane (iBTMS, 343 g/L) are getting close to the limit. At a limit of 250 g/L, the only common alkoxysilane that can still be used is n-octyltrimethoxysilane (nOTMS, 243 g/L).

To get much lower than 250 g/L, use of a pure silane or even a silane emulsion will not get there.

Formulated products can lower the overall VOC by introducing less volatile components, but the alkoxysilane still drives much of the performance. There are some premium formulated products on the market that can approach the performance on concrete that silanes get, but there are usually some tradeoffs in certain tests, or in penetration or durability. As the VOC goes even lower—getting to the level of less than 100 g/L—it gets even harder.

Fortunately, for applications other than reinforced concrete, some of the lower-VOC formulated products can do very well in standardized testing against water intrusion. As described earlier, silicone chemistry technologists have gotten very good at skillfully blending silanes, siloxanes resins, and other additives to achieve much better results than previously thought possible. The "trick" is to find the right balance of silane penetration and reactivity, siloxane mobility, and resin bulkiness. Because most formulated products work on this principle, it is possible to come up with less than 100 g/L formulations that work very well on multiple surfaces, and the field is only going to get better.

CONCLUSION

Silicon-based chemistry has many branches, and many different product forms. For water repellents, the staple of this chemistry has been silanes, and more specifically, alkoxysilanes. There is a good reason for this, as silanes have all of the attributes needed for effective concrete, masonry, and stone protection: penetration, breathability, UV, pH, and oxidative stability, and the ability to react to and within the substrates. Silicones, typically linear polymers, have many of these same attributes, and can even be functionalized to be reactive. Silicone resins can also contribute to the performance of water repellents. But the overriding element in all of this chemistry is that the reactivity needed to anchor this chemistry is a source of VOCs.

To keep viable water repellent products on the market, and to preserve the important protective aspects of these products, it is important to understand where the VOCs come from, what VOC content is allowable, and how we can further reduce the VOC content. As detailed in the chemistry overview, there is not an obvious way to completely eliminate the VOCs from alkoxysilanes, and, hence, durable silicon-based water repellents. Research is always ongoing to find new molecules or new ways to achieve the protection that silane-based chemistry can afford, but to this author's knowledge, the breakthrough has not yet occurred.

There is a brewing conflict in the industry because many highway departments and Departments of Transportation recognize that the use of silane-

based treatments can significantly prolong the life of reinforced concrete structures, which take considerable amounts of concrete, energy, and labor to rebuild or repair. It is probably inevitable that environmental regulation will eventually severely limit or eliminate the use of silanes. Until then, selecting the right silane or silane-based formulation for each application, or formulating the best protective silicon-based treatment possible that complies with regulations is still going to be the way to offer some of the best protection possible.

After all, *protecting* is usually more economical, environmentally responsible, and less energy intensive than *rebuilding*. **CT**

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This paper was presented at the 2009 ACSeries, "Coatings for Concrete," sponsored by NPCA/FSCT, February 2, 2009, in Las Vegas, NV.



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