Polysiloxanes

Norman R. Mowrer
Ameron International
Performance Coatings and Finishes

Inorganic silicon based polymers are inherently resistant to temperature, ultraviolet light and oxidation and are used as coating binders in the formulation of heat resistant silicones and zinc silicate primers. Many attempts have been made to utilize this chemistry to improve the properties of both inorganic and organic coatings. Progress has been slow primarily because of problems associated with film formation and the inability to obtain a balanced set of performance properties. Recent advances in siloxane chemistry and formulation technology have led to the development of ambient temperature curable polysiloxane coating systems with significant advantages compared to traditional inorganic and organic coatings.

Polysiloxanes are generally recognized as the newest generic class of high performance protective coating and include coating types based on inorganic siloxane and organic-inorganic siloxane hybrids.

Polysiloxane coatings based on pure inorganic siloxane binder are curable at ambient temperature and have high solids and low VOC, excellent temperature resistance and good resistance to certain acids and solvents. They are well suited for high-heat and selected chemical lining applications. Semigloss highly weatherable topcoats have also been formulated using this technology.

Polysiloxanes based on organic-inorganic siloxane hybrid binders have high solids and low VOC and provide an improved level of performance compared to traditional organic coating systems. Acrylic siloxane hybrids have superior weatherability and offer a cost effective, isocyanate-free alternative to aliphatic polyurethane topcoats. The epoxy siloxanes have very high solids and low VOC. They have outstanding resistance to corrosion and better weatherability than aliphatic urethane. These properties allow a single coat of epoxy siloxane to replace the standard 2-coat, epoxy/urethane system currently used over zinc rich primer systems. Elimination of the extra coat and the superior durability of the epoxy siloxane system provide lower application and life cycle costs compared to the traditional zinc/epoxy/urethane 3-coat systems.

TERMINOLOGY

For clarity, **Table 1** gives definitions of the chemical terminology used in this chapter. In coating compositions, the typical resins containing the silicon-oxygen bond as repeating unit in the backbone are silicates, silicones, oxysilanes and siloxanes.

Silicates are binders based on alkali metal salts of silicon-oxygen anions. Silicones are siloxane polymers with predominately two organic substituents on the silicon atom.

Oxysilane generally refers to silicon-based structures in which silicon is bonded with up to four alkoxide or hydroxyl groups, which enable certain condensation reactions. Oxysilanes can be monomeric or polymeric.

Silanes are monomeric silicon compounds with four substituents, or groups, attached to the silicon atom. These groups can be the same or different and nonreactive or reactive, with the reactivity being inorganic or organic. Inorganic reactive silanes have alkoxysilane groups and undergo hydrolytic polycondensation reactions. Organic reactive silanes contain amine, vinyl, epoxy, isocyanate or other functional groups that enable reactions with organic functionalities.

The term polysiloxane can include silicones but it is used herein in its broadest sense, that is, any polymeric structure that contains repeating silicon-oxygen groups in the backbone, side chains or cross links regardless of the substitution on the silicon atom. The presence of certain organic groups attached to the silicon atom in silicone and polysiloxane binders moderates physical, mechanical and chemical properties, typically in an advantageous way.

HISTORY

Inorganic Siloxane Coatings

Inorganic silicon based polymers have been used as coating binders for more than 50 years and there are a number of excellent reviews on the subject[1,2,3]. Heat curable zinc silicate primers were first introduced in the 1940's. Waterborne zinc silicate primers that required post-cure with acid solution were commercialized in the 1950's. Solvent based, ambient cure zinc-rich ethyl silicate primers became available in the 1960's. Zinc silicates provide the highest level of corrosion protection.

Silicone based coating formulations were developed during the same time period. The principal applications for these coatings included protective coatings for exhaust stacks, heat exchangers, boilers, ovens and furnaces, mufflers, cookware and aircraft components.

Silicate binders are not considered acceptable for broad use in coatings because of their poor film properties. Heat curing limited the practicality of silicone coatings, particularly on large structures.

A significant advance was made in 1978 with the introduction of ambient cure binders based on the hydrolysis of trialkoxysilane[4]. Subsequent development of new silane and silicate precursors led to formulation of polysiloxane coatings with improved film properties. Well formulated polysiloxane coatings based on these binders are capable of providing long term resistance to heat in excess of 1400F (760C) and are resistant to continuous immersion in virtually all solvents and most organic and mineral acids.

Organic - Inorganic Siloxane Hybrid Coatings

The first specification and earliest example of hybrid organic-inorganic coating is TT-E-490 (Enamel, Silicone Alkyd Copolymer). It was replaced by MIL-E-24635 (Enamel, Silicone Alkyd Copolymer), which is still used by the U.S. Navy and other government agencies as a weatherable topcoat on ships. Industrial analogs are used for the protection of tanks, chemical process equipment, bridges and other steel structures. Two specifications have been written by SSPC: SSPC Paint 21 (White or Colored Silicone Alkyd Paint and SSPC-PS 16.01(Silicone Alkyd Painting System for New Steel). Other early examples of organic-inorganic siloxane hybrids are the silicone polyesters used for high quality coil coatings and the silicone acrylics, which provide good color stability at high temperatures.

A breakthrough was made with the publication of a patent in 1981 which described binders based on interpenetrating polymer networks (IPN) comprising a polysiloxane network and an epoxy polyamine network[5]. Coatings based on this epoxy siloxane hybrid had excellent adhesion to steel and other coatings, good flexibility and improved acid and solvent resistance compared to conventional epoxy coatings.

Further progress was made with in the mid 1990's with the commercialization of patented, improved epoxy siloxane hybrids[6]. These coatings combined the corrosion resistance of an epoxy with the weatherability of polyurethane in one coating and are now widely used in new construction, industrial maintenance and marine applications. Acrylic siloxane hybrids appeared in the patent literature in 1994 and 1998[7, 8, 9]. Several commercial products are available. More recently, a number of patents have been published describing various methods and types of organic modified polysiloxanes.

A partial list of polysiloxane patents is shown in **Table 2**.

INORGANIC POLYSILOXANES

Some comment on the fundamental chemical characteristics of inorganic siloxane and organic binders is necessary to understand their performance differences. **Table 3** lists the important features of compositions containing the Si-O siloxane bond. The bond strength of the Si-O siloxane bond is about 108 Kcal/mole. It is considerably higher than 83 Kcal/mole for the C-C carbon bond of organic polymers. The stronger bond strength provides the basis for their improved durability and heat resistance compared to carbon based organic systems. Inorganic siloxane bonds are virtually unaffected by sunlight and ultraviolet attack. By comparison, organic coatings based on acrylic or polyurethane binders exhibit fading and gloss in 2 to 5 years exterior exposure. The Si-O bond is already oxidized and, consequently, atmospheric oxygen and most oxidizing chemicals do not affect coatings based on siloxane binders. Siloxane binders generally have low viscosity, which facilitates the formulation of very high solids, low VOC coatings. Further, inorganic siloxanes are not combustible while organic binders burn and generate smoke and toxic gases.

Inorganic Siloxane Binder Chemistry

Typical inorganic siloxane binders and precursors cure by a process called hydrolytic polycondensation in which an alkoxide silane hydrolyzes to generate silanol groups which subsequently condense to form the polymer network. See **Figure 1**. Silicone intermediates and alkyl silicates cure in the same manner

Recent advances in siloxane chemistry and formulation technology provide routes to better utilization of the siloxane group to significantly upgrade the performance of protective coating compositions. These recent breakthroughs have involved improved room/low temperature catalysis methods for polycondensation reactions, the availability of new reactive oxysilanes, silicone intermediates and prepolymers and the development of unique organic-inorganic siloxane hybrid binders. Formulation expertise involving selection of the appropriate binders, pigments and other ingredients has also been a factor in the development of commercially viable coating systems . A summary of technology advances is shown in **Table 4.**

Inorganic Siloxane Coating Formulations

The chemistry described above has been successfully applied to create pure polysiloxane binders and the formulation of coating systems with better film formation and improved thermal, chemical and UV resistance. The coatings are formulated by selecting an appropriate silane, silicate or siloxane binder precursor and pigment system to meet the performance and regulatory requirements of the intended application.

The following examples are intended to demonstrate the unique properties of inorganic polysiloxane coatings: .

Heat and Chemical Resistant Polysiloxane

Formulation and Coating Properties

Compositions that contain pure polysiloxane networks have been formulated that provide maximum heat and chemical resistance[10].

Table 5 gives a description of a typical formulation and its coating characteristics. This coating has about 90% volume solids, a pot life and dry through time of 6 hours and 24 hours, respectively, and is applied at 4 to 6 dry mils by conventional spray on SSPC-SP10 prepared steel. Typical heat resistant formulations contain the appropriate siloxane binder and micaceous iron oxide or aluminum as the major extender pigments. Successful formulations have pigment to binder ratios close to the CPVC. Heat resistance in excess of 1400F (760C) can be achieved. **Table 6** lists some of the coatings performance properties. **Figure 2** shows the thermogravimetric analysis of a typical heat resistant formula. The weight loss over the temperature range is about 10% and attributable to loss of the organic substituents on the siloxane binder and residual solvent. The remaining film maintains mechanical integrity and continues functioning as a barrier coat even after high temperature exposure. Examples of typical applications are stacks, tank exteriors and on piping under insulation. Cracking during thermal cycling can be a problem with some formulations. Recommendation for these applications should be made after testing under simulated use conditions.

The same binder can be used with a different extender pigment to achieve chemical resistance not obtainable with any organic coating. Indeed, because the binder is pure siloxane, it behaves like a zinc silicate coating without the reactivity and acid exposure limitations. **Table 5** gives a description of a typical formula and its coating characteristics. The coating has 80% volume solids and pot life and dry through time of 6 hours and 24 hours at 70F (21C), respectively. It is applied with conventional or airless spray in two 6-mil coats on SSPC-SP10 steel. **Table 6** summarizes the performance properties and representative chemical resistance of this formula. Inorganic polysiloxanes are resistant to virtually all solvents and a wide range of organic and mineral acids in certain concentration ranges and are well suited for tanklining applications. They are not resistant to alkali.

Weather Resistant Polysiloxane Topcoat

Formulation and Coating Properties

Topcoats have been formulated with pure polysiloxane binders that exploit the inherent UV resistance of the siloxane bond. The siloxane binder precursors are selected to provide balanced adhesion, package stability, mechanical properties and weathering resistance. High pigment loadings are generally required resulting in either a semigloss or flat finish. **Table 7** shows the formulation and coating characteristic of a typical polysiloxane topcoat. It is a one-package coating with volume solids of 63%. It cures by hydrolytic polycondensation on exposure to atmospheric moisture and has a dry through time of 12 hours at 70F. Application is by airless or conventional spray at 2 to 4 mils per coat. **Figure 3** offers a comparison of the QUV-B accelerated weathering resistance of a variety of generic coating types. The polysiloxane topcoat exhibits very little gloss loss after 15 weeks exposure. Prototypes have been exposed to Florida weathering for six years with no measurable chalking, film degradation or loss of gloss.

ORGANIC-INORGANIC SILOXANE HYBRIDS

Chemistry

The excellent heat, ultraviolet light and chemical resistance properties of inorganic siloxane binders make them obvious choices for improving the properties of organic coatings. Formulators have tried to utilize alkyl silicate and silicone resin chemistry for this purpose but success was limited by the peculiarities of their film forming mechanisms. Significant progress has been made in the last 5 to 8 years with the patenting of a range of methods for modifying a variety of organic binders with inorganic siloxane to produce hybrids with unique combinations of properties.

Formulators select the appropriate type and ratio of organic and inorganic siloxane constituents in an effort to achieve a balanced set of application and performance properties. Oxysilane and silicone resin precursors are selected for cure speed, degree of cross-linking, balanced film properties and compatibility with organic resin constituents. The types of silicon-based materials used are typically alkoxy or silanol functional silicone resin intermediates ranging in molecular weight from 600 to 10,00 and various types of organofunctional oxysilanes. An important feature of the oxysilane and silicone resin precursors is their very low viscosity. This feature has enabled development of very high solids coatings that meet all current and likely future regulatory requirements for volatile organic content. Organic resin precursors are generally chosen for their principal performance feature. For example, an aromatic epoxy resin would be used for applications requiring chemical resistance and an acrylic resin would be chosen for use in a coating requiring good weatherability. It has been found that organic-inorganic siloxane hybrid binders containing 20-50% organic resin give optimum performance in terms of film formation, adhesion, mechanical properties and chemical, corrosion and weathering resistance. Lower levels of organic resin result in coating films that exhibit undesirable properties e.g., low impact resistance and flexibility and loss of adhesion on aging. Higher levels of organic modification detract from important polysiloxane characteristics like resistance to ultraviolet light and oxidation.

The hybrids cure by complex multiple reactions involving oxysilane hydrolytic polycondensation (**Figure 1**), conventional organic reactions like epoxy and acrylate with amine and co-reaction of oxysilanes and polysiloxanes with organic functionalities. The cure rate for each reaction may be the same or different and is further complicated by the effects of temperature and humidity. At least some humidity is required to initiate hydrolytic polycondensation reactions, however, it is remarkably consistent over the range of 30 to 90% relative humidity.

The chemistry described above has been used to develop organic-inorganic siloxane hybrid coatings with performance properties, durability and reduced life-cycle costs not previously obtainable with conventional organic and inorganic coatings.

The following examples are intended to demonstrate the unique properties of organic-inorganic siloxane hybrid coatings:

Weatherable and Corrosion Resistant Epoxy Siloxane Hybrid

Formulation and Properties

Weatherable, corrosion resistant epoxy siloxane hybrid binders are formulated with aliphatic epoxy resins, silicone intermediates, oxysilanes and aminosilanes. The amine group on the aminosilane cures the epoxy resin in the usual manner and also participates in hydrolytic polycondensation reactions with silicone and oxysilane components. The curing reaction is shown in **Figure 4**. Hybrid resins with epoxy and alkoxysilane functionalities in the same molecule are also available. A description of the epoxy siloxane hybrid formula is shown in **Table 8** and its coating characteristics are shown in **Table 9**. The coating has ultra high volume solids of 90% and a VOC of 1.0 lb/gal (120 g/l). The coating is applied by brush, roll and airless or conventional spray at 3 to 7 mils per coat. Epoxy siloxane hybrids can be applied direct to sand blasted steel, hand or power tool cleaned, rusted steel, a variety of organic primers and properly prepared, previously painted substrates. An important feature of the epoxy siloxane hybrid is its compatibility with inorganic zinc silicate (IOZ) primers. Epoxy siloxane can be applied directly to IOZ without pinholing, thus eliminating the epoxy tie-coat required for aliphatic polyurethanes.

Another interesting aspect of epoxy siloxane hybrids is their excellent adhesion to steel and compatibility with inorganic substrates. High adhesion can be attributed to the epoxy siloxane binder's low viscosity, and excellent wetting characteristics as well as its ability to function as an adhesion promoter. Alkoxysilane groups on the binder hydrolyze and react with hydroxyl groups on metal inorganic substrates to form chemical bonds in a manner similar to the well-known silane adhesion promoters.

Epoxies are the workhorses of the corrosion protection coating industry because they are user friendly, have excellent corrosion resistance and adhesion to steel and provide good resistance to alkali and solvents. However, epoxy coatings have one major deficiency for exterior applications; poor weathering. On exterior exposure, conventional epoxy coatings exhibit chalking and color fade and lose most of their gloss in three to six months. If long-term retention of color and gloss are required, two to five mils of an aliphatic polyurethane topcoat must be used. The first commercially successful epoxy siloxane hybrid was developed to improve the weathering resistance of epoxy without compromising corrosion or chemical resistance. **Table 10** offers a comparison of the this epoxy siloxane with a commercially available epoxy polyamide coating. The epoxy siloxane hybrid has about the same resistance to corrosion as the epoxy polyamide but exhibits significantly better resistance to acid exposure and QUV-B accelerated weathering. Of note, the accelerated weathering resistance of the epoxy siloxane hybrid is actually better than aliphatic polyurethane. See **Figure 3**. **Table 11** offers a direct comparison of the following typical high performance coating systems:

- a single coat of epoxy siloxane with a 2-coat epoxy/urethane system and
- a 2-coat inorganic zinc/epoxy siloxane system with a 3-coat inorganic zinc/epoxy/urethane system.

The single coat of epoxy siloxane provides comparable resistance to corrosion and better resistance to Florida weathering compared to the 2-coat epoxy/urethane systems. The 2-coat IOZ/epoxy siloxane system has equivalent or better resistance to corrosion and better resistance to Florida weathering compared to the high performance, 3-coat, IOZ/epoxy/urethane system. Similar performance advantages are seen with epoxy zinc/epoxy siloxane compared to epoxy zinc/epoxy/urethane.

Limitations – Experience has shown that particular attention must be given to ensure adequate film thickness is applied. Three to four mils are required for long-term corrosion protection. Pull back from sharp edges can be a problem and stripe coating is recommended.

To summarize, epoxy siloxane hybrids provide the corrosion resistance of epoxy with weatherability better than an aliphatic urethane without the use of isocyanate in a single coat. The improved durability of the epoxy siloxane hybrid and elimination of epoxy primer and epoxy mid-coat in 2-coat and 3-coat high performance coating systems provides lower application and projected life-cycle costs for the protection of large structures[11]. The combination of cost and performance advantages of epoxy siloxane hybrids has resulted in widespread commercial acceptance with the coating of over 120 million square feet of steel since the mid-1990's.

Chemical Resistant Epoxy Siloxane Hybrid

Formulation and Coating Properties

Highly chemical resistant epoxy tanklinings and concrete surfacers are typically formulated from bisphenol-A, bisphenol F or novolac epoxy resins and modified aliphatic, cycloaliphatic and aromatic amines. They provide resistance to splash and spill or continuous immersion in a broad range of dilute and concentrated organic and inorganic acids, alkali, solvents and oxidizing chemicals. Aromatic amine cured epoxy is resistant to the broadest range of chemicals and is the only system suitable for continuous contact with organic acids like acetic and tall oil fatty acids.

Chemical resistant epoxy siloxane hybrids were introduced in the mid-1990's[12]. The formulation of a commercially available epoxy siloxane concrete surfacer is shown in **Table 8**. The aliphatic epoxy resin mentioned in the previous example was replaced with aromatic epoxy to provide optimum chemical resistance. As shown in **Table 9**, the surfacer has a resin, cure and filler component and is applied at 40-100 mils (1000-2500 microns) per coat by screed or trowel. It is ready for light traffic in 24 hours and chemical service in 72 hours.

The mechanical properties and chemical resistance of the epoxy siloxane surfacer are compared to commercially available methylene dianiline (MDA) and aromatic/cycloaliphatic amine cured epoxy systems in **Table 12**. Mechanical properties of the epoxy siloxane are higher than the other two systems. Chemical resistance of the epoxy siloxane hybrid is better than the aromatic/cycloaliphatic amine cured epoxy and comparable to the MDA cured epoxy. **Table 13** presents data on retention of compressive strength after one-week immersion in a wide range of chemicals. The high mechanical properties and broad range chemical resistance make the epoxy siloxane surfacer well suited for use in the chemical process industries and secondary containment applications.

Limitations – Like many chemical resistant epoxy and vinyl ester formulations, chemical resistant epoxy siloxane hybrids have high crosslink density and shrinkage that may result in cracking, delamination or disbondment from concrete, particularly at high thickness. Recently introduced elastomer modified epoxy siloxanes have greatly reduced this problem but still require application at recommended thickness.

Acrylic Siloxane Hybrid Topcoats

Formulation and Coating Properties

Aliphatic acrylic polyurethane topcoats have been the coating of choice for long-term gloss, color and appearance retention. Acrylic siloxane hybrids were developed primarily as isocyanate-free alternatives.

By combining acrylic resin with siloxane, formulators have developed high solids, low VOC, highly weatherable topcoats. Several products are commercially available and include self-curing, one-component and two-component types. One-package types are formulated from combinations of alkoxysilane or silanol functional acrylic resins, hydroxyl functional acrylic resins and silicone resin intermediates. The one-package acrylic siloxane hybrids cure via hydrolysis of alkoxysilane functionalities as suggested in **Figure 4**. Early versions of the single-package acrylic siloxane hybrid were about 55% volume solids and had relatively low siloxane content. Consequently, resistance to weathering was about the same as aliphatic polyurethane. Continued development has resulted in higher solids, single package acrylic siloxanes with significantly improved resistance to accelerated weathering.

Two-package acrylic siloxane hybrids have also gained acceptance in the market place. One component is formulated from acrylate or acetoacetate functional acrylic oligomers, acrylic resins and alkoxy or silanol functional silicone resin intermediates. The other component is typically an aminosilane. As suggested by **Figure 5**, the two-package acrylic siloxane hybrids cure via Michael addition reaction of amine and acrylate functional groups and hydrolytic condensation of the silicone resin intermediate.

The one-package acrylic siloxane hybrid offers advantages compared to the two-package type. As a self-curing coating, it is easier to apply with no need for mixing and no pot-life application restrictions. Further, there is no waste generated from unused, catalyzed material. One-package acrylic siloxane hybrids are well suited for marine and industrial maintenance applications, particularly for brush and roller application in difficult access areas.

Table 14 offers an overview of the considerations made in formulating acrylic siloxane hybrids. **Table 15** presents the coating characteristics of both the one-package and two-package acrylic siloxane hybrids. Both types have about 80% volume solids and a VOC of less than 250 g/l. They are applied at 4 to 5 mils (100-125 microns) per coat by brush, roll or spray over an epoxy, zinc-rich epoxy or other organic primer system. Both types have significantly better resistance to weathering than aliphatic urethane and, in fact, weather better than the epoxy siloxane hybrid. See **Figure 3**. **Table 16** presents data on the corrosion resistance of zinc-rich epoxy primer/acrylic siloxane topcoat and zinc-rich epoxy primer/aliphatic urethane topcoat systems. Both systems have the same performance.

It should be noted that acrylic siloxane hybrids do not provide the same level of corrosion resistance as the epoxy siloxane hybrid. .

The high-solids, low VOC, non-isocyanate curing mechanism and combination of superior weatherability and excellent corrosion resistance of acrylic siloxane hybrid coatings make them ideal as toxicologically more acceptable, cost effective alternatives to aliphatic polyurethane.

New Organic – Inorganic Siloxane Hybrid Technology

Siloxanes are one of the most rapidly expanding areas of materials research and coating development. The versatility of siloxane chemistry allows the formation of siloxane hybrids with a large range of organic polymers. In addition to acrylic and epoxy siloxane, hybrids with vinyl, fluoropolymer, elastomeric epoxy, phenol and urethane binder systems have been developed for use in tanklinings, flooring systems, anti-graffiti coatings and product finishes.

The versatility of siloxane chemistry extends to adhesives, sealants and composites. For example, an epoxy siloxane adhesive has been developed with improved temperature resistance for use on chemical and fire resistant composite pipes. Phenolic siloxane resin binders have been developed for use in composite fire resistant piping. The phenolic binder provides improved flexibility and resistance to cracking compared to conventional phenolic composites yet still meets IMO Level 3 requirements for hydrocarbon fires.

SUMMARY

Polysiloxane coatings are the newest generic coating type. Recent advances in molecular engineering chemistry and formulation technology have resulted in siloxane binders and coating systems which offer significant improvements in ultraviolet light, heat, chemical and oxidation resistance and longer term protection from corrosion and degradation.

Organic-inorganic siloxane hybrids represent the most significant advance in ambient cure protective coatings in many years. This chemistry allows the retention of desirable properties in existing systems while enhancing those areas needing improvement. Organic-inorganic siloxane hybrids have been formulated with performance properties, durability and extended service life not previously attainable with conventional inorganic or organic coatings.

Acrylic siloxane hybrid coatings have high-solids, low VOC and cure at ambient temperatures without the use of isocyanates. The superior weatherability and excellent corrosion resistance of acrylic siloxane hybrid coatings make them ideal as toxicologically more acceptable, cost effective alternatives to aliphatic polyurethane, acrylic epoxy and fluoropolymers.

Epoxy siloxane hybrids have ultra high solids, low VOC and cure at ambient temperature to provide coatings with an unsurpassed combination of resistance to weathering and corrosion. They provide the corrosion resistance of epoxy with weatherability better than aliphatic urethane in a single coat. The improved durability of the epoxy siloxane hybrid and elimination of epoxy primer and epoxy mid-coat in traditional multi-coat, high performance coating systems provides lower application and life-cycle costs for the protection of large structures.

Inorganic siloxane and organic-inorganic siloxane hybrid coatings provide new options and real value for end-users.

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