

Next Generation Coatings Update on Engineered Siloxane Hybrid Coatings

Summary

Over recent years engineered siloxane hybrid coatings have become established as the ultimate in durability and weather resistance for protective coating systems. Since their introduction in the mid 1990s polysiloxane topcoats have been used on numerous major projects worldwide for marine, offshore and onshore facilities. Research and development in the area of polysiloxane coatings chemistry has continued unabated and has resulted in the evolution of an even greater number of polysiloxane hybrids. This paper discusses these new inorganic-organic hybrids with details of their performance characteristics and their potential uses in protective coating systems.

Introduction

The chemistry and performance of polysiloxane hybrid coatings is well documented with a significant number of publications, papers and patents available not only from within the coatings industry but from other scientific establishments, institutes, universities and other seats of learning. This area of research has been one of the most rapidly expanding within the coatings industry over recent years. Their introduction provided the first new generic type of protective coating for over 25 years, since the introduction of polyurethanes for such coatings. Their superior durability, high solids, low VOC and non-isocyanate curing mechanisms have made them ideal as cost effective alternatives to polyurethane topcoats as well as epoxy-acrylics and other high weather resistant coatings, for example fluoropolymers.

In protective coating systems the use of a single high build polysiloxane topcoat to replace the standard two coat epoxy intermediate/polyurethane over a zinc rich primer has been proven both in the laboratory and in the field.

Test Description 3000 hours testing	Epoxy zinc/Epoxy siloxane @ 75/125 μm	Epoxy zinc/HB epoxy/PU @ 75/200/50 μm
Salt spray ISO 7253 - Scribe blistering ASTM D1654/A - Blistering/Rusting	2mm None/Ri0	2.5mm None/Ri0
Cyclic ISO 20340 Procedure A - Scribe blistering ASTM D1654/A - Blistering/Rusting	4mm None/Ri0	5mm None/Ri0
Cyclic ASTM D5894 - Scribe blistering ASTM D1654/A - Blistering/Rusting	2.5mm None/Ri0	2.5mm None/Ri0

Table 1: Comparison of performance of a 2 coat zinc rich epoxy primer/polysiloxane topcoat system against a 3 coat zinc rich epoxy primer/epoxy intermediate/polyurethane topcoat system.

Not that 2 coat systems can be without their flaws. Experience has shown that when applying a 2 coat system much greater care is needed to ensure adequate film thickness is achieved, particularly at edges.

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Stripe coating is good practice with any protective coating system and particular attention is required in this area for a 2 coat system. However even with this increased attention needed during application, the advantages of applying 2 coats instead of 3 coats and being able to provide an improved level of durability and performance provides significant reduction in both application and life cycle costs.

Polysiloxane binders themselves are insufficient in providing the all round properties required from a protective coating. Organic modification of the polysiloxane is necessary to achieve a balance of film properties, such as adhesion and flexibility. An optimum level of organic modification of around 20-30% has been identified to achieve this balance.

Present polysiloxane coatings technology

Aliphatic epoxy modified polysiloxane coatings have been commercially available since the mid 1990s and over 5 million square metres have been coated in Europe alone. More recently 2 pack acrylic modified polysiloxanes have also been introduced.

Test Description	Epoxy Siloxane	Acrylic Siloxane
Volume Solids ISO 3233	90%	76%
VOC EPA Method 24	120 g/l	172 g/l
Drying Times ASTM D1640		
Touch at 21°C	1 hr	4 hrs
Touch at 4°C	4 hrs	8 hrs
Through at 21°C	3 hrs	10 hrs
Through at 4°C	16 hrs	24 hrs
Pendulum Hardness ASTM D4366		
@ 7 days	78	33
@ 14 days	101	57
@ 21 days	103	60
@ 35 days	110	71
Direct Impact ASTM D 2794	48 lbs/sq.in.	42 lbs/sq.in.
Corrosion Resistance 3000 hours (125 µm over 75µm epoxy zinc rich) Salt spray ISO 7253		
- Creep	0.5mm	0.5mm (blisters 2 S4)
- Blistering/Rusting	0/Ri0	Blisters 2 (S2)/Ri0
Prohesion ASTM G85		
- Creep	0mm	0mm
- Blistering/Rusting	0/Ri0	0/Ri0
Cleveland Humidity ASTM D2247		
- Creep	0mm	0mm
- Blistering/Rusting	Blisters 4 (S2)/Ri0	Blisters 4 (S4)/Ri0

Table 2: General properties of typical examples of commercially available siloxane hybrids
Comparison of both these coating types and their performance characteristics have been carried out in detail. It could be concluded that both these hybrids have their relative merits. The epoxy siloxane shows higher solids and lower VOC, more rapid cure and hardness development. The acrylic siloxane shows

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improved UV resistance. Corrosion resistance of the epoxy siloxane is better in high humidity conditions. However in terms of impact resistance the data shows that when fully cured both materials show similar characteristics.

New Engineered Siloxane Hybrids

The versatility of siloxane chemistry allows the formation of siloxane hybrids with a large range of organic polymers. The original aliphatic epoxies and latterly acrylic siloxanes provide excellent performance as protective coatings. However combinations with vinyls, aceto acetates, fluoropolymer, elastomeric epoxy and phenol binder systems have also been developed. Self-curing siloxane hybrids also show potential. These new hybrids not only serve to improve the current polysiloxane coatings but also provide potential to expand their use in areas such as tanklinings, adhesives, flooring systems, laminates and single pack high solids, high build maintenance coatings, further expanding the limits of their performance.

Flexibilised epoxy siloxane hybrids

Although polysiloxane coatings exhibit excellent performance properties, as with nearly all coatings, application of excessive thickness can result in problems associated with shrinkage of the applied coating as it cures. This shrinkage imparts stresses within the coatings leading to reduction in properties such as impact resistance and flexibility. Investigations have been carried out to improve the tolerance of the epoxy siloxane hybrids to variations in applied dry film thickness. A variety of experimental modifications to epoxy siloxane formulations have resulted in some interesting improvements in both flexibility and impact resistance. The results show high increases in these properties with little compromise in film hardness development. These improvements have been made possible by varying the functionality of both the epoxy silicone and aminosilane within the formulation. This means that the internal flexibility of the crosslinked structure is increased and the improvement is not reliant on external plasticisation.

Test Description	Flexible epoxy siloxane	Control
Direct Impact ASTM D2794 4 weeks at 22°C	160 lb/sq.in.	90 lb/sq.in.
Reverse Impact ASTM D2794 4 weeks at 22°C	22 lb/sq.in.	2 lb/sq.in.
Elongation ASTM D522 2 weeks at 22°C	>27%	18%
Hardness development		
- 7 days	18	18
- 14 days	36	43
- 28 days	70	86
- 35 days	78	95

Table 3: Comparison of properties of flexible epoxy siloxane against control

Fluorinated epoxy siloxane hybrids

Coatings formulated with these hybrids show superior durability. The use of fluoropolymers for highly weather resistant coatings is well known, however they tend to be relatively low solids and high VOC products. This approach provides the UV resistance of the fluoropolymer together with the high solids and low VOC of the epoxy siloxane. Results of accelerated testing provide between 20-50% improvement in weatherability over the aliphatic epoxy polysiloxane and even better than the acrylic siloxane materials. This improvement is achieved with no compromise on the corrosion resistance afforded by epoxy siloxane material. The level of improvement is dependant on the type of fluorinated species used to modify the epoxy siloxane and a number of modifications have been tested.

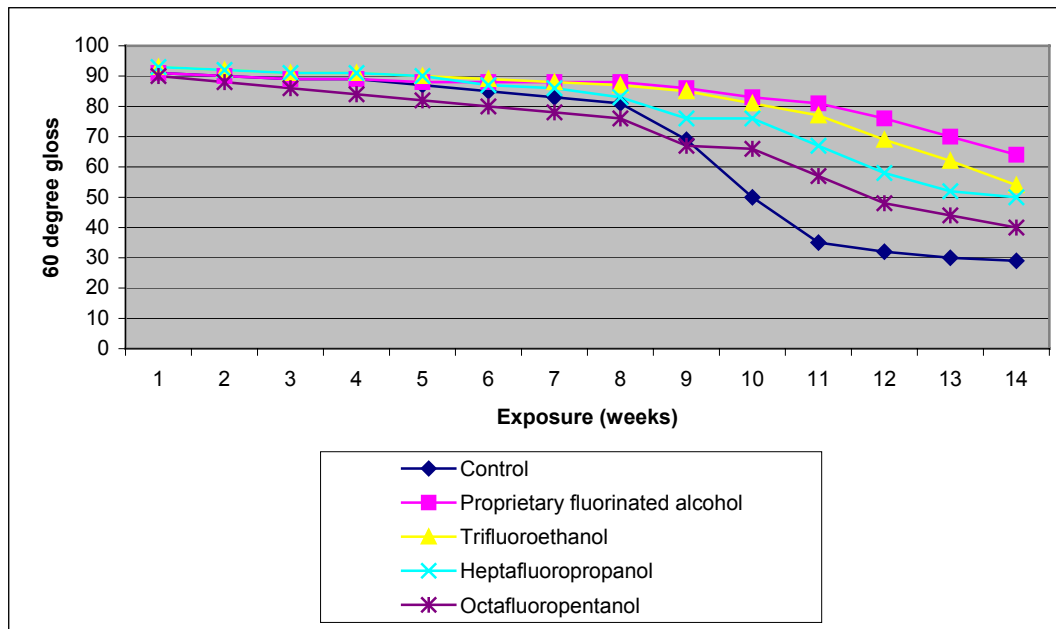


Figure 1: Comparative QUV-B data of pigmented fluorinated epoxy siloxane hybrids

Single pack high solids siloxane hybrids

Self-curing polysiloxanes offer advantages over 2 pack materials. As single component materials they lend themselves to easier application with no need for mixing, no restrictions in application time due to pot-life and also no waste from unused, catalysed material. In this respect these coatings are ideal for use in maintenance situations, particularly for brush and roller application in difficult access areas. A medium solids, high VOC self-curing acrylic siloxane material has been commercially available in the last 2 years. Further development of this technology has resulted in the formulation of a higher solids material with a potential VOC below 250g/l and volume solids around 80%. Improvement in weatherability over the lower solids acrylic siloxane materials was in the range of 20%.

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Test description	First generation 1 pack acrylic siloxane	Second generation 1 pack acrylic siloxane
Volume Solids ISO 3233	55%	80%
VOC EPA Method 24	384 g/l	262 g/l
Viscosity Kreb Units	80 ku	79 ku
QUV-B Weathering		
60° gloss, initial	84	90
60° gloss, 3 weeks	81	88
60° gloss, 6 weeks	75	86

Table 4: Comparison of properties of single pack acrylic siloxane hybrids

Elastomeric epoxy siloxane hybrid

These hybrid coatings exhibit excellent chemical resistance to acids, alkalis and solvents, together with excellent mechanical properties. They show potential as alternatives to MDA and aromatic amine containing epoxy coatings which are generally used where all round chemical resistance is desired. Elastomer modification is brought about by the introduction of carboxyl terminated butadiene-acrylonitrile (CTBN) epoxy resin. The curing agent is formed by the blending of aminosilane and aliphatic amine. These formulations provide not only outstanding chemical resistance but also excellent resistance to thermal cycling and cracking. The coatings provide solutions for chemical process, secondary containment and other industries where a high level of chemical resistance is required.

Conclusion

Engineered siloxane hybrid coatings are the first new generic coating type to be introduced to the protective coatings industry since polyurethanes more than 25 years ago. Since commercialization in the 1990s their use has grown rapidly and their performance proven. However the potential for the development of further siloxane hybrids is vast and new products continue to evolve. These new hybrids have been shown to provide improvements on the currently available materials and provide potential for use where previously polysiloxane coatings were restricted.