7. Silicones in Coatings

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Silicones are widely used in the coating industries as materials to protect and preserve but also to bring style to a wide variety of applications in our daily lives.

The unique combination of properties of silicones is well suited to coating applications. Two families of products are used: silicone polymers as additives and silicone resins as the main component, or binder.

At low levels, silicone polymers are used to ease application of paints. The surface properties of silicones enable a paint to wet a substrate easily and give it a smooth appearance once dry. Here silicones are behaving as performance-enhancing additives during the coating application. They are effective at an addition level of a fraction of a percent (see Table 1).

In contrast to the low-level use of silicone polymers as additives, silicone resins can be major components of the coating. Here they are used as binders or co-binders, imparting important benefits such as durability throughout the life of the coating. Silicone resins offer resistance to weathering in paints for exterior surfaces such as bridges and metal cladding on buildings. They also provide water repellence to masonry surfaces such as stone and brick.

Silicone resins have greater resistance to high temperatures than organic resins and are used in paints for ovens, chimneys, car exhausts and barbecues. In these examples, the resilience of the silicone materials allows reduced frequency of maintenance painting and consequently reduced volumes of paint used over the lifetime of the coated item (see Table 1).

Table 1. Silicones in Coatings and Associated Benefits

Silicones as performance-enhancing additives *(0.1 – 5.0 % w/w)*	***Silicone resins and intermediates*** *(30 – 100 % w/w)*
Foam control Substrate wetting Leveling Adhesion Surface slip	Weather resistance Heat resistance

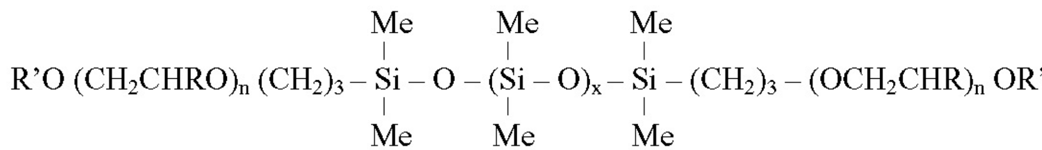
Silicones as Performance-Enhancing Additives

Polydimethylsiloxane (PDMS) fluids of low to medium viscosity were the first silicone additives to be used in coatings. They readily dissolve in solvent-borne paints, reducing the surface tension of the liquid and enabling it to wet substrates, even if contaminated with dust, grease or oil. This reduces the appearance of film defects known commonly as “fisheyes” and “pinholes.” The silicone also reduces surface tension gradients across the coating film as it dries so a smooth surface is obtained rather than the undesirable “orange peel” effect.

Silicone polymers can be modified by grafting polyether groups to give silicone-polyether copolymers. These behave as surfactants in aqueous media as they have both hydrophobic and hydrophilic components. Such surface active materials can perform many functions in inks, paints and coatings. The main uses of silicone surfactants are to provide defoaming, deaerating, improved substrate wetting, and enhanced slip properties [1].

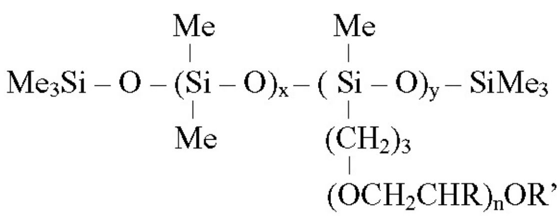
Silicone-polyethers are usually obtained by a platinum-catalyzed addition reaction of an unsaturated polyether onto a SiH functional silicone polymer. Therefore very many structures are possible, altering the SiH functional silicone polymer (DP, % SiH) and/or the nature of the unsaturated polyether (DP, unit type) (see Figure 1).

a) end-blocked or ABA type:



where: R = H (polyethylene oxide) or CH_3 (polypropylene oxide)
R'= H, CH_3, OAc (polyether end group)

b) raked/pendant or A_xB_y type:



where: R = H (polyethylene oxide) or CH_3 (polypropylene oxide)
R'= H, CH_3, OAc (polyether end group)

Figure 1. ***Molecular structures of silicone polyethers.***

Much versatility is possible here. A copolymer with a high proportion of ethylene oxide in the polyether chains is far more miscible with water than a copolymer with predominantly propylene oxide units. The former will act as a wetting agent since it reduces the interfacial tensions at the liquid-air and air-substrate interfaces. The latter behaves as a foam control agent since it matches the criteria cited as necessary for antifoaming, particularly immiscibility with the foaming medium and a lower surface tension than the medium [2, 3].

Limited miscibility with the coating film can also be used to design the silicone-polyether copolymer so it migrates towards the liquid-air surface during drying. This is beneficial in applications where surface slip is required. Cartons for food packaging often have a radiation-cured overprint varnish to protect the printed text and graphics on the exterior surfaces from water and frost during storage. A silicone-polyether copolymer added at 0.5 to 2.0% to the varnish reduces its coefficient of friction so the flat cartons slide easily from the stack in the production process rather than sticking together [4].

Silicone Resins and Resin Intermediates in Weather-Resistant Paints

Paints for exterior surfaces are exposed to sunlight in wet, dry, hot and cold conditions. The combination of UV radiation, variable temperature and humidity rapidly degrades organic polymers, roughening the coating surface and exposing the pigments. To the coating user, this is observed as loss of gloss and "chalking" (loose pigment on the paint surface). Since the 1940s, solvent-borne alkyds and acrylics have been blended with silicone resins to improve their weathering performance. In the 1950s, alkoxy- and silanol-functional silicone resin intermediates were developed which could be reacted with hydroxyl-functional organic resins to give even greater weather resistance. Chemically combining the silicone and organic resins gives a higher degree of compatibility, allowing a broader range of organic resins to be used.

A comparison of the bond strengths between atoms that compose silicones and their organic counterparts gives some insight into why the silicone backbone is so robust when exposed to energetic conditions such as UV radiation or heat (see Table 2).

Table 2. Bond Strengths for Some Common Combinations of Atoms in Coating Resins

Bond	***Bond strength*** *kJ/mol*
Si – O	445
C – C	346
C – O	358
Si – C	306

The Si-O bond has about 50% ionic character as calculated from Pauling's electronegativity scale. In aqueous media, Si-O bonds are more susceptible to hydrolysis than C-C bonds, especially in the presence of an acid or base. This might suggest that silicones would be expected to show less resistance to weathering than organic resins. The reason that this is not so is because the products of hydrolysis, silanol groups, rapidly condense to reform the silicone linkage. Moreover, the silicone hydrophobicity limits wetting and surface contact with any water-based media. However, water vapor can diffuse through most silicone polymer coatings, which is advantageous in some applications like masonry treatment.

Typical silicone resin intermediates used in solvent-borne alkyd or acrylic resin paints are oligomeric materials including T units with phenyl and propyl groups to improve their compatibility. They have some Si-OH or silanol groups that can be condensed with C-OH or carbinol groups of the alkyd or acrylic resin (see Figure 2).

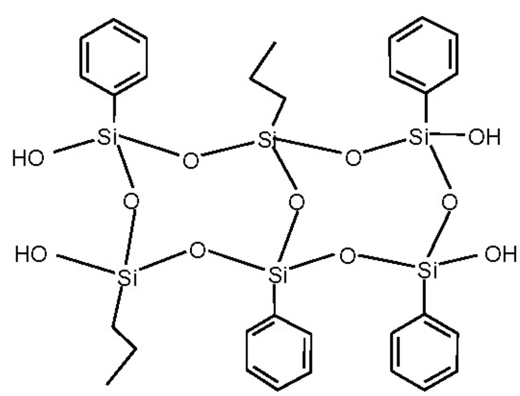


Figure 2. ***A phenyl-, propyl-functional silicone intermediate used to modify organic resins (idealised structure).***

These silicone-organic copolymers are used in industrial maintenance paints to protect a variety of metal objects and structures, including railway carriages, chemical plants and bridges. The biggest application in the US is the painting of naval ships according to specifications set by the federal government. Periods between recoating were extended from a maximum of one year for straight alkyds to three years for the silicone-modified versions. A typical silicone-alkyd copolymer for this type of paint contains 30% silicone based on resin solids.

The success of silicone-alkyds in naval applications led to the evaluation of silicone-organic copolymers in coil coatings for residential and commercial aluminum sidings. As these coatings can be cured at elevated temperatures, silicone-polyesters without drying oils were found to be most appropriate. At first, a 50% silicone content was the standard based on accelerated weathering data, but as more field experience was gained it became apparent that 30% silicone is sufficient.

Solvent-borne thermoplastic acrylic resins tend to have better chemical resistance than alkyds and can be cold blended with silicone resins to give weather-resistant paints for exterior applications. Addition of as little as 10% silicone can significantly increase the gloss retention and chalking resistance. The improvement that can be achieved in gloss retention of various organic coating resins through silicone modification is illustrated in Figure 3 [5].

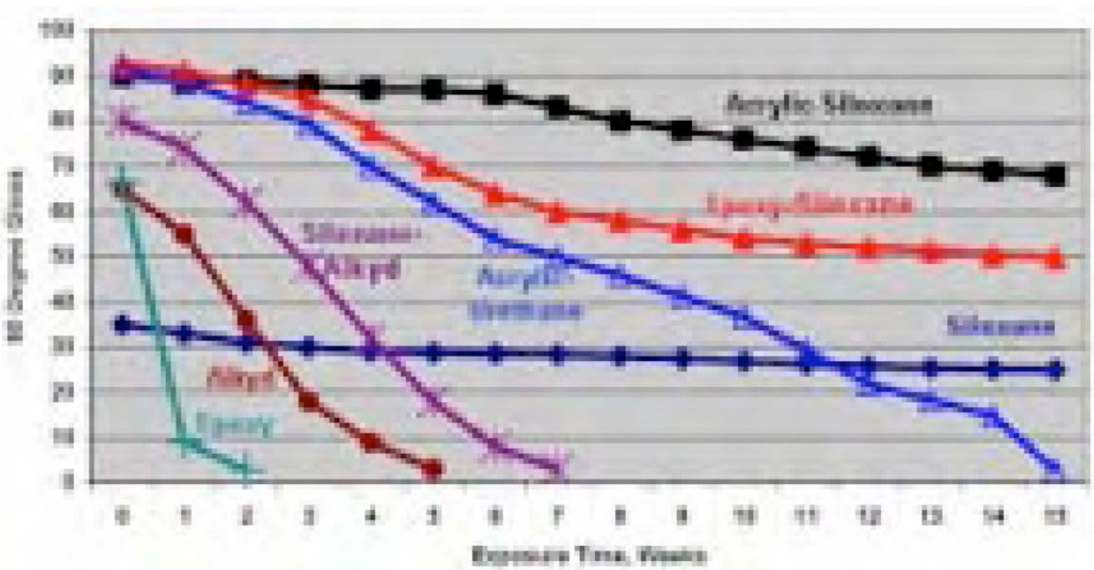


Figure 3. ***Gloss retention of coatings made from organic resins and silicone-organic combinations; QUV-B accelerated weathering.***

The modification of acrylic latexes (water-borne formulations) with silicones is proving to be an effective way to comply with regulatory restrictions on solvent use. Combinations of monomeric silicon intermediates with alkoxy functionality can be blended with hydroxyl functional acrylic latexes to give silicone-acrylic copolymers with excellent weather resistance. The ratio of alkyl- and aryl-bearing silicon monomers can be optimized to give the best balance of compatibility, film flexibility and durability. Gloss retention of paints formulated from acrylic latex with 10% modification is typically 50 to 70% after 30 months of south Florida exposure, compared to about 10% for the unmodified latex.

Silicone Resins in High Temperature Paints

Silicone polymers or resins can be regarded as already partially oxidized as they consist partially of Si-O groups. This is one of the reasons for the high thermal stability of silicones compared to organic materials. The bond strengths in Table 2 provide additional explanation of the observed stability.

Phenyl groups attached to silicon are far more resistant to thermal oxidation than methyl groups. So, most silicone resins for high temperature applications have a combination of methyl and phenyl substituents to achieve the required balance of heat stability, flexibility and compatibility with organic resins.

Blends of silicone and organic resins are suitable for applications up to about 400 °C. The proportion of silicone required increases vs. the expected upper operating temperature, as observed with the effect of adding a methyl/phenyl silicone resin into an alkyd paint exposed to various temperatures (see Figure 4) [6].

For temperatures above 400 °C, silicone resins are used only as binders. These can be formulated with aluminum pigments to form a ceramic film as the silicone organic substituents are burned off to give a very durable fully oxidized siliceous layer.

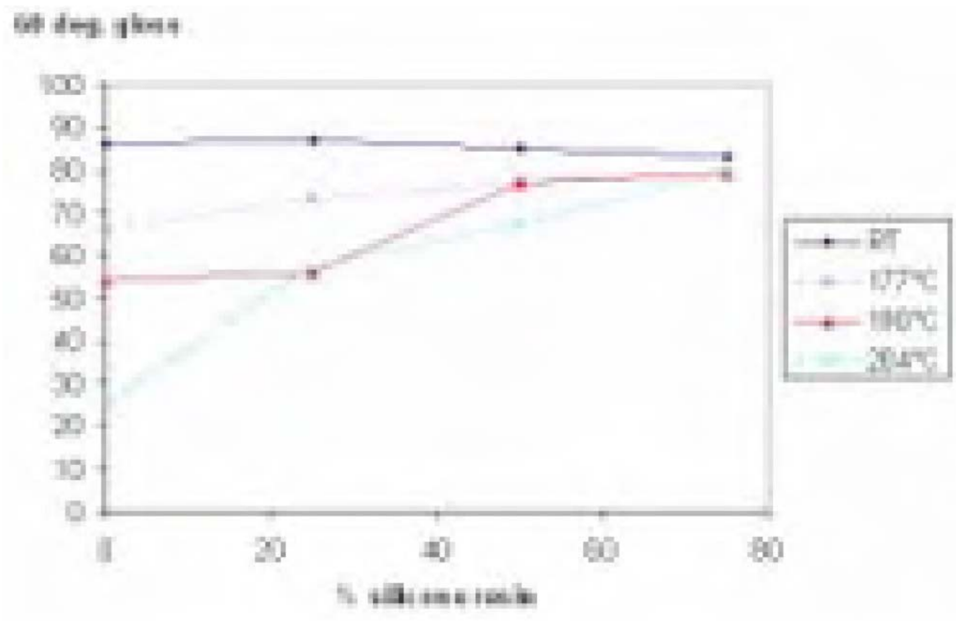


Figure 4. ***60° gloss vs. methyl/phenyl silicone resin content in an alkyd paint based on nondrying coconut oil after 16 hours exposure at different temperatures.***

Silicones for Marine Fouling Release Coatings

Solid surfaces immersed in seawater quickly become covered with algae, barnacles, tubeworms and other marine organisms. On ships this is referred to as fouling, which increases drag on the hull and raises fuel consumption by up to 40%. To prevent this, antifouling coatings are applied to the hulls. The most effective coatings were based on organo-tin compounds, and in the 1970s, 80% of the world's shipping fleet had this type of coating. Environmental concerns have motivated many countries to ban organo-tin coatings. So considerable research and development is taking place in government agencies and paint companies to find alternatives. Silicones have been identified as critical materials.

A typical silicone-based anti-fouling/release system consists of an epoxy or silane primer, an elastomeric silicone tie-coat and an elastomeric silicone top-coat that contains a release additive. The release additive must have limited compatibility with the coating so it will migrate to the surface. Organic oils and waxes have been shown to work as release additives, but the most effective materials are modified silicone polymers with a combination of methyl and phenyl substituents. The latter reduce the compatibility of the polymer with the predominantly PDMS network of the elastomeric coating. Figure 5 shows a system of this type applied to a test panel and immersed in the English Channel for two-and-a-half years. The panel is almost completely free of fouling organisms. Surprisingly, a comparison coating based on PTFE, which has also a very low surface energy, is completely covered. This indicates that a coating with a low surface energy is not a sufficient requirement for effective fouling release. The inclusion of a release additive, as in the silicone elastomeric system, has a dramatic and positive effect on performance.

Figure 5. ***Extent of fouling of coating steel panels submerged for two-and-a-half years in the English Channel. Picture courtesy Dow Corning Ltd.***

The ban on tin-containing anti-fouling coatings for marine applications has opened up an area that is surely a logical fit for silicone technology. This may well be the largest "release" application in the world, release being a function that silicones have provided for many years in bakeware, mold-making and adhesive label backing paper.

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