Silicone Organic Hybrid Coatings for the Industrial Maintenance Market

By
Gerald L. Witucki

November 17, 2006
Dow Corning Silicone Solutions

As the pioneer of silicon-based technology, Dow Corning has been improving customers’ products and profitability for more than 60 years. With a full range of product and application solutions, reliable supply, world-class manufacturing, and global reach, Dow Corning can meet virtually any silicone-related need through our total solution offering and technology leadership. For more information, call +1 989 496 6000.

Dow Corning (dowcorning.com) provides performance-enhancing solutions to serve the diverse needs of more than 25,000 customers worldwide. A global leader in technology and innovation offering more than 7,000 products and services Dow Corning is equally owned by The Dow Chemical Company and Corning, Incorporated. More than half of Dow Corning’s annual sales are outside the United States.
Silicone Organic Hybrid Coatings for the Industrial Maintenance Market

By Gerald L. Witucki
November 17, 2006

The utility of silicone-organic resin binder hybrid technology has enjoyed rapid growth in the protective coatings markets. A wide array of chemistries and applications provides opportunities for unique combinations and benefits to the end-user. Protecting the integrity and value of this technology benefits all participants of the value chain: raw material supplier, coating formulator, applicator, and the end-user. A readily accessible test method can be used to characterize silicone hybrids and communicate the expected level of performance, allowing for the selection of the appropriate coating system for the targeted application. In this paper, special emphasis is given to silicone-epoxy systems.

Introduction

In recent years, as coating formulators have worked to develop paint systems with enhanced performance, two global market drivers have impacted the success of the new product introductions more than any incremental performance improvement: reduced volatile organic content (VOC) and cost. With the rising price of the primary feedstock (oil) for many coatings ingredients, compliance with environmental regulations has become not only a government requirement, but also an economic imperative. Reducing the cost of a unit of coating is one means to improve market viability, but greater opportunities exist to reduce total end-user costs during the life cycle of the paint. Costs associated with process shutdowns, surface preparation, paint application and waste disposal often outweigh the price of the paint. In response to these market realities, silicone-organic hybrid coatings have risen from a niche technology to become an established market segment and a vital area of technology investment for the protective coatings industry. Variations of the technology are commercially available around the world and provide benefits including reduction in labor costs, overspray, emissions and required film-build, as well as long-term performance exceeding that of the industry standard of 2K urethane systems.

Background

Hybrids are composites formed or composed of heterogeneous materials. By that definition, most paints, combinations of organic binders, and inorganic particles (pigments and fillers) can be considered to be hybrid coatings. This paper will focus on resin binder hybrids. Many coatings derive performance benefits from combinations of organic and inorganic resins that form interpenetrating networks without interconnecting chemical bonds. True binder hybrids combine organic and inorganic polymers with compatible functional groups that react to form copolymer networks linked by stable, chemical bonds. For example, silicone-organic hybrid coatings have existed for more than 50 years, but in recent years have evolved to include a broader array of chemistries and applications (See Table 1).

Silicone binders (also known as silicone resins) are characterized by possession of a $\text{RSiO}_{3/2}$ matrix to which are attached various aryl and/or alkyl groups ($\text{R}$ typically = phenyl and methyl). This group of inorganic polymers is known to possess excellent resistance to thermal and ultraviolet radiation. The limitation of traditional silicone resins is their physical properties: hard, mar-resistant silicone resins are rigid and brittle; flexible silicone resins are soft and easily abraded. In addition, the solvent resistance of traditional silicone resins is marginal. Organic polymers have their

<table>
<thead>
<tr>
<th>Hybrid System</th>
<th>Application</th>
<th>Chemistry</th>
<th>Cure</th>
<th>Standard Si Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicone Alkyd</td>
<td>Above deckline on marine vessels, bridges, etc.</td>
<td>Hydroxyl-functional siloxane resin copolymerized with alkyd prior to paint formulation</td>
<td>Oxidation of fatty acid conjugated double bonds</td>
<td>30-50% silicone modification 14-23% silica ash content</td>
</tr>
<tr>
<td>Silicone Polyesters</td>
<td>Architectural coil coatings</td>
<td>Alkoxy-functional siloxane resin copolymerized with unsaturated polyester prior to paint formulation</td>
<td>Melamine – carbinol</td>
<td>30-50% silicone modification 14-23% silica ash content</td>
</tr>
<tr>
<td>Silicone Epoxy</td>
<td>Industrial maintenance</td>
<td>Alkoxy-functional siloxane resin blended with aliphatic epoxy</td>
<td>Amino-alkoxy-functional silane</td>
<td>50-80% silicone modification 23-38% silica ash content</td>
</tr>
</tbody>
</table>
own performance limits (e.g., ultraviolet (UV) and thermal degradation). Early (1950s) hybrid innovation focused on modification of alkyd resins with silicone resins to improve the UV radiation resistance of industrial maintenance coatings. In those cases, the copolymerization of the silicone and alkyd resin is performed prior to paint formulation and is done to ensure stable, long-term miscibility of the silicone in the organic matrix. Benefit to the physical properties is also gained by the copolymerization, owing to the increased molecular weight of the copolymer. The cure mechanism of the alkyd, by oxidation of conjugated double bonds, remains unchanged by the hybridization. Silicone-alkyd technology continues to find utility around the globe. One particular application suggests an approach to establishing performance standards for other silicone-organic hybrid systems that may be necessary to protect the integrity and value of this branch of coatings technology.

A concern arises from the idea that merely adding a nominal level of silicone into a binder system justifies labeling the coating as a silicone-hybrid. The benefits of silicone content are derived by dilution of the less stable organic binder; there is minimum insular effect on the remaining organic portion. United States Military Specification E-24635 provides the standards by which silicone alkyd enamel must be formulated. This coating is utilized as a weatherable topcoat on United States Navy ships. The specification calls for a minimum level of silicone modification and details a simple analytical means to verify the modification.

For silicone alkyls meant to comply with the U.S. Navy specification, the minimum silicone content is 30 percent of a silicone intermediate (such as XIAMETER® RSN-6018 Resin) into the resin binder solids. Reducing the level of silicone below the specification reduces the coating’s level of performance, thereby diminishing the perceived utility of the technology and the formulator’s ability to capture the value of the coating application.

Coating formulators who verify and communicate the silicone resin component level of the coating system can aid the specification process without compromising their competitive advantage. The information can be conveyed in terms of the weight percent of silicone binder or as a measurement of the silica ash content. Either of these numbers can be provided without disclosing an undue level of intellectual property. Appendix A details a procedure to quantify the level of silicon dioxide ash content of a coating formulation. Suppliers of silicone resins provide the theoretical levels of silicon dioxide for their typical silicone resins. From that information, a formulator or resin cooker can calculate the level of silicone needed to comply with either the silicone or residual silica standard. The wide array of applications utilizing silicone-organic hybrid technologies requires that a range of silicone modification be correlated to differing levels of performance expectations.

With the numerous applications utilizing silicone-organics, there are many technical avenues of approach to improve the physical properties of UV and heat-resistant coatings. Acid equilibration of siloxane precursors with organic polyols before hydrolysis produces resins with a unique combination of hardness, flexibility, and solvent resistance. Investigators have also studied copolymers of epoxy-functional materials with siloxanes for improved flexibility, butanolized polyphenyl siloxane for improved adhesion, polyperfluoroalkylene siloxane resins for resistance to oxygen etching, and silane hydrolyzates combined with polyester resins for reduced discoloration after weathering. One of the most widely cited patents related to silicon-organic hybrid technology in protective coatings (more than 60 citations) documents the benefits of silicone-organic copolymers in a wide array of systems including epoxies, urethanes, amide-imides, sulfones, polyesters, polyphenylene sulfides and polycarbonates. Additional work is being done with silicone-acrylics, acrylosilane polymers and solgel-based hybrids. Of all these systems, the silicone-epoxy technology has gained more widespread acceptance in the industrial maintenance applications such as storage tank exteriors, offshore platforms, ship and railcar exteriors, and bridges.

**Recent Innovations**

Traditional modification of epoxy resins with silicone resins relies on cold blend mixtures with the potential for reaction between silanol (SiOH) or alkoxy (SiOR) groups with available hydroxyl groups on the epoxies, but this reaction is not chemically favored. The Si-bonded reactive groups are more likely to homopolymerize, rather than react with the epoxy. This can result in a heterogeneous polymer with distinct organic-inorganic domains and reduced film performance. In addition, co-reaction results in the formation of Si-O-C bonds. While these bonds are hindered sterically within the final resin matrix, they are ultimately hydrolyzable – creating a potentially weak link in the resin matrix. Still, silicone-epoxy bonds of this form of copolymer are widely utilized in the industry. Other formulators have sought to ensure stable bonds between the epoxy and the silicone resin. Utilizing the functional groups available from silane monomers, resin formulators have created organofunctional (e.g., epoxy and amine) silicone resins for epoxy resin modification.
Combining the rapid cure and excellent barrier properties of epoxy resins with the thermal and UV stability of silicon-based materials, formulators created high-performance coatings with excellent resistance to corrosion and chemical attack, as well as thermal and UV degradation, as early as 1959. These innovations relied on a broad spectrum of silicon-based technologies. Monomeric alkoxy silanes, silicone resins, and fluids of various molecular weights and chain lengths with a myriad of functional groups provide numerous options with which to tailor the organic epoxy resin system to meet specific performance requirements for industrial maintenance coatings.

In some applications the coating is exposed to high temperatures that result in a lowering of film integrity. A blend of an epoxy resin, a curing agent for epoxy resins, an amine-functional alkoxy silane and a catalyst for effecting condensation polymerization of a silane compound was found to provide high heat resistance and excellent mechanical strength. Similarly, complete or partial hydrolysis of alkyl/phenyl alkoxy silanes to form silanol or alkoxy-functional siloxane resins and the subsequent reaction with epoxy resins have been shown to produce copolymers with improved water and moisture resistance. Compatibility of the epoxy and silicon-derived materials is critical to formulation success. Bis-Phenol A epoxies have limited acceptance of silicones. Aliphatic epoxies are more tolerant, while cycloaliphatic epoxy systems are very compatible with silicones. Monomeric silanes are generally compatible, while polymeric silicones require a high phenyl content to ensure miscibility in the organic matrix.

The complicated cure chemistry includes four primary reactions (and several less significant reactions including interactions with catalysts and other possible, but not favored, reactions):

1) Epoxy + Amine → Amine-ol polymer
2) Alkoxy + Water → Silanol + Alcohol
3) Alkoxy + Silanol → Siloxane + Alcohol
4) Silanol + Silanol → Siloxane + Water

While these (reversible) reactions occur simultaneously and are impacted to differing degrees by ambient conditions, they react to relative completion in the order shown. The technology is designed to provide the desired physical properties at the tack-free state within hours via primarily the reaction of the silane amine groups and the aliphatic epoxy functionality. Long-term properties are generated over time (days to weeks) by the hydrolysis of the alkoxy groups on the silanes and siloxanes to form silanol groups, and subsequent condensation of those silanol groups to crosslink the siloxane network. This reaction scheme can lead to potential issues. If the formulation is designed to rapidly (e.g., within 8 hours of application) create a film with a high glass transition temperature via the epoxy/amine reaction, the subsequent siloxane crosslinking can lead to high internal stress and embrittlement. It is therefore critical to formulate the coating with a balance of short- and long-term property expectations.

While the use of silicone resin modifiers (RSiO₂) exploits the stability of the SiO₂ matrix, modification of epoxy resins with silicone fluids (R₂SiO₂) takes advantage of other physical properties of silicones, such as flexibility. The chain length of telechelic (linear) siloxanes possessing terminal reactive groups impacts the function of the silicone in the epoxy matrix. Silicone fluids with shorter chain lengths are inherently more reactive and miscible with the epoxy resin. This allows for modification of the bulk properties of the epoxy matrix such as toughness and impact resistance. Formulating with siloxanes with longer chain lengths decreases the miscibility in the epoxy and the properties of the siloxane are governed less by the terminal organo-functional groups versus the siloxane portion of the molecule. In those cases, the siloxane becomes more of a surface modifier, contributing lubricity, low surface energy and water repellency.

Conclusions
Silicon-organic hybrid technology has demonstrated broad utility across the coatings markets. In particular, silicone-epoxy industrial maintenance coatings have generated a high level of interest in hybrid technology. The varied forms of this technology offer multiple economic and performance benefits to the industry. Compared to the industry standard of three- to four-coat 2K urethane systems, silicone epoxy hybrid technology offers reduction in VOCs; elimination of isocyanate health effects; and improved durability against weathering, corrosion and chemical attack. These long-term benefits mitigate the higher unit cost of a silicone-organic hybrid coating. The level of siloxane modification in the binder system is directly related to the level of anticipated performance. Characterization of silicon-organic hybrid binder systems can be readily performed by residual ash content to provide a standard by which to support performance claims and protect the value of this versatile technology.
Appendix A

Analysis of Formulated Paint for Silicone Resin Content

Procedure:
Approximately 250 grams of paint are needed.

1) Centrifuge the paint to remove the majority of the pigments and fillers.

2) If needed, filter the upper layer to achieve a clear solution.

3) Test the percent non-volatile content (% NVC).
   A. Tare an aluminum weighing dish (triplicate samples).
   B. Into the dish, weigh approximately 0.3 gram of resin solution. Note the sample weight to the nearest one-tenth milligram (0.0001).
   C. Add approximately 3 grams of toluene to dissolve the sample.
   D. Dry the sample in a convection oven at 110°C for 60 minutes.
   E. After cooling, reweigh the dish to the nearest one-tenth milligram.
   F. Calculate the percent non-volatile content: \((\frac{\text{Final weight} - \text{dish tare weight}}{\text{resin sample weight}}) \times 100\).

4) Determine silicon dioxide content:
   A. Thermal cleanse (7 mm) porcelain evaporating dishes (triplicate samples) by heating to 800°C for at least one hour. Cool.
   B. Tare the dish.
   C. Into the dish, weigh approximately 3.0 grams of the clarified resin solution. ADD approximately 3 mL of sulfuric acid (to digest the organic portion).
   D. Note the sample weight to the nearest one-tenth milligram (0.0001).
   E. Heat the samples in a convection oven at 110°C for three hours.
   F. Move the samples to a COLD furnace and heat slowly (over at least a one-hour period) to 800°C. Hold at 800°C for three hours. Cool. All that should remain is a white, crumbly powder of silicon dioxide.
   G. Reweigh and calculate the percent silicon dioxide.
Endnotes


Two brands to serve you

Whether you need industry-leading innovation or greater cost efficiency, Dow Corning can help. Dow Corning® brand solutions are dedicated to meeting your needs for specialty materials, collaborative problem-solving and innovation support. Learn how we can help you at dowcorning.com/coatings.

If you need to buy high-quality, standard silicone materials at market-based prices, we can help you achieve that through our Web-enabled XIAMETER® brand and business model. Learn more at www.xiameter.com.

North America
1-866-739-7224 (Toll-free) – Midland

Latin America
+55 19 3887 9112 (Spanish) – Campinas

Europe
+32 64 511157 (English) – Seneffe

Greater China
+86 21 38997922 (Chinese) – Shanghai

ASEAN-ANZ
+65 6359 3394 (English) – Singapore

Korea
+82 2 6411 7600 (Korean) – Seoul

India
+91 22 66946868 (English) – Mumbai

HANDLING PRECAUTIONS

PRODUCT SAFETY INFORMATION REQUIRED FOR SAFE USE IS NOT INCLUDED IN THIS DOCUMENT. BEFORE HANDLING, READ PRODUCT AND MATERIAL SAFETY DATA SHEETS AND CONTAINER LABELS FOR SAFE USE, PHYSICAL AND HEALTH HAZARD INFORMATION. THE MATERIAL SAFETY DATA SHEET IS AVAILABLE ON THE DOW CORNING WEBSITE AT DOWCORNING.COM, OR FROM YOUR DOW CORNING SALES APPLICATION ENGINEER, OR DISTRIBUTOR, OR BY CALLING DOW CORNING CUSTOMER SERVICE.

LIMITED WARRANTY INFORMATION – PLEASE READ CAREFULLY

The information contained herein is offered in good faith and is believed to be accurate. However, because conditions and methods of use of our products are beyond our control, this information should not be used in substitution for customer's tests to ensure that our products are safe, effective and fully satisfactory for the intended end use. Suggestions of use shall not be taken as inducements to infringe any patent.

Dow Corning's sole warranty is that our products will meet the sales specifications in effect at the time of shipment.

Your exclusive remedy for breach of such warranty is limited to refund of purchase price or replacement of any product shown to be other than as warranted.

DOW CORNING SPECIFICALLY DISCLAIMS ANY OTHER EXPRESS OR IMPLIED WARRANTY OF FITNESS FOR A PARTICULAR PURPOSE OR MERCHANTABILITY.

DOW CORNING DISCLAIMS LIABILITY FOR ANY INCIDENTAL OR CONSEQUENTIAL DAMAGES.

Dow Corning is a registered trademark of Dow Corning Corporation.

XIAMETER is a registered trademark of Dow Corning Corporation.

We help you invent the future is a trademark of Dow Corning Corporation.

©2007, 2012 Dow Corning Corporation. All rights reserved.

Printed in USA  AD15014  Form No. 26-1469A-01