

HIGHLY DURABLE SOLVENTBORNE SILICONE ORGANIC HYBRID FOR PROTECTIVE COATING APPLICATIONS

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ABSTRACT

In high-performance protective coating applications, traditional systems often require three distinct layers of different composition/formulation for optimal protection of the structure against degradation. Polyurethane topcoats have been widely used as high performance and durable coatings in these applications; however, they typically contribute little to corrosion protection and therefore are not useful as primers. In these applications, a two-coat system providing similar performance as the three-coat system would yield labor and material savings as well as reduced environmental impact. Advances in understanding the compatibility between silicone and organic resins has led to the development of a new isocyanate-free hybrid resin technology that combines the advantages of silicones (e.g., outstanding weather resistance, hydrophobicity) with the benefits of an organic binder (e.g., corrosion protection, adhesion). Excellent corrosion resistance is observed after 3000 hours (as a two-coat system) or 1000 hours (as a single coat system) salt fog exposure with no evidence of blistering, cracking or rusting. Weathering tests show exceptional gloss retention over 4000 hr QUV A or Q-Sun exposure and after >2 years South Florida exposure. The hybrid technology also has low VOC and favorable hazard labelling when compared against those of standard PU coatings.

Key words: metal protection, layer reduction, corrosion resistance, weatherability, isocyanate-free

INTRODUCTION

The impact of corrosion on society is enormous. The National Association of Corrosion Engineers (NACE) estimated that the global total cost of corrosion is ~\$2.5 trillion (USD), approximately 3.4% of global GDP.¹ In 2016, NACE released the “International Measures of Prevention, Applications, and Economics of Corrosion Technology” which estimates that implementing corrosion prevention best

practices could result in global savings between 13-15 percent of the cost of damage, or a savings between \$375-875 billion (USD) annually on a global basis.² One important aspect of this strategy is implementing state-of-the art corrosion control through advanced painting/coating technology and use of corrosion-resistance materials, resulting in competitive advantages and warranties against corrosion. A second study noted that if indirect costs of corrosion (costs incurred by lost productivity, taxes, and costs of others than the owners and operators) were also accounted for in these calculations, the total estimated cost is closer to 6% GDP.³

Coating systems used in protective coating (PC) and general industrial finish (GIF) applications are chosen to reduce the detrimental effects of corrosion on property, plants, and equipment, while offering a beautiful weatherable finish. The topcoat chemistry of choice is often a 2K solventborne polyurethane. This chemistry, however, is under pressure due to the presence of isocyanates, high levels of solvent (VOC), and the need for improved durability. For these reasons, some regions have begun to limit the use and sale of polyurethanes and it is expected that other regions will follow suit in the future. Hybrid polysiloxane resins⁴ have offered formulators a highly durable, isocyanate-free (iso-free) alternative chemistry choice to standard polyurethanes. The hybrid nature of the final coating is the basis for superior weathering and corrosion resistance associated with this technology. The technology, however, can be difficult to apply properly and suffers from the release of latent volatile organic content (VOC) formed during the condensation of residual alkoxy groups on the silicone resin which can lead to coating shrinkage, cracking, and adhesion loss.

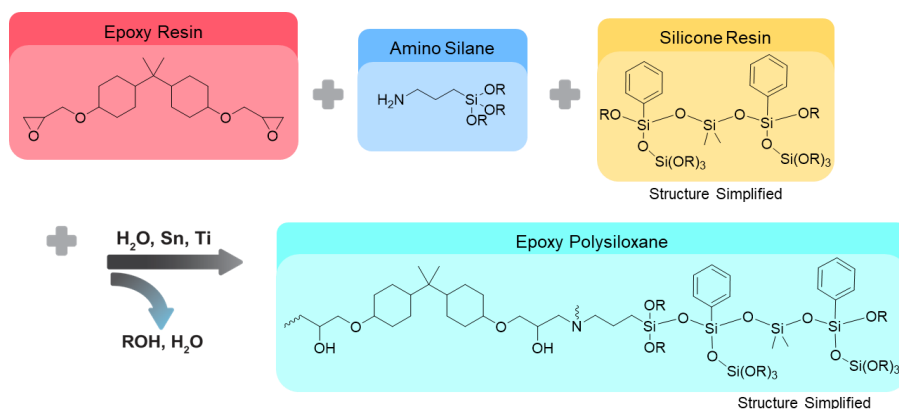


Figure 1: Schematic Illustration of hybrid polysiloxane technology.

Recently, a different approach was taken to develop a new hybrid 2K coating system that combines the advantages of silicones with those of organic chemistries to address top needs in the PC and GIF applications: excellent 2-coat or direct to metal (DTM) corrosion protection, exceptional weatherability, improved coating application robustness, low VOC, and isocyanate-free labeling. Using condensed functional siloxane resins as a component of the hybrid helps to maximize weathering resistance and maintain the appropriate flexibility/hardness balance in a cured coating while avoiding the cracking and shrinkage issues observed in standard polysiloxane technology.

One key for success in hybrid technology is managing the compatibility of the disparate components (silicone and organic in this case) in the formulation, during cure, and in the final coating. Conventional approaches for compatibilization of silicone resins with organic polymers typically rely on expensive silicone building blocks such as phenyl substituted instead of methyl substituted repeat units. Without this modification, the silicone material often phase separates from the organic phase and leads to poor coating properties.⁵ To expand the practicality of using silicone hybrid coating systems in cost sensitive applications, we envisioned new strategies for controlling the compatibility of silicone materials with organic polymers by simultaneously tuning the structure of the silicone and organic resins. We hypothesized that new hybrid materials could be developed that would have small microphase separated

domain sizes that could give properties approaching those of miscible resin systems but at lower cost. Examples of some of the potential scenarios with organic continuous phase morphology are illustrated in Figure 2. We also hypothesized that coatings with silicone continuous phase and organic microphase separated domains could be reasonable to consider as well.

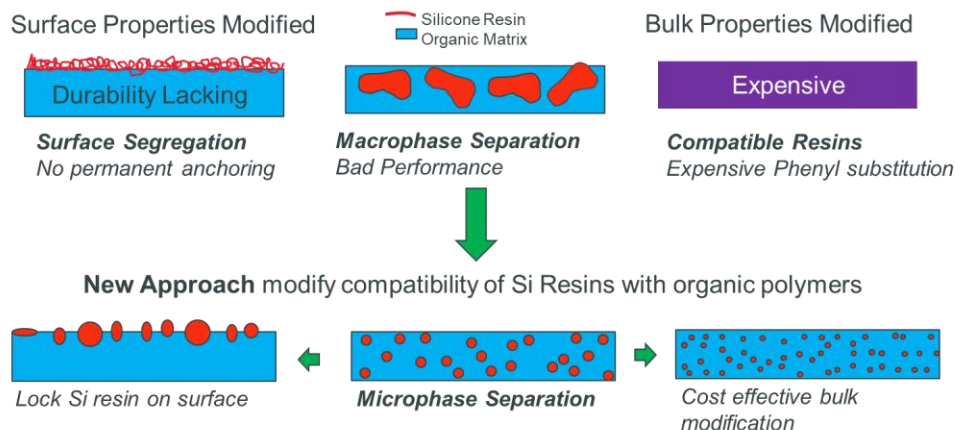


Figure 2: Illustrative cross sections of silicone hybrid coatings with microphase separated silicone domains in a continuous organic matrix. Red = silicone material. Blue = organic polymer. Purple = compatible blend.

EXPERIMENTAL PROCEDURE

Coatings were formulated into 15% PVC coatings using TiO_2 as the only pigment (note: anticorrosive pigments are compatible with technology, but not used in examples within the paper). The coatings were applied either by drawing down using a 10 mil ($\sim 250\ \mu\text{m}$) coating bar or by spray using HVLP spray gun onto phosphate pretreated steel substrates or on aluminum substrates to ultimately achieve $\sim 50\text{--}75\ \mu\text{m}$ DFT, and then cured at $23\ ^\circ\text{C}$ and 50% relative humidity (RH) for 7 days before testing.

Gloss was measured using a BYK micro-TRI-gloss instrument at 20° , 60° , and 85° angles. Color measurements were taken using a BYK Spectro Guide using CIELAB. Coating dry time was measured using a BYK drying time recorder according to ASTM D5895-03. Coatings were applied with a wet film thickness of $76\ \mu\text{m}$. Pendulum hardness was measured using a pendulum hardness tester from BYK Gardner equipped with a König pendulum. The tester was run according to ISO 1522 and set to measure hardness in seconds. Pencil Hardness was measured in accordance with ASTM D 3363. Methyl ethyl ketone (MEK) double rub tests were conducted according to ASTM D5402 using a semi-automatic MEK Rub Test machine made by DJH DESIGNS INC. Adhesion of the coatings to the specified substrate was measured according to ASTM D3359-09, test method A or B, depending on the total coating thickness. Chemical resistance was determined according to ASTM D1308.

Clear coatings were investigated by means of optical microscopy and scanning electron microscopy (SEM). Samples of the films deposited on transparency films were cryo-microtome at -120°C . Nonconductive coatings were applied to the cross-sections to maximize the backscatter contrast.

Accelerated weathering tests were conducted according to ASTM D4587 and SAE J2527. Coatings were applied on aluminum panels ($\sim 75\ \mu\text{m}$ DFT) and tested for 4000 hr. The QUV chamber was illuminated by UVA-340 bulbs and chamber cycled between 60°C at $0.89\ \text{W/m}^2$ irradiance for 8 hours and a condensation cycle at 50°C for 4 hours following ASTM D4587. The Q-SUN Xenon arc test method was conducted according to SAE J2527 using extended UV-Q/B filters, 340nm UV sensors and an uninsulated black panel. Salt fog tests were conducted according to ASTM B117. One coat systems

were applied on cold rolled steel panels at ~75 μm dry film thickness (DFT) and tested for 1000 hours. Two and three coat systems were applied to either cold rolled steel or blasted hot rolled steel panels (~75 μm DFT/layer) and tested for 3000 hours.

Outdoor exposure tests were conducted at four sites in the United States. At each site, the panels were mounted in four orientations: north and south vertical, and north and south at 45°.

RESULTS

To address resin compatibility, several design criteria were considered for each resin component. These factors were considered through a series of designed experiments (DoE) that helped ascertain the role of the variables on compatibility and overall system performance. Some of the factors that were considered in the design included: percent phenyl substitution on the silicone resin, degree of crosslinking, molecular weight and T_g of silicone and organic resins, and the potential for latent VOC generation. A series of four DoEs (example shown in Figure 3) with additional expansion points were conducted, which led to the synthesis and evaluation of >50 resins and resin combinations. The resins were evaluated in clear, additive-free, coating formulations.

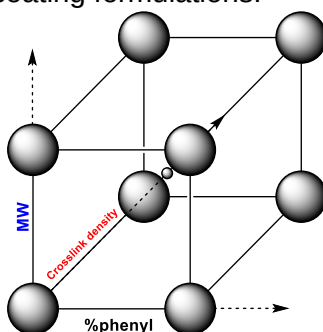


Figure 3: Target compositional space for one Design of Experiment.

Compatibility

Incompatible systems often form large phase separated domains that scatter light, giving a hazy appearance to the coating. Incompatibility can also be observed in coating properties such as poor solvent resistance, slow hardness development and long dry times. Figure 4 shows an example of how silicone resin characteristics can affect coating compatibility (left = incompatible, rightmost = compatible) in a hybrid system with a single organic polymeric partner.

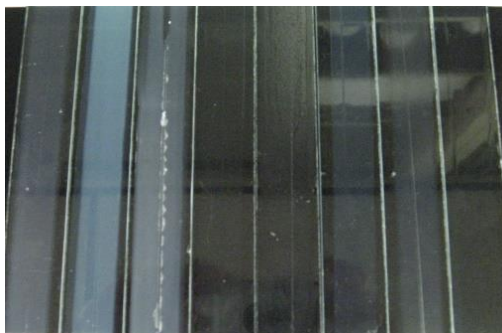


Figure 4: Degree of compatibility as indicated by level of haze evident in clear film.

Comparison of the coating properties of compatible and incompatible systems is shown in Table 1. The incompatible coating system had lower gloss, long dry times, low coating hardness and poor solvent resistance. Upon QUV exposure, the incompatible system also showed very rapid gloss loss within the first cycle (Figure 5).

Table 1
Performance of compatible and incompatible unpigmented coatings.

Sample	Compatible	Not compatible
Clarity	Clear	hazy
Dry Time (hr)		
Set-to-Touch	0.2	0.2
Tack-Free	1	4
Dry-Hard	2	>24
Dry-Through	15	>24
Initial Gloss		
20°	94	51
60°	103	92
Thickness (μm)	65	65
König Hardness (sec)		
1 Day	51	13
7 Day	104	29
Pencil Hardness	F	2B
MEK double rubs	>200	175

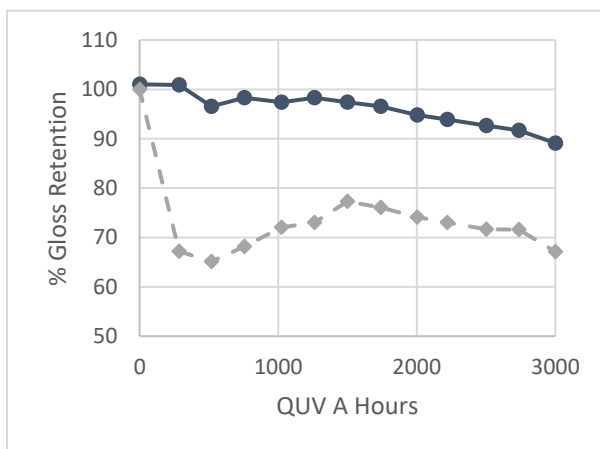


Figure 5: Gloss retention upon QUV A exposure (solid blue line: compatible, dashed gray line: incompatible hybrid coating systems).

Compatibility can also be visualized on the micron scale using scanning electron microscopy (SEM). Figure 6 shows SEM images of the cross-section of compatible and incompatible coating systems. Very little phase separation can be seen in the left image (clear compatible film) whereas in the right image (hazy incompatible film) significant phase separation has occurred throughout the entire film. In the phase separated film, the lighter regions are the silicone domains and the darker regions are the organic resin. In some areas, the silicone phase is dispersed within the organic matrix and others where the organic phase is dispersed within the silicone matrix. There is also significant silicone enrichment evident at the surface of the coating.