# The Fascinating World of Silicones

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*Silicones were commercialized in the 1940s in the United States and ever since their introduction, they have expanded remarkably not only in terms of economic growth but also by an amazingly diverse assortment of product types and applications. Silicones represent a class of compounds that are based on silicon and they exist in a variety of forms including oils, fluids, high viscosity polymers, gums, elastomers, resins, and silanes. Silicones' involvement in coatings began with the early stages of silicone product development and today they are used extensively in coatings mainly as either modifiers or additives. Typical modified coatings contain around 30% of the binder as silicone and these coatings exhibit improved weatherability, increased moisture vapor transport, and improved heat stability. Silicone additives are used in small amounts in coatings, usually less than one percent and even lower, to achieve various enhanced properties such as improved flow and leveling, slip and antimar, improved abrasion resistance, improved adhesion, foam control, and water repellency. Although silicones are useful for eliminating or diminishing surface defects, they are also capable of producing surface defects. An understanding of phenomena surrounding surface defects can aid the coatings formulator in avoiding surface defects caused by silicones.*

*Part I of this article, which was published in the April issue of* CoatingsTech, *presented a brief history of silicone development and detailed their preparation and properties. Part II focuses on how silicones are used in coatings.*

## SILICONES IN COATINGS

Silicones find many uses in the developed world due to their unusual surface properties, their resistance to the effects of weather, and their ability to function in both high temperature and low temperature environments. It is also because of these properties that silicones are used in coatings. The use of silicones in coatings falls into the following four categories:

1. Silicone additives, in which a small amount of silicone is used (< 10%)
2. Silicone polymers, where 10–50% silicone is used
3. 100% silicone coatings, where 100% of the coating or binder is silicone
4. Silicone water repellents

Silicones are added to coatings to primarily achieve one or more of the following property enhancements: improved adhesion, improved wetting, foam control, to obtain slip, improved

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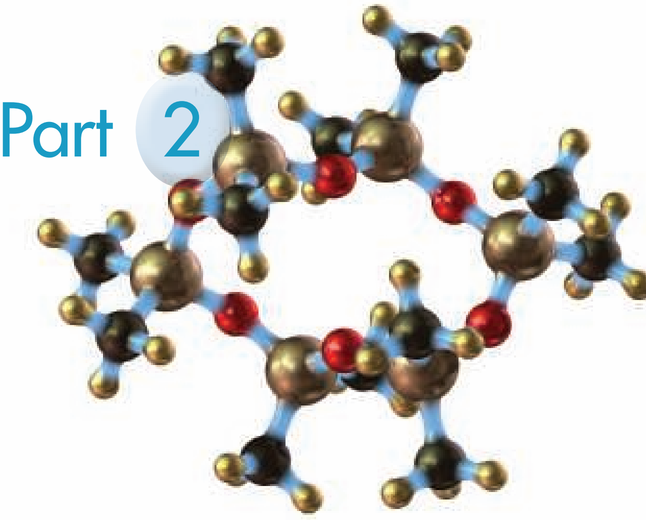
Presented as the Plenary Lecture at the 39th Waterborne Symposium, sponsored by the School of Polymers and High Performance Materials, The University of Southern Mississippi, February 13–17, 2012, in New Orleans, LA.

# and Their Impact on Coatings: Part 2



flow and leveling, improved mar and abrasion resistance, to obtain waterproofing, increased $H_2O$ vapor permeability, improved weather resistance, and improved high temperature stability.

The types of silicones that fall into the additives category are silanes, silicone surfactants, silicone foam control compositions, and silicone polymers (resins, fluids, and elastomers). When silicone polymers are used in small amounts (< 10%), they are classified as additives; above this amount, they are simply classified as polymers since their level may approach 50% of the organic binder in the coating. Silicone polymers, when incorporated into coatings in such high levels as these (10–50% of binder solids; more typically > 30%), are usually used to obtain improved high temperature properties, improved weatherability, or improved water vapor permeability. On the other hand, small amounts of certain silicones are very effective at modifying surface properties of coatings including water-based coatings. Such additives, when used at levels of 10% or less (in many cases on the order of one percent or less), can have a significant impact on properties such as adhesion, wetting, flow and leveling, slip, mar and abrasion resistance, and foam control—these are all related to surface properties of the silicone.

One hundred percent silicone (binder) silicone elastomeric coatings are used as architectural coatings, textile coatings, and paper coatings; the silicone in these applications provides for good weatherability, good high temperature properties, and enhanced surface properties, respectively.[61,63] Silicones used in 100% binder applications can be in the form of neat polymers, polymer solutions in solvent, or as aqueous emulsions, with the latter being used as is or as a component in water-based coatings. Silicone resins can also be used as 100% silicone (binder) coatings. These are usually solvent-based coatings and they are used in high temperature applications such as cooking (baking) pans, outdoor cooking appliances, industrial exhaust stacks, and high temperature chemical process equipment. Although some water-based silicone resins are currently available, there is still a need for satisfactory water-based resin coating systems for high temperature applications that will meet existing and future volatile organic compound (VOC) requirements.

Finally, silicone water repellents are used to treat a variety of substrates to obtain waterproofing and/or hydrophobic surfaces. These water repellents can be used either alone or admixed into organic coatings, either solvent-based or water-based, depending upon the nature of the silicone. Each of these four categories is discussed individually.

## Silicone Additives

Silicone additives are distinguished from other silicones used in coatings by their level of use. Silicones are classified as additives when their level falls under 10% of the coating or binder weight. This is a rough classification employed to distinguish use of silicone as an additive or as a binder modifier, and in fact most silicone additives are used at levels of one percent of the coating or even less.

During the early development of commercial silicones in the 1940s, silicones were found to be useful as additives in paints and inks. Addition of small amounts of polydimethylsiloxane (PDMS) to solvent-based coatings lowered surface tension of the coating and prevented some surface defects such as cratering, crawling, floating, and orange peel.[73] In addition, the silicone provided cured films with improved slip and mar resistance. As more silicone products were developed, they were tested in paints and inks and several product types were found to give unique and beneficial properties to coatings. Today, silicone additives are firmly established as their ability to provide benefits to coatings is well understood; these benefits are listed in *Table* 7.[74] Several of these properties may not be as well known and are briefly discussed.

**Antiblocking:** Blocking is when coating surfaces adhere to themselves, usually after two freshly coated articles are placed in contact with each other. The most

**Table 7**—Benefits of Silicone Additives in Coatings

| | |
|---|---|
| Adhesion | Pigment Dispersion |
| Antiblocking | Release |
| Flow | Slip |
| Foam Control | Texturizing |
| Gloss | Water Resistance |
| Leveling | Wetting |
| Mar Resistance | Abrasion Resistance |

common example of blocking occurs with painted window frames and doors. Even after a painted window sill or door appears dry, closing it then reopening it later can cause the painted surfaces to stick to themselves and peel paint from one or both surfaces. Polymer (binder) molecules diffuse from one coating to another and create a strong bond between the two layers of coatings. Silicones are useful for providing antiblocking to coatings. However, at the same time, the silicone can interfere with paint recoatability.

**Wetting, Flow, and Leveling:** When a liquid coating is applied, the liquid should flow over a substrate and wet it evenly. Thus wetting is the process whereby one fluid is displaced from the substrate by another liquid—for example, air is displaced by liquid coating. Generally, surface tension of the liquid should be less than surface tension of the substrate; otherwise, wetting will not occur.[75]

After wetting the substrate, the coating should "flow out" or, in other words, should flow to create a uniform (hence level) surface, thus eliminating surface irregularities, such as brush marks. However, many things can go wrong when a coating is applied and dried and in many of these cases it is due to surface tension gradients that arise from temperature and concentration gradients; these surface tension gradients are likely to cause surface imperfections upon film drying.[76] By lowering the overall surface tension of liquid coatings, silicones can aid in wetting, flow, and leveling.[77]

**Slip, Mar, and Abrasion:** Marring is a disturbance of a surface that changes its appearance while abrasion is the wearing away of the surface. Slip corresponds to lubrication of a dry coating surface.[78] Marring is usually a near-surface phenomenon that occurs at less than 0.5 μm depth while abrasion is the result of deeper penetration.[79] The physics of marring and abrasion are complex and various models have been proposed to describe events when a hard object is moved over a viscoelastic material such as coating binder.[80,81] Certain silicones have been found to provide excellent slip, mar resistance, and abrasion resistance in a number of coatings. The reason for this is believed to be due to silicones' ability to accumulate at the coating surface and provide for a low coefficient of friction.[82]

Silicone additives are classified as coatings additives when their use level is 10% or less. However, in most cases, their use is far less than this as it is normally less than one percent. There are numerous cases whereby silicone additives are used at levels as low as 0.1% and even some applications whereby their use is 0.01% or 100 ppm. The types of silicones used as additives fall into the following categories:

1. Silicone polymers (resins, fluids, elastomers)
2. Silicone foam control
3. Silicone surfactants
4. Silanes

### *Silicone Polymer Additives*

Silicone polymers are used as additives in coatings to provide slip and to improve mar and abrasion resistance. They also can impart antiblocking, release, water resistance, and texturizing. These polymers consist mainly of aqueous dispersions or emulsions of silicone resins, linear siloxane polymers, or elastomers. In the case of linear siloxanes, both medium viscosity polymers (100–1,000 cP) and higher viscosity polymers (60,000–>$10^6$ cP) are typically used. These polymers almost always afford coatings with slip, antiblocking, and improved mar and abrasion resistance due to the low surface energy of the silicone additive. During the 1940s, when silicone additives were first used in coatings, neat PDMS was used, as the coatings were solvent-based. The preferred viscosity of the silicone fluid (PDMS) is around 350 centistokes for solvent-based coatings.[83] Today, neat PDMS has mainly been supplanted by aqueous emulsions of PDMS and/or silicone surfactants. Most likely, neat PDMS would never be added to a waterborne coating as it would be highly prone to cause surface defects such as craters or fish eyes.

The silicone elastomer additives are aqueous dispersions of silicone elastomer, or neat, solid particles of silicone elastomer. These silicone aqueous dispersions are used in coatings and inks to obtain hydrophobicity and waterproofing. They can also provide slip to coatings which should positively impact mar resistance and antiblocking. Particle size of silicone elastomer dispersions is usually sub-micron. The solid silicone elastomer particles are typically 2–5 μm in size and they are used for texturizing coatings as their large particle size leads to coatings having textured surfaces.[84]

Recoatability of paints and coatings can be an issue when using these silicone polymers, especially if too much silicone is present. The coatings formulator is advised to seek a minimum effective level of silicone via designed experiment when evaluating these additives. If recoatability becomes a problem when using silicones, in some cases silane coupling agents when used as a primer may be helpful.

### *Silicone Antifoam Additives*

Silicone foam control compounds provide defoaming properties to coatings and can also provide deaeration. Silicone antifoam compositions are sometimes composed of hydrophobic silica dispersed in silicone oil and supplied as an oil-based compound or as an aqueous emulsion.[85] Although very effective at controlling foam in numerous applications including coatings, silicone antifoam compounds and some silicone antifoam emulsions are also capable of creating surface defects in coatings. This is because the silicone antifoam is mainly incompatible with the coating composition and due to its low surface tension, it is capable of producing surface imperfections caused by surface tension driven flows.[86] Recent advances in silicone foam control for coatings involve the use of certain silicone surfactants which are less prone to causing surface defects.[87]

### *Silicone Surfactant Additives*

Silicone surfactants or silicone polyethers (SPEs) are used in coatings to lower surface tension in liquid coating films; this can lead to reduced surface defects, improved leveling, and improved substrate wetting.[76,78,88] Some silicone surfactants also provide slip to coatings and give improved mar resistance, abrasion resistance, antiblocking properties, and at times improved gloss.[89] In these cases, it is believed that orientation of the SPE at the film surface is responsible for these benefits. Levels of silicone polyether used in coatings vary by the type of coating and the desired benefit, but typical levels are usually lower than 1.0% and even levels as low as 0.10% can impart significant positive effects to the coating. Silicone polyethers are less likely to cause surface defects than other types of silicones and some of them are even useful as defoamers in coatings.[86] Silicone polyethers also provide for improved recoatability as compared to PDMS when used in coatings.[90] In addition, silicone surfactants can help to overcome some surface defects by lowering surface tension of the coating, thus minimizing surface tension differentials.[91]

Surface active silicones or silicone surfactants are derived from siloxanes modified with polyethers. The two most common structures of SPE or silicone surfactant are shown below.

SPEs are used extensively in polyurethane foam manufacture as foam stabilizers and, after years of use in that regard, they were found to provide excellent mar resistance in a number of organic coatings systems.[92,93] SPEs are prepared by reacting functionalized polydimethylsiloxanes with polyalkylene oxide oligomers derived from either polyethylene oxide or polypropylene oxide or both (copolymeric).[94] The early SPEs for coatings contained SiOC linkages and thus they were prone to hydrolytic instability. Improvements in hydrolytic stability came about by preparing SPEs from the reaction of SiH functional siloxanes with allyl functional polyalkylene oxides to provide a non-hydrolyzable SPE as shown in the structures below.[89] The allyl polyether oligomers can be entirely ethylene oxide (OEt), entirely propylene oxide (OPr), or copolymers of both. End groups of the polyethers are normally either OH or capped with methoxy or acetate.[89]

A large variety of silicone polyether structures is possible based on the ratio of dimethyl siloxane and polyether groups, their molecular weights, as well as the type of polyether and structural type of the siloxane, the latter of which includes chain-end substitution, pendant chain substitution, or various branching structures.[95] SPEs are used in both solvent-based and waterborne coatings.[90]

Another silicone polyether that is in a class by itself is the trisiloxane polyether, nicknamed "super wetter." The trisiloxane is highly potent as it is capable of lowering surface tension in water-based coatings by a significant degree with relatively low levels of the surfactant.[96] A typical trisiloxane super wetter is shown:

$$\begin{array}{l} \qquad\quad Me \\ \qquad\quad | \\ Me_3Si\text{-}O\text{-}Si\text{-}O\text{-}SiMe_3 \\ \qquad\quad | \\ \qquad\quad CH_2CH_2CH_2[OEt]_n\text{-}OH \end{array}$$

n = 7-12

The trisiloxanes are used as adjuvants in some herbicide compositions to obtain improved wetting of the herbicide to waxy plant leaves and they are also used in coatings to achieve wetting to some difficult to wet substrates.[97,98]

### *Silane Additives*

Silanes are used as additives in coatings for pigment treatment, for improved adhesion, and to effect crosslinking in certain types of coatings. Silane use in solvent-based coatings usually is straightforward, provided that the level of water in such coatings is small and can be controlled.[99] Although silanes are normally hydrolyzed by water, some silanes are compatible with water and thus can be used in certain waterborne coatings to obtain improved adhesion. A large number of organofunctional silanes are commercially available, but only a few of them are water compatible. Even though alkoxy silanes will react with water to ultimately form silsesquioxane resins which can precipitate, several of them are compatible with water in that they form water dispersible oligomers that remain dispersed in water. The three most common water compatible silanes have amino or epoxide functionality.[67,68]

$$(C_2H_5O)_3SiCH_2CH_2CH_2NH_2$$

$$(CH_3O)_3SiCH_2CH_2CH_2NHCH_2CH_2NH_2$$

$$(CH_3O)_3SiCH_2CH_2CH_2OCH_2\overset{O}{CH\text{–}CH_2}$$

$$\begin{array}{ll} Me_3Si\text{-}[OSiMe_2]_x\text{-}[OSiMe]_y\text{-}OSiMe_3 & \\ \qquad\qquad\qquad\quad | & \\ \qquad\qquad\qquad\quad CH_2CH_2CH_2(OEt)_n(OPr)_m\text{-}OR & R = H, Me, Ac \\ R'O\text{-}(CH_2CHRO)_n)\text{-}(CH_2)_3SiMe_2\text{-}(OSiMe_2)x\text{-}SiMe_2(CH_2)_3\text{-}(OCH_2CHR)_n\text{-}OR' & R = H, Me; R' = H, Me, Ac \end{array}$$

Structure of SPE or silicone surfactant.

The amino functional silanes in some cases are not compatible with anionic emulsions or anionic latexes as they can cause coagulation of anionically stabilized latex particles. Silanes are typically used in coatings to obtain improved adhesion to substrates and also for pigment treatment. Silanes are capable of bonding to pigment surfaces and providing improved chemical bonding between pigment particles and organic polymer binder.[65-67] Silanes also provide improved pigment dispersion in some cases and help to keep pigment particles from re-agglomerating. Silanes are typically used at a level of one percent of the binder in coatings.[67,68,100]

When silanes are used for crosslinking in coatings, they can be added to the coatings or they can be grafted or copolymerized with the organic binder.[101,102] In either case, reaction of the silane with organic polymer binder followed by hydrolysis and condensation reactions of the alkoxy groups on Si is responsible for the crosslinking.[102,103] In waterborne coatings, it is desirable to have crosslinking occur after application and hence after removal of water. In some cases, silicon alkoxides react prematurely and this leads to pre-cured or pre-crosslinked polymer latexes. To get around this, organofunctional silanes having bulky alkoxy groups (and hence slower reacting) such as $RSi(O\textit{i}–Bu)_3$ were developed.[104] It is also possible to crosslink reactive organic polymers using certain organofunctional silanes. For example, carboxylic acid functional acrylic latex can be crosslinked using an epoxy functional silane.[105]

It should be understood that not all silicone additives will provide all of the benefits listed since different types of silicones provide different benefits. It should also be emphasized that silicones used in one type of coating may behave differently when used in another type of coating. Finally, it should be realized that some silicone additives may be incompatible in certain coatings and could lead to surface defects.

## Silicone Polymers in Coatings

This category describes coatings in which 10–50% of the coating binder is silicone. Modification of coatings with this amount of silicone results in improved high temperature properties and also improved weatherability. For improvements in these properties to be realized, the minimum level of silicone required is about 15% of organic resin weight with typical values being about 30–50%.[106] The type of silicone used in these coatings is almost always silicone resins. The silicone resins used in these applications are based primarily on a combination of phenyl and methyl groups. Two basic methods of preparing silicone–organic coatings exist: cold blends and copolymerization. Cold blending of silicone resins with organic coating binders, such as alkyds, occurred first during the 1950s and this resulted in coatings having substantially improved weatherability. Copolymerized versions of silicone alkyds were developed next and these provided coatings with weather resistant properties that were superior to the cold blends. These copolymerized silicone–alkyds are made by "cooking" silicone resin with the alkyd (in solvent) which causes SiOH groups on silicone resin to react with carbinol groups of the alkyd resin. Later silicone-acrylic coatings were developed and used as architectural coatings. Other organic coating systems used with silicone resins include phenolics, epoxies, epoxy esters, and saturated polyesters.

In the 1960s, the U.S. Navy began painting ship superstructures with silicone alkyd paint and its use has expanded ever since.[107] Silicone alkyds saw success in numerous other coating applications such as communication towers, bridges, rail cars, storage tanks, and metal building exteriors.[103]

Another type of resin used in coatings is sometimes referred to as silicone intermediates and consists of alkoxyfunctional siloxane oligomers or polymers. These silicones have been around for quite some time and they have been optimized to give good weatherability performance while minimizing cost. They are based on monophenyl, phenyl/methyl, and dimethyl units.[108]

All these coatings were of course solventborne and although they provided excellent weatherability, their chief drawback was a high VOC level.[59] Higher solids versions of silicone resins were developed later in the interest of obtaining lower VOC coatings.[109] Next, water-reducible silicone resins were developed to meet more stringent VOC requirements.[110] Although great progress has been made in the field of silicone resins for lower VOC coatings, the technical advancements in this field have in reality not kept up with the pace of regulation. In other words, many silicone resins that provide excellent weatherability to coatings are approaching VOC levels that are too high by today's standards or regulations. In some applications, solvent-based silicone resins can still be used, such as in coil coatings whereby solvent is captured and used as fuel to help dry the coatings.[111]

Even though many silicone resin applications in coatings require solvents and hence are limited by current VOC regulations, some progress has been made in the area of aqueous silicone resin emulsions or dispersions. Some aqueous methyl silicone resin dispersions have been developed and are used to modify acrylic latex in architectural coatings for building facades.[112] These resins impart hydrophobicity to the facade and they also provide improved water vapor transport. Other aqueous silicone resins have been developed for high temperature coatings and by proper choice of ingredients; such coatings are serviceable to temperatures of 600°C.[113] Silicone aqueous dispersions can be inherently different from solventborne silicone resins and hence they are not necessarily a direct replacement. Their use requires careful consideration and much experimentation and, in many cases, performance of aqueous silicone resins has just not been acceptable for certain coatings applications.

## 100% Silicone Coatings

This category of silicones in coatings involves those coatings whereby the entire coating or the binder is all silicone. Typically these coatings are based on silicone resins or silicone elastomers and they exist as both solvent-based coatings and as water-based coatings. In the case of silicone resins, some solvent-based and waterborne resins were discussed in the previous section on silicone polymers in coatings. Some of those resin solutions and resin aqueous dispersions can also be used as 100% silicone coatings, or, in other words, the binder is all silicone. Even though all-silicone coatings based on silicone resins have excellent weatherability, they are not used that extensively in exterior (architectural) coatings. They are, however, used to a significant extent as high temperature coatings.

Thus, film formers based on 100% silicone resin are used in high temperature paints and coatings, abrasion-resistant coatings, and as bakeware coatings while 100% silicone elastomer film formers are used in architectural coatings, fabric coatings, paper coatings, and marine antifouling coatings. Resin-based coatings and elastomeric coatings are discussed individually along with several coating types.

### *Silicone Resin Coatings (100% Silicone)*

Coatings based entirely on silicone resins are mainly solvent-based coatings of reactive silicone resins that can be cured upon removal of solvent, usually by heat. These coatings undergo a thermoset cure, which typically involves silanol condensation to produce a resin film of infinite molecular weight. In some cases, the resins are alkoxy functional which also undergoes a cure to form hard, resinous films. These coatings have found widespread use as high temperature coatings and for release coatings for bakeware. Although most silicone resin coatings are solvent-based, there are some aqueous dispersions of silicone resins that have been developed that are low VOC, in particular for high temperature coatings. Several of these coatings are covered in more detail.

#### *High Temperature Coatings*

Use of silicone resins as the binder in heat-resistant coatings began in the late 1940s. These silicone resins provide coatings formulators with means for preparing high performance coatings for a number of high temperature applications such as exhaust stacks, ovens, furnaces, barbeque grills, cookware, wood-burning stoves, camp stoves, lighting fixtures, and heat exchangers. *Table* 8 gives an indication of heat stability of silicone resins based on different organic substituents on silicon.[114] The half-life of the coating in *Table* 8 means the time for one half of the organic substituents to be eliminated from the resin due to oxidation.

From *Table* 8, it can be seen that phenyl-containing silicone resins possess the best thermal stability. Thus coatings based on phenyl silicone resin have an upper temperature limit of around 260°C. For extended times or at elevated temperatures (> 400°C), all organic groups on silicon will become oxidized, leaving silica in its place. In those cases, resins based on phenyl will experience a greater weight loss than resins based on methyl. This higher level of weight loss can lead to increased cracking and hence coating failure. For very high temperature coatings, silicone resins along with a judicious choice of pigment provide the best result. Aluminum (leafing) pigment improves the heat stability of all paints, including organics, but if silicone resin is included in the paint, heat stability up to 315°C can be achieved.[115] Presumably, silicon dioxide from silicone resin forms bonds with aluminum oxide to create a durable, heat-resistant coating. Still higher coating service temperatures up to 760°C can be obtained by using ceramic frits and silicone resin; the silicone resin oxidizes to silica over time, which can fuse with the frits and form a durable and heat-stable coating.[112,115]

**Table 8**—Thermal Stability of Organic Substituents on Si

| Group Bonded to Si | Approximate Half-Life in Hours @ 250°C in Air |
|---|---|
| Phenyl | >100,000 |
| Methyl | >10,000 |
| Vinyl | 100 |
| Ethyl | 6 |
| Propyl | 2 |

#### *Food Contact Release Coatings*

The first silicone coatings for food release were silicone resin coated bakery pans for commercial bread baking. Prior to 1946, commercial bakers used lard on metal pans to provide release to baked bread.[116] Silicone bakery pan coatings—"silicone pan glaze"—were introduced in 1946 and are still used today as they are the most cost-effective release system for the baking industry.[117] A line of baking pans coated with silicone resin is also available to consumers at low cost. This is not to be confused with recently introduced silicone rubber baking and cooking utensils, which have become very popular with consumers. Silicone resin coated baking tins will eventually become fouled; for the commercial baking industry, silicone resin is removed from the pans using hot alkali and the pans are recoated.[118] Silicone resins for baking pans have traditionally been applied as low solids (~20–40%) solventborne coatings. As VOC regulations become more stringent, a need still exists for compliant, low-VOC silicone resin coatings for baking pans.

#### *Abrasion-Resistant Coatings*

Coatings having excellent abrasion resistance can be prepared by hydrolyzing $MeSi(OMe)_3$, methyltrimethoxysilane, in the presence of colloidal silica.[119] The composition cures to form clear, hard coatings that deliver outstanding abrasion resistance and they are used primarily to coat plastics such as polycarbonate and polymethylmethacrylate. The coatings cure via silanol condensation to form a highly crosslinked network. The coating is supplied as a solution in alcohol–water and although it possesses a moderately short shelf life, it is manageable. There is an unmet need to convert this system to an all-aqueous coating in order to meet current VOC regulations, however.

### *Elastomeric Coatings (100% Silicone)*

Silicone elastomeric coatings can be divided into solventless, solventborne, or waterborne. Solventless silicone coatings consist of reactive siloxane polymers that have a low enough viscosity that they are capable of forming films upon application and afterwards they react to form crosslinked silicone polymer or silicone elastomer.[120] These materials are used primarily in paper coatings applications for creating release liners for organic adhesives. They are normally two-part coatings systems and they have very fast curing rates at elevated temperatures. These coatings usually employ Pt catalyzed addition reactions or Sn catalyzed condensation reactions to obtain cure. Another type of silicone elastomeric coating is commonly referred to as LSR or liquid silicone rubber. Although LSR is primarily used to form molded silicone rubber articles, it can also be used as a coating, such as in textile coatings.[121] LSR is a two-part heat-curable composition consisting of fillers and reactive siloxane polymers and it is typically cured via Pt catalyzed addition reactions. LSR is also used as coatings in high performance airbags (automotive).

Solventborne silicone elastomeric coatings are typically reactive siloxane polymers with fillers and pigments dispersed in a solvent. They are normally RTV coatings and cure by ambient moisture. Architectural coatings and roof coatings are typical applications. As expected, these coatings have come under pressure from regulations as they do contain substantial amounts of volatile solvent.

Water-based silicone elastomeric coatings consist of aqueous emulsions of precured or pre-crosslinked silicone polymer.[122] Dispersions of reinforcing fillers and pigments also make up part of the coatings. Removal of water leaves a silicone elastomeric film. These silicone elastomer coatings are used as architectural coatings, textile coatings, and as coatings additives. The presence of the surfactant, which remains with the coating upon drying, may detract from some of the silicone's otherwise outstanding properties in some cases.

#### *Marine Antifouling Coatings*

As tin-based marine antifouling coatings have been banned in many parts of the developed world due to aquatic toxicity, a search for suitable replacements has been ongoing for the past 25 or so years. Silicones have emerged as materials of great interest due to their performance against marine antifouling.[123-125] Silicone coatings based on silicone elastomers that contain a release additive appear to be the most effective.[126] The release additive is designed to have limited solubility in the coating so that it will migrate to the coating surface. Although organic oils and waxes also work as release additives, the most effective additive is a siloxane composed of methyl and phenyl substituents.[127] Silicone elastomer antifouling coatings are still evolving.

## Silicone Water Repellents

Silicones are inherently hydrophobic and, coupled with their excellent weather resistance, make very effective water repellents. Silicone water repellents function by creating a hydrophobic, durable surface on top of and within the pores of substrates. Unlike silicone elastomeric coatings, they do not form a continuous film on the substrate surface, but rather silicone water repellents render the surfaces of substrates hydrophobic. Silicone water repellents allow for transport of water vapor, but inhibit liquid water from migrating through substrates. This is particularly important to building facades whereby trapped moisture within or behind the substrate can escape.

Silicone water repellents can be divided into two basic categories: solvent-based and water-based. Most silicone water repellents are reactive siloxane polymers or precursors such as silanes, although in some cases, medium to high molecular weight PDMS will function as a water repellent.

Although some non-reactive polydimethylsiloxanes can function as water repellents in some instances, most of the silicone water repellents, in particular the higher performing ones, are based on reactive siloxane polymers or silanes. Several of the more important water-based silicone water repellents are discussed individually.

### *Siliconates*

Alkali metal siliconates are water soluble and make excellent water repellents for mineral surfaces like brick, limestone, masonry, ceramics, mortar, glaze, and tile.[128] Siliconates are prepared by reaction of an alkyl–alkoxy silane with sodium or potassium hydroxide in water:

$$RSi(OMe)_3 + KOH + 2H_2O \longrightarrow RSi(OH)_2OK + 3MeOH$$

Alcohol is removed and the aqueous siliconate is usually supplied as an aqueous concentrate up to about 40%. Alkyl groups on Si can be methyl, ethyl, or propyl; alkyl siliconates beyond propyl have limited solubility in water. Sodium or potassium methyl siliconate is applied as a dilute aqueous solution to the substrate and, within several days to a week, is fully cured and functional. Siliconates cure by reacting with ambient $CO_2$ to form a silsesquioxane resin and alkali carbonate salt, the latter of which washes away during weathering.

$$2RSi(OH)_2OK + CO_2 \longrightarrow 2RSiO_{3/2} + K_2CO_3 + 2H_2O$$

### *Emulsions*

Aqueous emulsions of siloxane polymers including linear siloxanes, resins, and elastomers can function as water repellents either neat or when used as additives in organic coatings. In some cases, the siloxane polymers possess functionality such that they can react to some extent with substrate surfaces or among themselves. Functionality of siloxane polymer water repellents usually consists of either silanol (SiOH), alkoxy (SiOR), or silicon hydride (SiH). Although the latter two of these functional groups are reactive towards water, under the right conditions, they can be stabilized in aqueous emulsions and made to react upon application to a particular substrate. Silicone rubber latex forms a waterproof coating and as such is not considered a water repellent. However, when used at an additive level in some organic coatings, it can enhance water repellency of those coatings.

### *Silanes*

Alkyl–alkoxy silanes make particularly effective water repellents as they form alkyl silsesquioxanes upon hydrolysis and condensation.[128] The SiOH groups condense with themselves and also can condense with other hydroxyls on mineral surfaces, forming a tight bond between silsesquioxane resin and the substrate:

$$RSi(OR')_3 + 2H_2O \longrightarrow RSi(OH)_3 + 3R'OH$$

$$RSi(OH)_3 \longrightarrow RSiO_{3/2} + 3/2H_2O \quad R = CH_3, C_3H_7, C_8H_{17};\ R' = Me, Et$$

The product of choice for hydrophobing concrete is *n*-octyltriethoxysilane. It can be applied neat, applied as a solution in solvent, or emulsified and applied as an aqueous emulsion. Some substrates such as concrete contain residual alkalinity which acts as a catalyst for promoting hydrolysis and condensation of the silanes and reactive siloxanes. For neutral substrates, in particular wood, catalysts may need to be added to the silicone water repellent in order for it to function properly.

### *Other Silicone Hydrophobing Compositions*

Water-soluble or water-reducible siloxane compositions have been prepared by incorporating a certain level of hydrophilic moieties within the siloxane structure. Such hydrophilic groups are usually based on amine or amine salts of carboxylic acids.[129] Removal of water deposits the siloxane and, a short time later, the salt breaks down leaving a hydrophobic siloxane.

## SILICONES AND SURFACE DEFECTS

Due to their unusual surface properties, silicones are quite capable of causing surface defects in coatings. The most common undesirable effect of silicones is an inability of the coating to properly wet the intended substrate while certain silicones are present, in particular if the silicone has pre-wet the substrate. For a coating to wet a substrate, surface tension of the liquid coating must be lower than the surface tension of the substrate.[76,78] PDMS, with a surface tension of 21 mN/m (dynes/cm), is significantly lower than surface tension of most coatings and if PDMS is absorbed on the substrate, the coating will not wet where PDMS resides. This phenomenon is not limited to silicones as any substance with a lower surface tension than the coating, such as organic oils or resins, will behave similarly.[130] In the case of silicones, it may be difficult to detect visually if silicone is present, however. At the same time, silicones can be helpful for wetting low energy surfaces, such as certain plastics.[131,132] Silicone surfactants, when added to coating, are capable of lowering surface tension enough such that the coating will wet the low energy surface. Ordinary surfactants can perform the same function, but silicone surfactants are usually more potent in this regard and thus can be used at lower levels to achieve a desirable surface tension compared to many organic surfactants.[133]

The second most common surface defect associated with silicones is craters and/or fisheyes. Craters and fisheyes originate from a substance having a lower surface tension relative to the coating and also being either undispersed within the coating (non-homogeneous) or residing on the substrate surface.[134] As pointed out by the 19th Century physicist Carlo Marangoni, liquids flow from regions of low surface tension to regions of high surface tension.[135] An example of the Marangoni effect is the "tears of wine" which occur when a glass of wine is tipped or swirled and drops of wine form above the liquid level and fall back down into the liquid.[136] Alcohol evaporating from the meniscus of the wine leads to a region of higher surface tension. Since surface tension of the remaining liquid is lower than at the meniscus, a flow develops which pushes liquid up the walls of the glass. As more alcohol evaporates from the thin film of liquid on the walls of the glass, surface tension becomes higher and the flow increases. Drops form from coalesced liquid at the top of the film, well above the liquid level and when drops' mass overcomes the force of upward flow, they fall back down into the glass.

This simple example of Marangoni flow is highly relevant to coatings because quite often, surface tension driven flows or surface tension differential driven flows develop in coatings as they dry and this can lead to highly detrimental imperfections in the applied coating. An impurity such as a speck of dust or a minute drop of oil residing on the substrate and having a lower surface tension than the coating liquid will cause coating to flow away from the impurity quite quickly. This results in a crater in the film upon drying. A particle of undispersed substance within a coating that possesses a surface tension lower than that of the liquid coating will likely lead to the same phenomenon. Diameter of craters caused by Marangoni flow can be as much as 10 times and even higher than the diameter of the low surface energy impurity.[137]

Silicones, being incompatible or insoluble in most coatings compositions coupled with their low surface

**Table 9**—Coating Defects Aided by Silicone Surfactants

| Defect | Si Surfactant Help | Defect | Si Surfactant Help |
|---|---|---|---|
| Air entrapment | Y | Haze | N |
| Benard cells | Y | Orange peel | Y |
| Bumps and sinks | Y | Picture framing | Y |
| Cratering | Y | Rub up | N |
| Crawling and dewetting | Y | Sagging | N |
| Fish eyes | Y | Silking | Y |
| Floating | N | Telegraphing | Y |
| Flooding | Y | | |

energy, can be quite capable of causing surface defects. However, if the silicone is properly dispersed within the liquid coating and remains stable during dry down, little, if any, surface defects can be attributed to the silicone. Some silicone compositions when added to coatings are not stable and tend to coalesce or coagulate. In such instances, surface defects will invariably occur if the coagulum particle size is significant, which it usually is. In many cases, the formulator correctly associates surface defects with the presence of silicone and summarily dismisses all silicones as prone to causing these surface defects. On the other hand, if the reasons for the apparent instability of silicone can be understood and a means can be found to overcome the instability, a coatings formulator may be able to reap the rewards of using silicones in his or her coating without the annoying problem of surface defects. To reiterate, some of the benefits silicones are capable of providing to coatings are improved flow and leveling, slip and improved abrasion resistance, improved mar resistance, increased hydrophobicity, defoaming, and increased adhesion. It should be understood that not one silicone will lead to all of these attributes; rather, a different silicone is normally used to accomplish each of these benefits.

While silicones are certainly capable of causing surface defects, they can also be very useful for preventing surface defects. As numerous surface defects are caused by flows of coating liquid that originate from surface tension differentials, lowering the overall surface tension of the coating can eliminate or minimize these flows and lead to elimination or a reduction in coating defect severity.[88] Silicone surfactants are the best known of the silicone additives for this purpose. Of all the silicones used in coatings, silicone surfactants are perhaps the least prone to causing surface defects.[138] A list of common surface defects which silicones are capable of rectifying is provided in *Table* 9.

## ENVIRONMENTAL FATE OF SILICONES

Silicones are of completely synthetic origin, and hence they have never been found to exist in nature. The fact that they do not exist in nature suggests that they will eventually revert back to their fully oxidized state, which is $SiO_2$ and $CO_2$. Even though silicone polymers are able to withstand extreme temperatures and they have excellent durability against outdoor exposure, silicones will eventually fail as they do not last forever. In extreme high temperature applications, silicone coatings form protective coatings by oxidization of the organic groups on silicon to leave a film of silica combined with pigment as the coating.

The outcome of silicones in the environment has been studied in the past and the results were essentially non-alarming.[139] The reason for such little concern is that silicones degrade in soils as a result of contact with clay minerals, as further studies have illustrated.[140,141] Clay acts as a catalyst to depolymerize the siloxane chain into primarily $Me_2Si(OH)_2$ regardless of PDMS molecular weight.[142] The silane diol degrades further in the soil or it evaporates into the atmosphere where it oxidatively degrades.[143] Thus it is apparent that PDMS is converted back into its oxidized constituents: amorphous silica, carbon dioxide, and water.[144]

Recently, the topic about silicones in the environment resurfaced and it has been the subject of interest, in particular about volatile silicone compounds such as $D_4$ and $D_5$.[145,146] Governmental regulatory agencies are reviewing PBT (persistent, bioaccumulative, and toxic) properties of these volatile silicones and it remains to be seen what will be the outcome. At this time, an abundance of studies have been conducted on the health and environmental effects of products that contain $D_4$ and $D_5$ and the overall consensus is that silicone polymers and volatile siloxanes such as $D_4$ and $D_5$ are not harmful to human health or the environment.[147] The major silicone producers together with silicone industry associations are working with government regulatory agencies to help them understand the unique nature and environmental fate of $D_4$ and $D_5$.

## FUTURE OF SILICONES IN COATINGS

As previously stated, silicones are capable of providing a wealth of benefits to coatings such as improved weather resistance, high temperature stability, increased abrasion resistance, improved mar resistance, improved flow and leveling, foam control, improved water resistance, and improved breathability. In some applications, desired results cannot be achieved without the use of silicone. Thus, silicones have become a vital element in the coatings formulator's toolbox to achieve certain desired properties of coatings. As VOC regulations have become more stringent and as market and global trends continue to exert their influence, coatings with still lower volatiles than those of today will be desired in the future. Increased performance and improved durability will likely also be important. The outcome appears bright for silicones in coatings as their ability to meet high performance demands is quite good. The challenges, however, appear to be able to meet these demands using compositions that contain lower volatile content. This is particularly true for silicone resins. In many water-based coatings applications, it is the presence of surfactant(s) that detracts from the performance of the coating system. The same is true with water-based silicones. Thus, means still need to be discovered that provide water-based silicones having the same performance as neat or solvent-based silicones in coatings. The author is of the opinion that these discoveries are actually there and they are merely waiting to happen.

## SUMMARY AND CONCLUSIONS

Silicones, some of their illustrative history, their preparation and properties, and their use in coatings have been described in this two-part article. Silicones are a class of compounds or their precursors that possess at least one silicon–carbon bond and a siloxane unit. Silicones exist in a large variety of forms that include oils or fluids, high viscosity polymers, gums, elastomers, resins, and silanes. Silicones were commercialized in the United States in the early 1940s and have experienced strong growth ever since. Silicones are used in coatings to achieve high temperature properties and coatings with improved outdoor durability and also improved water vapor transmission. They are also used in coatings as additives to obtain slip and antimar properties, improved abrasion resistance, improved adhesion, improved pigment dispersion, improved wetting, flow and leveling, foam control, and water repellency. Although silicones can help coatings to eliminate or reduce the severity of surface defects, they can also cause surface defects and an understanding of the phenomena leading to surface defects can aid in successful use of silicones in coatings.

## ACKNOWLEDGMENTS

The author would like to thank the organizers of the Waterborne Symposium for inviting him to present this lecture and also would like to thank and acknowledge the support of the School of Polymers and High Performance Materials at The University of Southern Mississippi, Hattiesburg, MS. The author would also like to acknowledge Dow Corning Corporation for support.

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