

CL12- Covalent Bonding of Si Coatings, Making Infrastructure Maintenance Easier

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ABSTRACT /INTRODUCTION

Silicone polymer based coatings were designed with maintenance, and extending asset design life in mind. 100% polysiloxane RTV technology to meet some of the most demanding challenges relating asset management. This technology has can be tailored to be used for Anti-Corrosion, Water proofing, Building Envelope or as a Hydrophobic Hight voltage insulator.

Demands on protective coatings to meet longer service life have led to the devolvment of Silicones of RTV maintenance coatings. Since very few 100% polysiloxane polymer coatings are on the market today a comprehensive set of either ASTM ISO or NACE standards for accelerated performance indication exist. Historically these have been used for either epoxy or polyurethane coatings. A combination of accelerated laboratory testing, natural exposure testing and historical installations have been used to innovate technology that will push the performance limits of today's silicone maintenance coatings.

The basic philosophy behind the development of Silicone polymer based coatings as an anti-corrosion coating was to minimize the need for surface preparation by using covalent bonding rather than mechanical adhesion. In the early stages of development, the model of the metal substrate employed in engineering the product was one that takes full advantage of the natural state of exposed metals, versus metals that have been forced into an unnatural state (i.e. metal that has been sandblasted and profiled). As a result, the Silicone polymer based coatings products have been developed to have superior adhesive properties when compared to conventional coatings and, in turn, eliminate the need for sandblasting and/or profiling of the substrate.

Before an adequate illustration of Si-Polymer coatings adhesion superiority can be made, the modes of bonding a coating to a substrate (particularly metal substrates) must be discussed.

It was once rather fashionable to draw two broad categories of adhesion mechanism — chemical adhesion or mechanical adhesion. In the case of chemical adhesion, it was said the coating bonded to the metal surface by means of a chemical reaction. In the case of mechanical adhesion, the adhesion of the coating to the metal was thought to take place through an interlocking of the coating with the metal as it flowed into the microscopic pores and cavities of the metal surface and, in turn, “hooked on” to the irregular surface.

Proposed thinking, however, discounts the theory of mechanical adhesion except in the special cases of extremely porous surfaces. Instead, adhesion of a coating to its host surface is explained via various forces that exist at the molecular level.

Objective: The purpose of this paper is to introduce through case histories and lab results the benefits of a coating that is bonded to a surface at the molecular level rather than the mechanical bond usually found in traditional coating systems.

Results: Although not always the best option using a coating that needs minimal surface preparation it can result in equal or greater corrosion protection to a coating system requiring high levels of surface perperetration

Analysis: Cost saving, minimizing maintenance time and extending asset life can be achieved without the need for costly sandblasting and surface preparation

Fundamental Chemistry

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Modern thinking, however, discounts the theory of mechanical adhesion except in the special cases of extremely porous surfaces. Instead, adhesion of a coating to its host surface is explained via various forces that exist at the molecular level.

This use of silicone polymer chemistry (breathable, adhesion, UV stability, hydrophobicity) backbone has led to using the natural characteristics of silicone for a variety of different coating types such as for high voltage insulator coatings as well as for building envelope.

Tailoring properties and performance by varying the -Si-O chain lengths, side groups and cross linking. Silicone can be synthesized with a wide variety of properties and compositions. Silicone elastomers contain linear silicone polymers cross linked in a 3D network containing fillers that act as reinforcing agents or as additive for certain mechanical, chemical or physical properties.

A proper understanding of the many phenomena involved in a coating's adhesion to a surface is gained through a working understanding of the chemical and physio chemical forces acting to hold the coating to the metal or concrete (or any other substrate).

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Molecules form the building blocks of any coating material. These molecules are complex groups of atoms, which are held together by chemical bonds. This is true whether speaking of the long-chained, carbon-based polymers that make up the resins of conventional systems (epoxy, urethane, alkyd, etc.) or when considering the silicone-oxygen-based polymers of the Silicone polymer based coatings products.

The nature of the chemical bonds that hold atoms together depends on the types of atoms (elements) involved. All elements have an atomic structure in which the positively charged nucleus, can be thought to exist in “shells” surrounding the nucleus. The electrons in the outermost shell of the atom are named the “valence” electrons. The number of electrons residing in this valence shell is critical, because it dictates the number of chemical bonds the atom can then make.

Chemical bonding occurs between two atoms when they get close enough to share (covalent bonding) or transfer (ionic bonding) valence electrons.

Covalent Bonding

Bonding between atoms is also achieved through sharing of electrons (as opposed to the donation of electrons in ionic bonding) and is termed covalent bonding. Examples of covalent bonds include carbon-carbon bonds (C-C), carbon-hydrogen bonds (C-H) and the extremely strong silicone-oxygen bond (Si-O) found throughout the Silicone polymer based coatings polymer backbone.

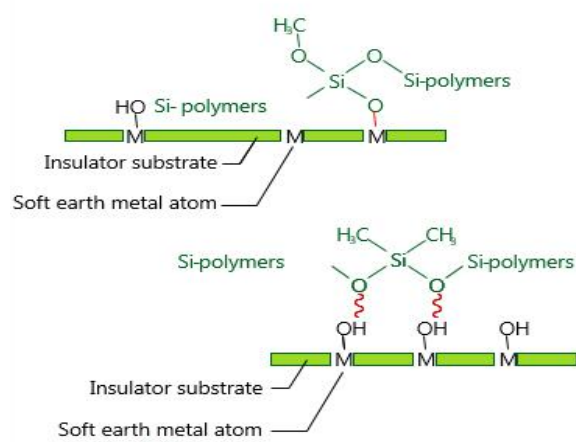
Whatever the exact nature of a chemical bond holding molecules together, they are very strong linkages and can only be broken with great difficulty.

Superior Bonding Mechanism of Silicone and Oxygen

As might be expected, the true chemical bond that is achieved through primary valency bonding provides a much stronger bond than the physio-chemical bonds of secondary valency bonding. In the case of primary valency bonding, the bond is so strong that the interface between coating and substrates may be regarded as disappearing entirely.

Strength of Silicone polymer based coatings Bond to Metal and Other Substrates

It is essentially through primary valiancy bonding that Silicone polymer based coatings adheres to the metal substrate.



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While primary valiancy bonding is preferred, the majority of conventional coatings (including epoxies and urethanes) rely on the weaker secondary valence bonds to adhere to the metal substrate. These secondary valiancy attractions are reversible, and because there is not actual chemical linkage between coating and substrate to be cleaved, they are all much weaker forces than the primary valiancy forces and, hence, more easily broken.

Thus, conventional coatings, which adhere via secondary valiancy forces, are not nearly as resistant to subsequent delamination as the primary bond, which adheres via primary valiancy forces. In various tests, adhesion produced by primary valiancy bonds has been measured at approximately six times the adhesion strength of secondary valence bonds.

In silicone, adhesion is based on the heavy concentration of groups on the polymer backbone that will react with the metal (or other substrates) to form primary valiancy bonds.

The Relative Weakness in Epoxy Adhesion

Secondary valence bonds utilize polar groups such as hydroxyls, ethers, amino compounds, etc. The adhesion of epoxy, perhaps surprisingly, is directly related to the abundance of polar groups in the epoxy molecule and in the curing agent. In each low molecular weight Bisphenol, A type epoxy, for example, a polar hydroxyl and two polar ether linkages can be found, which will form secondary valiancy bonds with the metal substrate.

As a direct result of their poorer wetting characteristics and the fact they rely so heavily on the weaker secondary valence forces to adhere to metal substrates, epoxies will better adhere to a surface if they are given more opportunities to bond to that surface. A greater number of bonding opportunities can be achieved by abrasive blasting and/or profiling the substrate.

Abrasive blasting and profiling a metal surface increases the actual surface area (versus the “apparent” surface area). This process creates deeper crevices in the metal surface when viewed at a microscopic level. Hence, the actual surface area is increased and a greater number of potential bonding sites on the metal are exposed. In turn, this offers a greater number of opportunities for a coating to bond to the substrate.

Engineered to Eliminate the Need for Abrasive Blasting and Profiling

The successful engineering of a high-performance coating system begins from the ground, up. That is, it is essential to first study the substrate to which the coating will be applied.

In the case of conventional coatings, including epoxies, inherent weaknesses in the physical and chemical characteristics of the resin (inadequate degree of wetting, dependency on weak secondary valence forces of attraction for adhesion) forced engineers to create a model of the metal substrate that would allow the coating sufficient opportunity to adhere. This model included the preparation of the metal substrate to a level that was free of dust, oils, all traces of rust and which had been profiled to increase its actual surface area.

While it is highly unlikely the need to remove dust and oils will ever be eliminated, the engineers and chemists behind the creation of Silicone polymer based coatings chose to create a coating that would fully utilize the natural characteristics of exposed metal surfaces, rather than forcing unnatural state of metal to accommodate a coating.

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Silicone coating film

Though silicone-based materials are generally viewed as hydrophobic, that hydrophobicity relates to liquid water, not water vapor. The structure-permeability relationship holds true for both organic and silicon-based materials. For example, non- or low-filled silicone sealants and elastomers which possess relatively low crosslinking levels are known to be vapor and gas permeable, which can create a “breathable” film.

In the case of the coating film being applied onto steel is allow all trapped water to diffuse back through the film as a vapor.

The ability to control the silicone polymer chain length allows for control over the physical properties that might be needed for specific application. In coatings being applied to concrete a long polymer chain length is desirable to add to the coatings ability accommodate the movement of the concrete while the coating will not crack due to the elongation properties.

Environmental

UV light does not have any visual or structurally effects of most silicone oxygen bonds this overcomes inherent issues that can come from epoxies as they will chalk and loose thickness and color over time with exposure.

EXPERIMENTAL PROCEDURE

Exposure Testing in accordance with ISO 20340

Procedure A: Standard procedure with low temperature exposure (thermal shock). The exposure cycle used in this procedure lasts a full week (168 hours) and includes 72 hours of QUV Accelerated Weathering Tester, 72 hours of Salt Spray test (SST) and 24 hours of thermal shock (-20°C ; -4°F) The QUV exposure is according to ISO 11507, accelerated weathering, by exposure to fluorescent ultraviolet (UV) light and condensation in order to simulate the deterioration caused by sunlight and water as rain or dew. UV cycle: 4 hours UV-light at 60±3°C (140°F) with UVA-340 lamps and 4 hours condensation at 50±3°C (122°F).

The SST exposure is according to ISO 9227, exposure to constant spray with 5% NaCl solution at 35°C (95°F). The thermal shock exposure consists of placing the panels in a freezer, at -20±2°C. Total period of exposure: 25 cycles equal to 4200 hours. Before the panels are started in the climatic cycle, they are given a 2 mm (0.079 in) wide score placed horizontally, 20 mm (0.79 in) from the bottom and sides. When the test is stopped, the paint film is removed from the score, and the width of the rusting is evaluated.

After removing the coating by a suitable method, the width of the corrosion is measured at nine points (the midpoint of the scribe line and four other points, S mm apart, on each side of the midpoint).

The rust creep M is calculated from the equation

$M = (C - W)/2$ (1), where C is the average of the nine width measurements and W is the original width of the scribe.

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Florida Fence Test

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Testing Overview

For the three year period starting in Spring 2000, a major power utility in Florida, USA conducted the “Florida Fence Test” on a series of 29 anti-corrosion coatings, including Si coating #1 | Anti-Corrosion Protective Coating.

The 29 coating systems tested included two-coat systems and three-coat systems. The only one-coat system in the field was the Silicone polymer based coatings⁵⁷⁹.

Two-coat systems included, from various manufacturers:

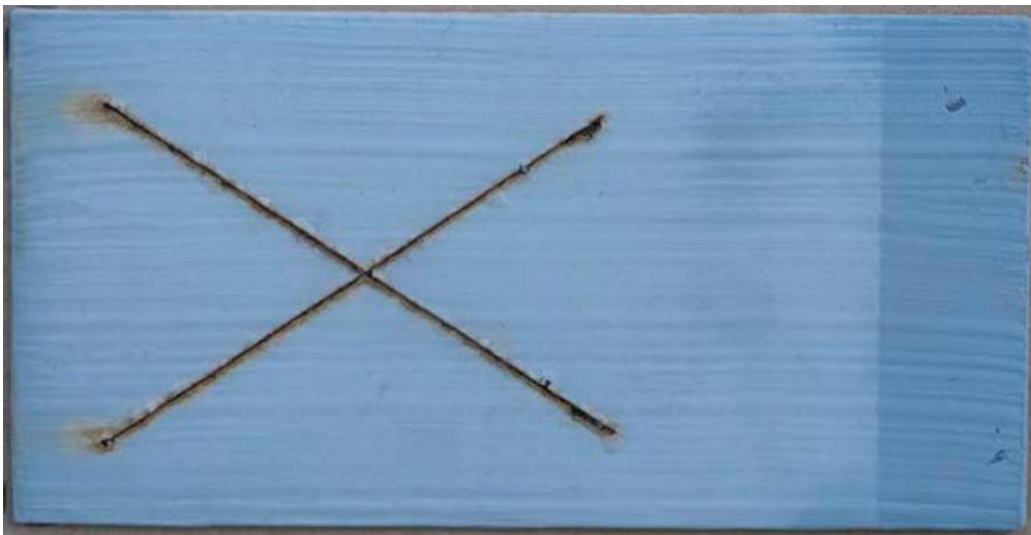
- zinc-rich epoxy/polyurethane,
- moisture-cured polyurethane/polyurethane,
- epoxy/polyurethane,
- moisture-cured polyurethane/acrylic,
- epoxy-polysiloxane copolymer/ epoxy-polysiloxane copolymer, and
- zinc-rich epoxy/epoxy-polysiloxane copolymer.

Three-coat systems included, from various manufacturers:

- zinc-rich epoxy/epoxy/polyurethane,
- zinc-rich epoxy/epoxy-polysiloxane copolymer/epoxy-polysiloxane copolymer, and
- zinc-rich epoxy/epoxy/epoxy-polysiloxane copolymer.

The parameters followed in this test were identical to those employed by NASA in their exceptionally harsh corrosion testing carried out in Cape Canaveral, Florida.

The test station owned by the utility that conducted the test is located on Melbourne Beach, 45 miles south of the test station used by NASA. This is the same beach on which the NASA test station is situated. As a result, both test stations experience identical UV radiation, wave break (salt spray) and weathering conditions. NASA and the utility both ran the test for the same three year duration with panels facing due south at a 45° angle.



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Coating: *Silicone polymer based coatings* One-coat system
PP

Details: self-priming, proprietary, 100% polysiloxane

DFT: 7 mils (178 microns) total

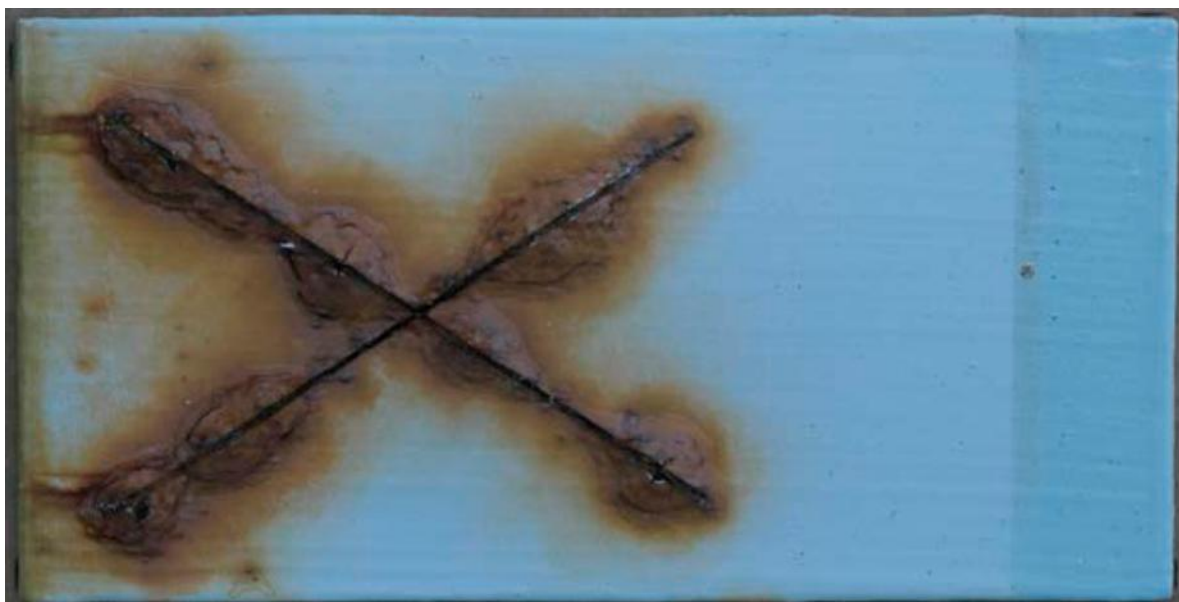
Observations: *Discoloration* = medium† *Loss of gloss* = 80.77%† *Rust creep* = none *Bleed-through rusting* = none *Pinhole rusting* = none *Adhesion loss* = none

Exposure: 36 months

† Loss of gloss and discoloration seen in photograph are due to unknown contaminants deposited on coating surface during testing and are not indicative of Silicone polymer based coatings polymer degradation as is common with epoxy coatings that exhibit chalking. Such surface deposits are unobserved on Silicone polymer based coatings in real applications extending beyond ten years service.

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Coating: *Two-coat acrylic system*

AA

Primer: waterborne acrylic emulsion *Finish coat*: water-reducible acrylic

DFT: 8 mils (203 microns) total

Observations: *Discoloration* = medium *Loss of gloss* = 94.79% *Rust creep* = heavy *Bleed-through rust* = slight *Pinhole rust* = slight *Adhesion loss* = medium

Exposure: 36 months



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Coating: *Two-coat polyurethane system*

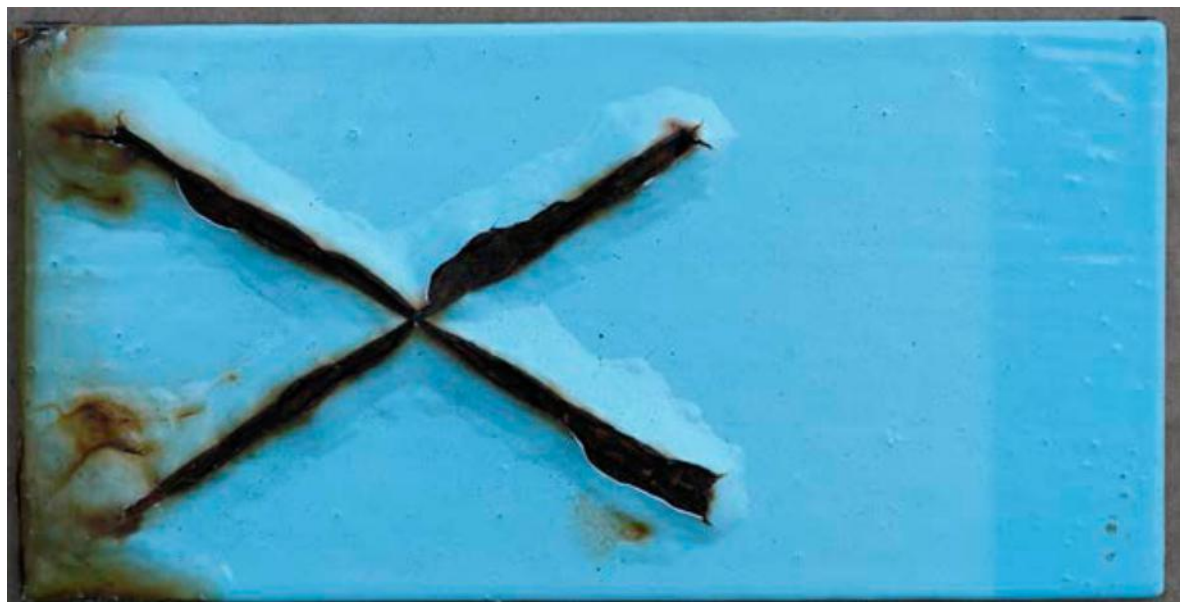
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Primer: micaceous iron oxide, one-component, moisture cure polyurethane *Finish coat*: one-component, aliphatic, moisture cure polyurethane

DFT: 8 mils (203 microns) total

Observations: *Discoloration* = heavy *Loss of gloss* = 81.75% *Rust creep* = very heavy *Bleed-through rust* = very heavy *Pinhole rust* = heavy *Adhesion loss* = heavy

Exposure: 36 months



Coating: *Two-coat epoxy-polysiloxane copolymer system*

FF

Primer: two-component, high solids epoxy *Finish coat*: two-component epoxy-polysiloxane copolymer

DFT: 12 mils (305 microns) total

Observations: *Discoloration* = slight *Loss of gloss* = 43.63% *Rust creep* = medium *Bleed-through rust* = medium *Pinhole rust* = none *Adhesion loss* = medium

Exposure: 36 months

Field Data

Escondida, Chile, Processing Plant

Product: Silicone RTV Coating for Corrosion

Color: Tennis Court Green (custom color match)

Location: Antofagasta, Chile

Date Installed: November 2016

Environment: High and low humidity, desert conditions, high altitude, high UV exposure, dry and extreme temperatures, high salinity.

Issues: OEM-coated structures with epoxy ended their service life cycle and need a more durable coating to endure such aggressive environmental conditions.

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CONCLUSIONS

Silicone RTV have proven to be able to withstand a variety of real world and accelerated testing for both corrosion protection and weatherability.

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