NOVEL HIGH SOLIDS SYSTEMS BASED ON SILICONE-EPOXY RESINS

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ABSTRACT

Silicone-Epoxy coatings are of increasing interest for the industrial, marine, and industrial maintenance markets due to their potential widespread applications. The epoxy component in the resin matrix offers the advantages of mechanical toughness and adhesion while the silicone component provides the coating with its hardness and UV stability properties. This paper will present an overview of the development of the silicone-epoxy systems which offer an environmentally friendly alternative to existing anti-corrosion coatings. In this study, novel coatings technology has been formulated on the basis of silicone-epoxy systems combining outstanding weathering resistance with excellent chemical resistance in a two-pack system. The use of silicone-epoxy resins enables formulation of isocyanate-free coatings with a VOC content below 100 g/L. The anticorrosive, mechanical and weathering properties of the primers and top-coat systems have been studied and compared to the current commercial systems using testing aspects like adhesion to steel substrates, flexibility and hardness, UV resistance, and improved anticorrosive properties.

Introduction

Corrosion protection for the industrial, industrial maintenance and marine markets can be an expensive and overwhelming task. Protecting objects such as oil platforms, bridges, storage tanks, steel structures, concrete walls and floors, and ship decks from corrosion requires high costs and intensive investment of labor. One of the best methods to protect objects from corrosion is by the use of protective coatings.

Coatings provide corrosion protection by one or a combination of three basic mechanisms. These mechanisms are:

- Barrier
- Inhibitive
- Sacrificial

The first mechanism may act as a physical barrier between the substrate and its environment by keeping oxygen and moisture away from the substrate. Examples of these coatings are coal tar enamels and vinyl coatings. The second mechanism may act as an inhibitive coating by passivating the metal and interfering with the corrosion process. Examples of these coatings are mostly based on epoxies and urethanes. The final mechanism may be a sacrificial coating which will corrode instead of the metal or steel structure. Examples of these coatings would be zinc-rich or metallized.

Coatings systems can be classified as organic or inorganic in nature. Coatings systems used in the protective coatings industry traditionally rely on organic resin systems. Due to the variety of properties needed, a multiple coat system is usually required. An example of a multiple coat system may be a zinc-rich primer, an epoxy mid-coat and a polyurethane top-coat. This enables the formulator to provide multiple levels of protection by utilizing the sacrificial protection of the zinc-rich primer, the corrosion resistance of the epoxy, and the weather resistance of the urethane topcoat.

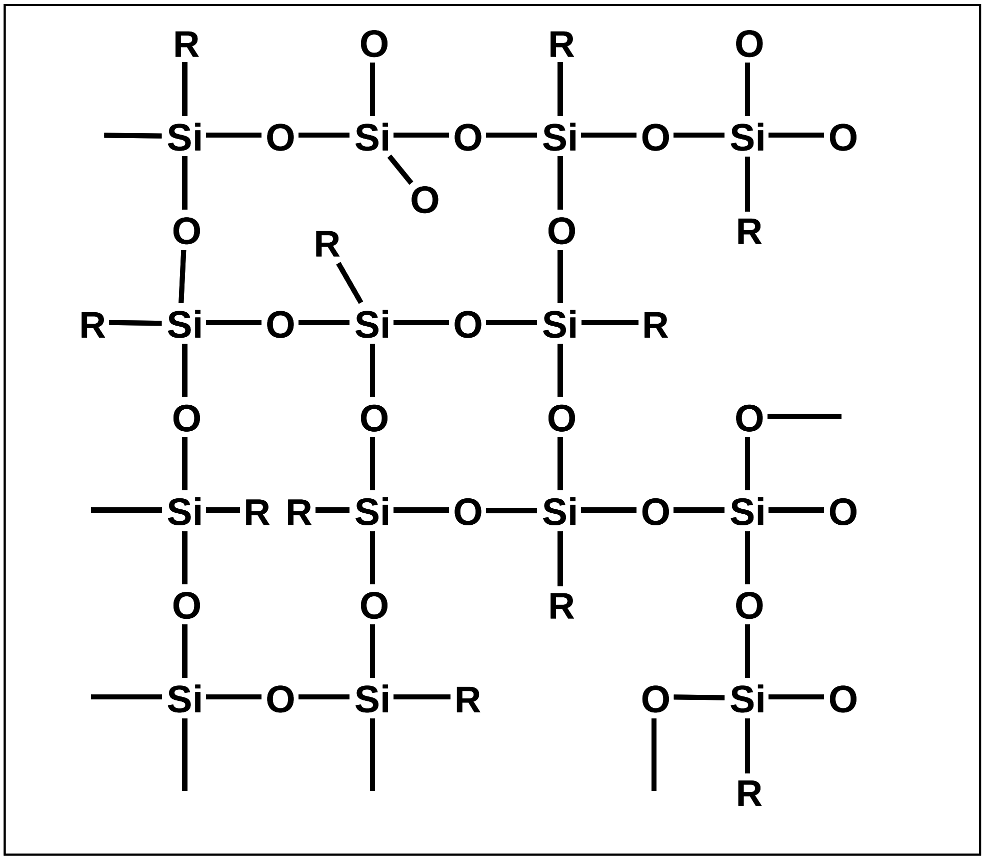
By exploring inorganic silicone based chemistry, a silicone-epoxy hybrid polymer has been developed which combines the properties of organic and inorganic compounds into a new class of resins for protective coatings. This paper will discuss the benefits of the novel silicone-epoxy resin systems.

Polysiloxane Chemistry

As mentioned earlier, most protective coatings are based on organic resin systems. Unfortunately, these organic coatings are subject to degradation by thermal and photo-induced oxidation as well as chemical attack. The silicone inorganic systems are much more resistant to these degradation mechanisms.

These silicone inorganic resin structures as seen in Figure 1 are comprised of polysiloxanes due to the stable $[-(Si\text{-}O)_n\text{-}Si\text{-}]$ backbone. The Si-O inorganic groups in the polymer backbone provide a bond strength of 108 kcal/mole compared to the C-C organic bond strength of only 83 kcal/mole. The higher energy needed to break apart the Si-O bond compared to the C-C bond gives improved resistance to weathering and thermal degradation. Because the silicone is already oxidized, it is not subject to the same oxidative degradation that affects the C-C bonds.

Figure 1. Example of a Typical Silicone Resin Structure



Silicone resins exhibit properties and characteristics that make them an excellent component for protective coating technology. Some of these properties include:

- Thermal Stability
- Weather and UV Resistance
- Color Stability
- Low Surface Tension
- Hydrophobic Nature
- Excellent Release Properties
- Good Insulator
- Low Influence on Health

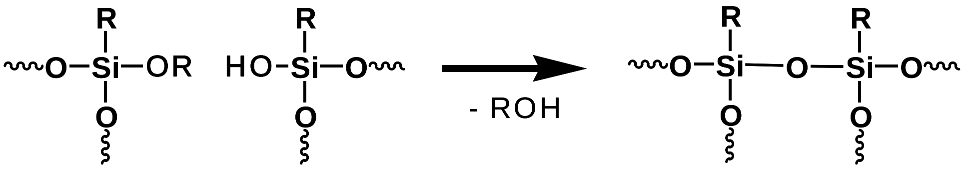
Coupled with an organic component, the properties can be improved even further. The next section outlines the combination of the inorganic polysiloxane and the organic epoxy polymer to achieve improved protective coating characteristics.

Silicone-Epoxy Resins

Silicone-Epoxy systems are generally referred to as “hybrid coatings” due to the organic epoxy functionality coupled with the silicone inorganic functionality. The term "hybrid coating" reflects the nature of two binder systems having distinct properties and curing mechanisms that work together to form one novel resin system.

In this polymer system, the siloxane forms the matrix with epoxy and alkoxy functionality in the side chains. The novel chemistry of the silicone-epoxy polymer is achieved by the condensation reaction of an aliphatic epoxy with a polysiloxane. As discussed with the "hybrid" nature of the polymer, two reactions take place. The amine group of the aminosilane cures the epoxy resin in a typical manner. At the same time a competing polycondensation reaction takes place with the silicone alkoxy groups of the hardener and resin. The silanol condensation reaction is shown in Figure 2 below.

Figure 2. Example of a Silanol Condensation Reaction

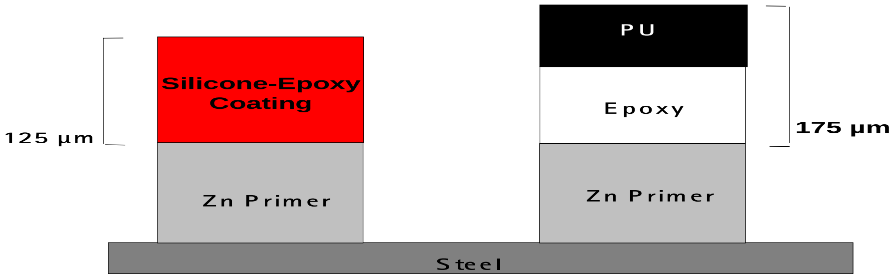


The advantages of the epoxy combined with the strength of the polysiloxane provide for a two-component ambient cure thermoset coating. The low viscosity of this polymer allows for the formulation of a low VOC, high solids, non-isocyanate coating.

Results and Discussion

A major focus in the protective coatings market is to reduce material and labor costs while maintaining corrosion resistance. We tested a two-coat system consisting of 75 microns zinc-rich primer top-coated with 125 microns of a silicone-epoxy coating. This was compared to the traditional three-coat system consisting of 75 microns of a zinc rich primer, 125 microns of an epoxy mid-coat, and 50 microns of a polyurethane top-coat (Figure 3).

Figure 3. Comparison of Test Coatings



This paper encompasses two different experiments. The first experiment was to evaluate how the two-coat zinc rich primer/silicone-epoxy technology performed against the traditional three-coat zinc rich primer/epoxy mid-coat/urethane top-coat technology. The second experiment determined the performance of the first generation silicone-epoxy technology against the more flexible second generation silicone-epoxy technology. The main difference between the first generation silicone-epoxy and the second generation is the alkoxy content on the silicone side. These changes are evident in the number of alkoxy units as well as the types of alkoxy groups used. Both experiments utilize the same starting point formulation shown in Figure IV. In experimentation, it should be noted that the traditional system utilized the standard 250 microns of coating thickness as compared to the cost saving 200 microns associated with the silicone-epoxy system.

Figure IV. Two-Component Silicone-Epoxy Coating Formulation

1. Component A:	Wt.%
Silicone-Epoxy Resin	32.4
UV Light Stabilizer	1.0
Deaerator	0.5
Titanium Dioxide	26.1
Micro Talc	2.0
Silica	1.0
Butyl acetate	5.0
Grind to Hegman 7+	
Silicone Epoxy Resin	32.0

2. Component B: (Hardener)	Wt.%
Aminosilane	16.0

Solvent 5 %!

As you can see from the starting point formulation, very little solvent was used. Other solvents such as t-butyl acetate or acetone may be substituted in place of butyl acetate to even further lower the VOC content. The silicone-epoxy resin exhibits a low viscosity at a nonvolatile content by mass of approximately 98%. Due to the high solids content and low viscosity, a sprayable formulation may be achieved with a minimal amount of solvent allowing the formulator to achieve a VOC content of less than 100 g/L.

A number of different experimental tests were examined to determine the performance of the two different silicone-epoxy resin systems as well as the traditional three-coat systems used in protective coatings. The comparative tests performed include physical properties, chemical resistance, resistance to corrosion via salt spray and humidity testing, Florida exposure and QUV testing for weatherability.

The physical properties were evaluated with both the first and second generation silicone-epoxy resins. This was able to give us an impression of how the modification of the alkoxy content would influence the formulated protective coating properties. The physical properties are listed below in Table I.

Table I. Physical Properties

Test Properties	Zinc Primer Silicone-Epoxy *First Generation* 200 Microns Dried	Zinc Primer Silicone-Epoxy *Second Generation* 200 Microns Dried
Pot life (25°C)	4.5 hours	5.5 hours
Drying time	Touch dry: 4 hours Through dry: 8 hours	Touch dry: 5 hours Through dry: 9 hours
Gloss (60°)	87	92
Hardness	Pencil: F Pendulum 1 Day: 27 Pendulum 35 Day: 115	Pencil: F Pendulum 1 Day: 13 Pendulum 35 Day: 106
Recoat time	Minimum: 6 hours Maximum: 48 hours	Minimum: 6 hours Maximum: 48 hours
Adhesion to primer	Crosshatch: 4B-5B	Crosshatch: 5B

As seen from the physical property table, the second generation resin system exhibits better initial gloss, crosshatch adhesion, and a longer pot life. The first generation has a higher development of hardness as well as a shorter cure time. This data helped confirm the theory that the modification of the alkoxy content was able to develop a more flexible second generation silicone-epoxy resin. Recoat time is also an important characteristic of these coatings. As you can see from the 48 hour recoat window of the system, silicone-epoxy systems exhibit a certain degree of anti-graffiti properties due to the high crosslink density and the siloxane backbone. Therefore, as the crosslink densities of these systems build, the more difficult it is to apply multiple coats. Although the recoat time can make it difficult for the novice applying silicone-epoxy technology to a structure, these anti-graffiti properties are of benefit to many formulators for steel structures, bridges, rail cars, and other industrial and industrial maintenance coatings.

Chemical resistance plays a crucial role in determining the performance of protective coatings. Protective coatings are not only exposed to rust and corrosion but also a number of different acids, bases, and solvents. Table II illustrates the differences between the traditional technology and the novel silicone-epoxy approach. This table also compares the first generation silicone-epoxy to the second generation to determine if any benefit or decrease in performance is seen by changing the alkoxy content.

Table II. Chemical Resistance

Test Method Chemical DIN 68 861	Zinc Primer Silicone-Epoxy *First Generation* 200 Microns Dried		Zinc Primer Silicone-Epoxy *Second Generation* 200 Microns Dried		Traditional Zinc Primer Epoxy Urethane 250 Microns Dried	
Chemical	24 Hrs	7 Days	24 Hrs	7 Days	24 Hrs	7 Days
Sodium Hydroxide 50%	2	3	2	3	2	5
Ammonium Hydroxide, conc.	2	3	2	3	3	4
Hydrochloric Acid 1M	1	3	2	4	2	5
Sulfuric Acid 1M	3	3	2	3	4	6
Nitric Acid 1M	2	3	2	3	4	6
Citric Acid 1M	1	1	1	2	2	3
Acetic Acid 1M	2	3	2	4	2	4
Acetone	1	1	1	1	1	1
MIBK	1	1	1	1	1	2
Xylene	1	1	1	1	1	1
Butyl Acetate	2	2	2	2	2	2
Ethyl Alcohol	1	1	1	1	1	1
Mineral Spirits	1	1	1	1	1	1
Crude Oil DRO	1	1	1	1	1	1

Note: Substrate: Bare Steel
Substrate Preparation: Sand Blasted to SA 2.5
Cure Before Test: 10 Days Air Dry at Room Temperature
Testing: After 24 Hours and 7 Days
Rating: 1 (Excellent), 3 (Fair), 6 (Poor)

As seen in the table above, the silicone-epoxy coating systems outperformed the traditional three-coat system with regard to chemical resistance with most acids and bases. It can also be seen that in testing various solvents, equal outstanding performance was observed. The differences in chemical resistance were more pronounced when it came to seven day testing. There was only a minor decrease in chemical resistance of acids in the second generation resin but it still outperformed the traditional three-coat system.

Other important properties of the protective coating systems include the salt spray, humidity, and QUV testing. These tests show the ability for each coating system to withstand the elements and to protect against environmental factors such as corrosion and light. Tables III, IV, and V show the results of these tests.

Table III. Salt Spray Testing

Test Method Salt Spray Test DIN 53 210 (Rust Grade)	Zinc Primer Silicone-Epoxy *First Generation* 200 Microns Dried	Zinc Primer Silicone-Epoxy *Second Generation* 200 Microns Dried	Traditional Zinc Primer Epoxy Urethane 250 Microns Dried
2000 Hours	2	2	1-2

Note: Substrate: Bare Steel
Substrate Preparation: Sand Blasted to SA 2.5
Cure Before Test: 10 Days Air Dry at Room Temperature
Rating: 0 (No Rust), 5 (Total Rust)

Table IV. Humidity Testing

Test Method Humidity Test DIN 50 021	Zinc Primer Silicone-Epoxy *First Generation* 200 Microns Dried	Zinc Primer Silicone-Epoxy *Second Generation* 200 Microns Dried	Traditional Zinc Primer Epoxy Urethane 250 Microns Dried
5000 Hours	1	1	1-2

Note: Substrate: Bare Steel
Substrate Preparation: Sand Blasted to SA 2.5
Cure Before Test: 10 Days Air Dry at Room Temperature
Rating: 1 (Excellent), 5 (Poor)

Table V. QUV Weathering/Gloss Retention

Test Method QUV B 3000 Hours Cycle: 4 Hrs/4 Hrs	Zinc Primer Silicone-Epoxy *First Generation* 200 Microns Dried	Zinc Primer Silicone-Epoxy *Second Generation* 200 Microns Dried	Traditional Zinc Primer Epoxy Urethane 250 Microns Dried
Initial Gloss (60°)	80.1	89.2	90.3
Gloss After 3000 Hrs	26.1	36.8	9.5
ΔE After 3000 Hrs	4.0	4.8	10.5
Chalking	1	1	5

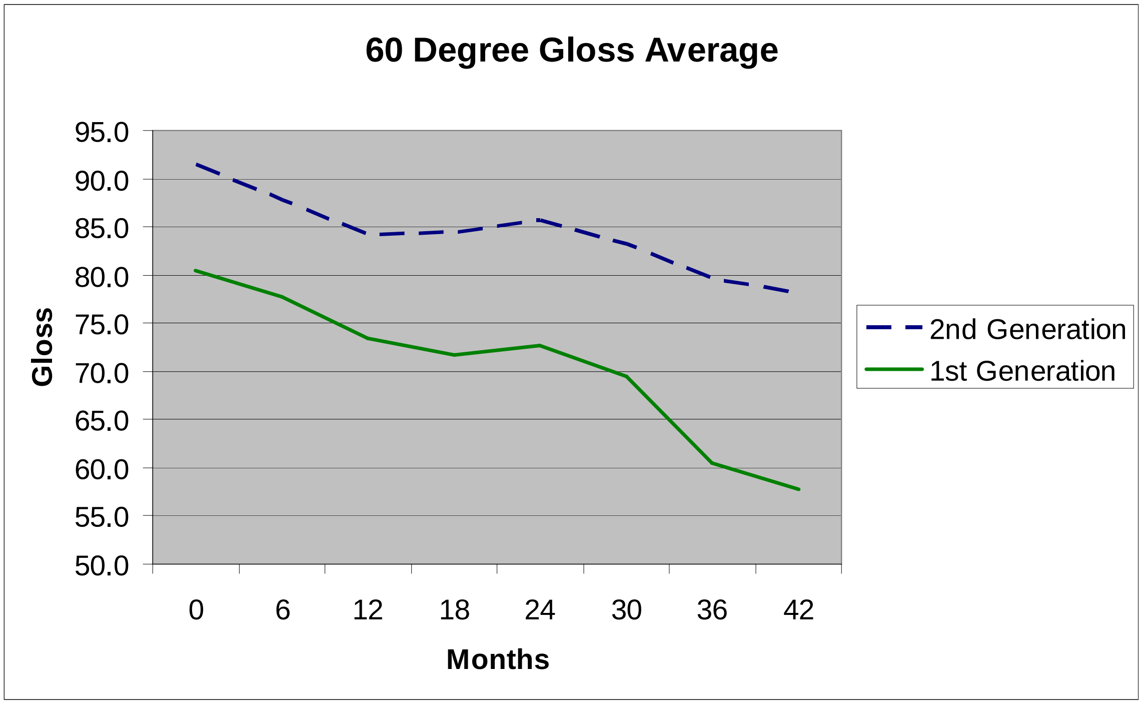
Note: Substrate: Bare Steel
Substrate Preparation: Sand Blasted to SA 2.5
Cure Before Test: 10 Days Air Dry at Room Temperature
Rating: 1 (Excellent), 5 (Poor)

As seen in the three tables above, both generations of silicone-epoxy resins outperform the traditional system with regard to QUV gloss retention, chalking, ΔE, and with regard to humidity testing. The traditional system slightly outperforms the silicone-epoxy technology with regard to salt spray.

When comparing the first and second generation silicone-epoxy resins, the salt spray and humidity testing were very similar. The main differences found were in QUV testing. The initial gloss of the second generation resin has a higher initial gloss and seems to maintain slightly higher gloss retention after 3000 hours of QUV-B testing. The ΔE of the first generation is slightly better for color retention.

Although many other experiments and studies were performed, the final study worth noting is the weathering data. Salt spray, humidity, and QUV-B are all great forms of accelerated testing but sometimes they do not show realistic and reliable data. Often, the accelerated testing does not directly correspond to real world exposure. As a result, we decided to prepare these two silicone-epoxy systems in the same experimental starting point formulation and submit for Florida exposure testing. Currently 42 months of Florida exposure has been completed. The following figures will show the performance of the first and second generation silicone-epoxy systems.

Figure V. 60° Gloss for Silicone-Epoxy Systems – Florida Exposure



As seen from Figure V above, the second generation silicone-epoxy system starts at a higher initial gloss. As you may recall, this was also seen in the QUV-B data. After 42 months of exposure, the second generation system also continues to maintain a much higher gloss level than the first generation resin.

Figure VI. 60° Gloss Retention for Silicone-Epoxy Systems – Florida Exposure

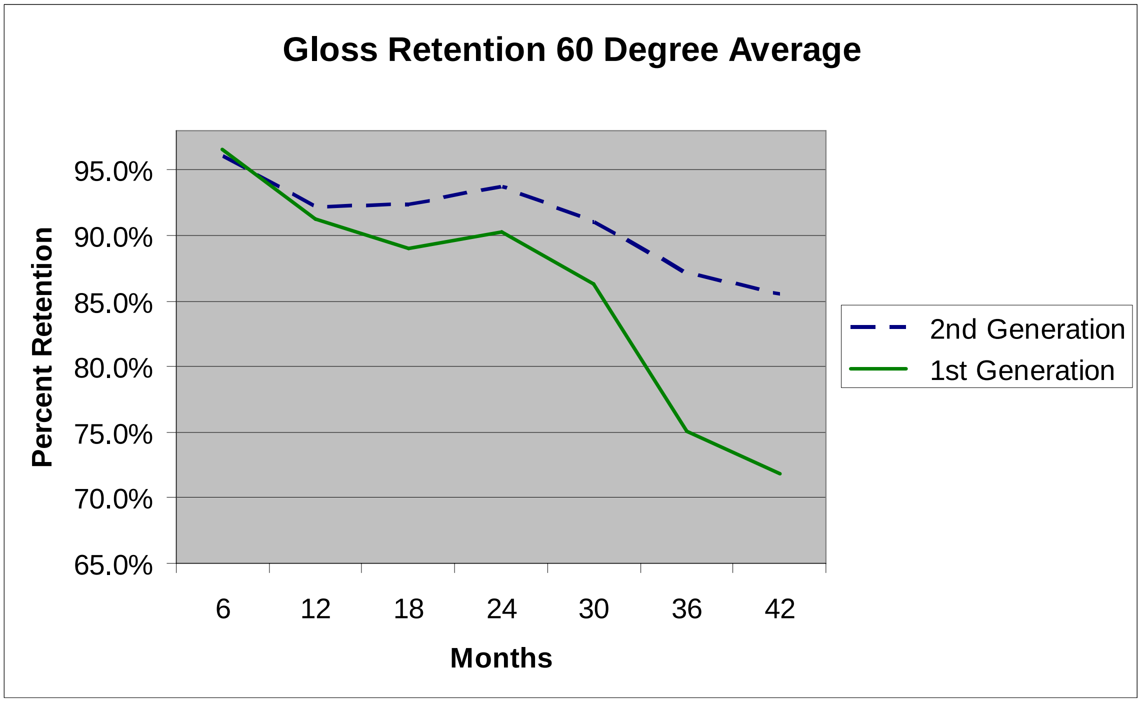
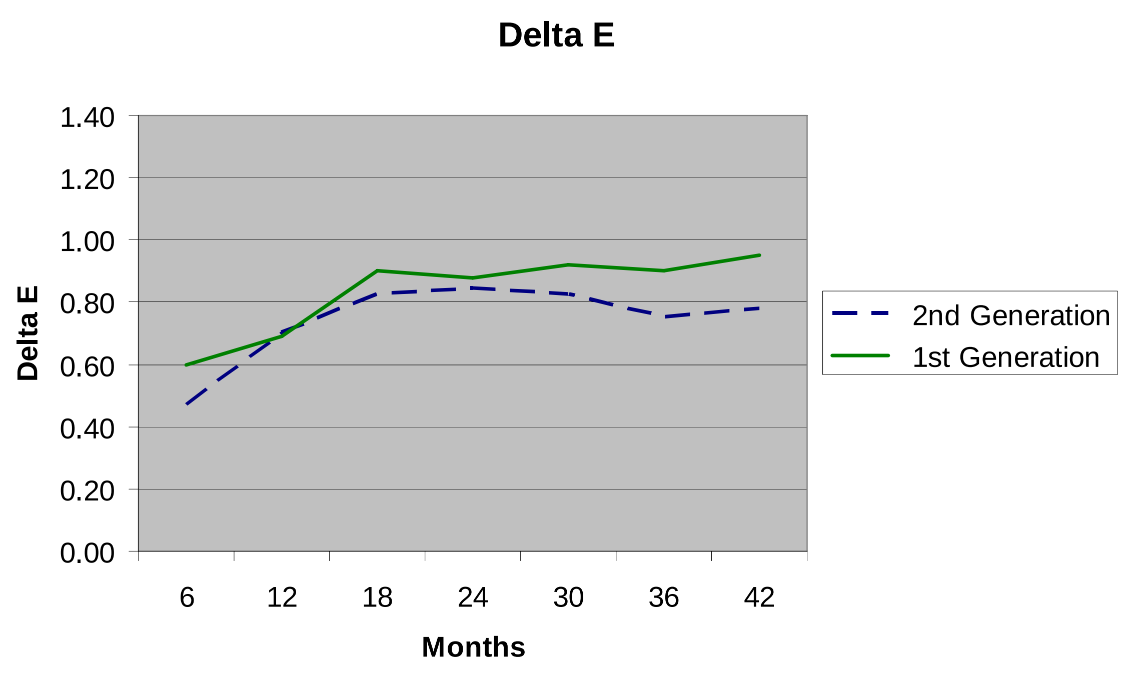


Figure VI above shows exactly what we expected with regard to gloss retention. Gloss retention is much greater for the second generation system than for the original silicone-epoxy system developed.

The final aspect we will look at for Florida exposure will be with regard to ΔE and color retention over the 42 month time frame. Equally as important as the protective nature of the coating is the appearance. As seen in Figure VII below, the color retention was excellent. The ΔE of both silicone-epoxy systems was outstanding. Both systems exhibit a ΔE of less than 1 after a severe level of outside exposure. Although not included in this paper, it should be noted that the Florida exposure of this silicone-epoxy technology outperforms most other competitive technological platforms we have tested.

Following the trend of the gloss numbers in the charts above, the second generation silicone-epoxy outperforms the first generation with regard to ΔE. The difference between both resins, in this regard, is much more subtle with a difference of approximately 0.2 after 42 months.

Figure VII. **ΔE for Silicone-Epoxy Systems – Florida Exposure**



Conclusion

The novel “hybrid” chemistry achieved by combining an aliphatic epoxy with a polysiloxane allows the formation of a silicone-epoxy resin that performs better than an organic or inorganic polymer alone. This allows for a durable binder for the protective coatings industry. The first experiment shows the benefits of a two-coat system over the traditional three-coat system while the second experiment shows how modifying the alkoxy content can achieve performance improvements with a more flexible system. Due to this novel class of material, the following performance benefits are observed:

- High Volume Solids
- Low VOC
- Excellent Color and Gloss Retention
- Excellent Corrosion Resistance in Two-Coat Systems
- Cost Effective Two-Coat Alternatives to Multiple-Coat Systems
- Compliance with Health and Safety
- Isocyanate Free
- Excellent Chemical Resistance
- Provides a Degree of Anti-Graffiti Properties
- Tolerance to High Humidity due to Nature of Curing Mechanisms

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