An Improved Class of High-performance Coatings with Reduced Toxicity and Hazards: Patented Polysiloxanes

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Recent advances in protective coating technology for the high-performance/heavy-duty industries are reviewed. A new generic class of high-performance binders based on siloxane chemistry is described that offer the potential for quantum improvements in various performance categories. Non-combustible formulations are possible, as well as products with lower solvent content and toxicity. The compositions offer significant increases in heat, chemical, and weathering resistance compared to the state of the art.

Key words: protective coatings, patented siloxane, polysiloxane, heat, chemical, ultraviolet resistant coatings.

Introduction

Steel and concrete need to be protected from corrosion and degradation in a variety of operational and atmospheric environments in general industrial and mining applications, ranging from simple atmospheric exposure to marine environments, chemical/fume contact, splash and spillage of chemicals, and continuous aqueous or chemical immersion. Further variables include the existence of continuous or cycling heat exposure and/or the need to possess mechanical and physical durability.

From the protective coating standpoint, each generic type of coating possesses certain unique features and benefits, as well as certain limitations. Table 1 highlights these.

Discussion

With the exception of the zinc silicate compositions, the features and limitations result from the fact that the binder systems used are organic in nature (based on carbon-carbon bonds in the binder backbone). The silicone and silicates display notable differences in heat, ultraviolet and, in many cases, chemical resistance. A consideration of these fundamental chemical characteristics provides the basis for advancing the state-of-the-art to higher levels of performance through binder and formulation redesign. By incurporating siloxane, high-solids, low-solvent content coatings can be formulated out of previously non-compliant technologies.

Weatherable finish coats can be developed without toxic isocyanates and totally inorganic, non-combustible products can be developed. Table 2 gives a comparison of the essential chemical properties of the siloxane bond and the organic bonds found in typical coating resins.

Terminology

For clarity, Table 3 gives definitions of the chemical terminology used in the following discussion. In coating compositions, the typical resins using the silicon-oxygen bond as the repeating unit in the backbone are silicones and silicates. 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. The presence of certain organic groups bonded to the silicon atom in silicones and polysiloxanes moderates physical, mechanical, and chemical properties.

Silicones. Silicone copolymers (containing either alkyd, acrylic, or polyester coresins) are well known. The amount of silicone resin incorporated in the copolymer defines the properties of the composition. These compositions are manufactured by condensation at high temperature and their curing and drying properties are dominated by those of the organic components.

Recent advances in siloxane chemistry. Recent advances in siloxane chemistry have provided routes to the better utilization of the siloxane group to significantly upgrade the performance of protective coating compositions. For example, the incorporation of polysiloxane with epoxy improves significantly epoxy gloss retention and bond strength to various surfaces. These recent breakthroughs allow formulation of a wide range of upgraded coating systems meeting from general industrial to even the most severe of performance requirements. Further, this patented siloxane technology can be utilized to create formulations and systems that fully comply with ever more stringent environmental, health, and safety requirements without downgrading performance.

Siloxane formulations. The chem.-istry has been applied successfully to create pure polysiloxane network compositions having maximized thermal and chemical resistance; pure polysiloxane compositions offering extended weatherability and appearance retention; and "hybrid" systems in which properties of a traditional resin have been selectively and significantly upgraded.

Heat-resistant polysiloxanes. Compositions that contain pure polysiloxane binder networks have been formulated that provide maximum heat and/or chemical resistance. Heat resistance in excess of 1100ºC (2000ºF) can be achieved. Figure A shows thermogravimetric analyses for this type of formulation. The weight loss over the temperature range is around 10%; this accounts for the loss of the organic substituent groups, absorbed water, and residual solvent. The remaining film maintains mechanical integrity and continues functioning as a barrier coat even after high-temperature exposure. Table 4 is a summary of representative properties of this type of formulation. Typical applications would include stacks, the exterior of reactors, and on piping under insulation.

Chemically resistant polysiloxanes. The same binder system can be used with an optimized pigment package to

**Table 1:
General Coatings
Features and Limitations**

	Feature	Limitations
Epoxy	Corrosion Barrier Durability Adhesion	Poor Weathering Heat Resistance (will burn) Slow Cure Chemical resistance dependent on cure type
Polyurethane	Appearance Durability Weatherability	Toxicity (isocyanates) Moisture Sensitive Heat Resistance (will burn)
Silicone	Weatherability Heat Resistance Copolymer Resistance	Baking required to function
Zinc Silicate	Corrosion Resistance Heat Resistance Durability Solvent Resistance	Appearance Acid/Base Sensitive

**Table 3:
Terminology**

Silicon	The element (Si)
Silicate	Metal salt of silicon-oxygen anion
Silica	Sand; silicon-oxygen compound
Siloxane	Compounds with 2 or 4 oxygens bonded to silicon
Poly-Siloxane	Polymer with silicon-oxygen backbone
Silicone	Polysiloxane with organic substituents on each silicon, typically 2
Organic	Carbon based compounds; polymers with carbon-carbon units in backbone.

**Table 2:
Comparative Properties
Siloxane and Organic Coatings**

1. Binder Backbone
   C - C 83 Kcal/mole
   Si - O- 108 Kcal/mole
2. Si-O is UV resistant.
3. Si-O is already oxidized.
4. Si-O is not combustible
5. Organic groups bonded to Si Tailor Properties

Achieve chemical resistance of a scope not given by organic systems. See Table 5. Indeed, because this type of formulation is essentially inorganic, it behaves like a zinc silicate without the acid exposure and chemical reactivity limitations. These patented polysiloxane tanklining prototypes are resistant to virtually all solvents, organic acids, and mineral acids in certain concentration ranges. However, pure polysiloxanes are not resistant to alkali. Table 5 is a summary of representative properties of this type of formulation. Hybrids of polysiloxane with other chemistries allow formulation of tanklinings with broad chemical resistance, including alkali resistance.

Polysiloxane topcoats. By using the appropriate blends of silicone intermediates and a cross-linking agent, topcoats similar in appearance to polyurethanes have been formulated without the use of toxic isocyanates. Figure B offers a comparison of the accelerated UV resistance of a variety of generic coatings. The polysiloxane performs according to expectation, the effect of the addition of non-siloxane components to the formulation can be seen by the decreasing UV resistance going from pure polysiloxane to acrylic polysiloxane to silicone alkyd. Only polysiloxane and fluorocarbon-based formulations (not shown on plot) show such extreme UV resistance. Semi-gloss prototypes of the pure polysiloxane compositions have been exposed to Florida weathering in excess of six years with no measurable chalking, film degradation, or loss of gloss.

Zinc silicate compatibility. Another interesting property of the polysiloxane compositions described above is that they are inherently compatible with inorganic zinc silicate (IOZ) primers. This offers the possibility of eliminating the require-

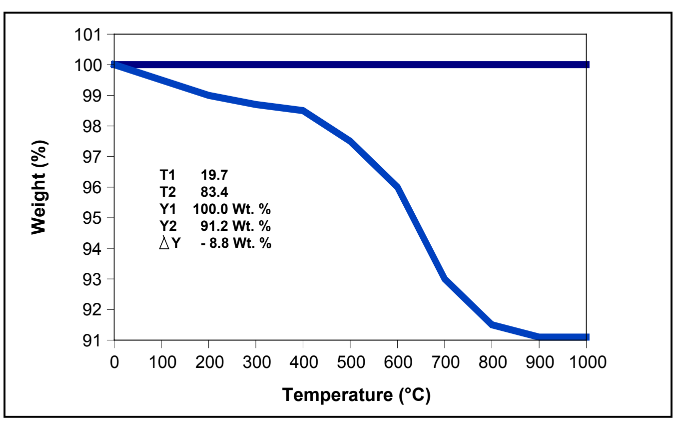

Figure A: Thermogravimetric Analysis of Heat-resistant Polysiloxane

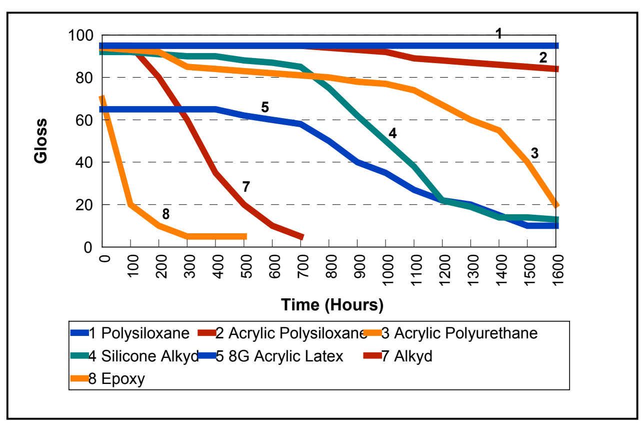

Figure B: Comparison of the Accelerated Ultraviolet Resistance (QUV) of Various Generic Classes of Coatings

Table 4:
Patented Polysiloxane Coatings Heat Resistant Formula

1.	Salt Spray	
	5000 Hrs	
	Blistering (ASTM D714)	10
	Corrosion (ASTM D1654)	9
	Scribe (ASTM D1654)	10
	Adhesion	Excellent
2.	Heat Resistance	
	TGA – Total Weight Loss, to 1000°C	
	10%	
	Torch – 1510°C, Discoloration	
3.	Condensing Humidity	
	4500 + Hrs	
	Blistering	10
	Corrosion	9
	Adhesion	Excellent
4.	Atlas Cell (Salt and Deionised Water)	
	1000 Hrs	
	Vapor Phase	Pass, No Blisters
	Liquid Phase	Pass, No Blisters
5.	Chemical Resistance (Representative)	
	Immersion at 25°C (Test time, hrs.)	
	Acetic Acid	(4000)
	50% Sulfuric Acid	(4000)
	19% Hydrochloric Acid	(3000 +)
	Acetone	(8000)
	Methylene Chloride	(8700)
	JP-4	(1200 +)

Table 5:
Patented Polysiloxane Coating Immersion Formula Representative Chemical Resistance

Acetone
- Ketones

Methanol
- Alcohols

Xylene
- Aromatics

Methylene Chloride
- Chlorinated Hydrocarbons

Fatty Acids

Acetic Acid
- Organic Acids

Triethanol Amine

50% Sulfuric Acid

83% Phosphoric Acid

10% Nitric Acid

10% Hydrochloric Acid

Not Resistant to Alkali

ments for the mid-coat in the IOZ-based systems where appearance and chemical protection of the zinc primer are required. Currently testing and demonstration of such systems are underway, with outstanding results for systems tested. Table 6 offers a comparison of the two systems. The advantages of the two approaches are obvious, especially when the same or better performance level can be achieved from a simpler system. The environmental and cost advantages of the patented polysiloxane system are appreciable: lower VOC emissions and reduced waste generation are achieved. In addition, lower VOC's means lower solvent emissions that can pollute the environment and result in a fire hazard. Table 7.

Conclusions

In summary, it should be emphasized that a new formulation and molecular engineering chemistry has been described. The products used as examples typify the first generation of polysiloxane-based systems. This chemistry offers the opportunity for quantum improvements in such performance areas as toxicity and flammability reduction, heat resistance, chemical, ultraviolet resistance, durability and longer term protection from corrosion and degradation. The use of this chemistry is consistent with the need for developing high-performance protective coating systems that extend service life and offer reduced environmental, health, and safety hazards.

Table 6:

A.	Inorganic Zinc Silicate Primer	Epoxy Midcoat	Polyurethane Topcoat
	Corrosion Control	Adhesion Promotor; Tie coat	Appearance Weatherability Toxic isocyanates
	Three coats required to make the organic coatings, notably polyurethane compatible with IOZ.		
B.	Inorganic Zinc Silicate Primer	Polysiloxane Topcoat	
	Corrosion Control	Barrier Appearance Weatherability Reduced toxicity	

- Two coats because polysiloxane is inherently compatible with IOZ
- No need for epoxy midcoat to make system compatible
- Epoxy film not needed for corrosion control; IOZ is sufficient.

Table 7:
IOZ / Polysiloxane System Advantages

Better weatherability
Same corrosion resistance as three coat
Easy field touch-up / repair
Faster manufacturing turn-around
Lower solvent emissions
Reduced waste generation / disposal
No toxic isocyanates