NEW TECHNOLOGY COATINGS FOR CORROSION CONTROL

A **JPCL** eBook

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Introduction

This eBook consists of articles from the *Journal of Protective Coatings & Linings (JPCL)* on recent technological advancements in heavy-duty coatings for corrosion control.

photo courtesy of Lumiflon

Spanning 25 Years of Development in Heavy-Duty Coatings

By Michael Donkin,
International Paint Ltd.

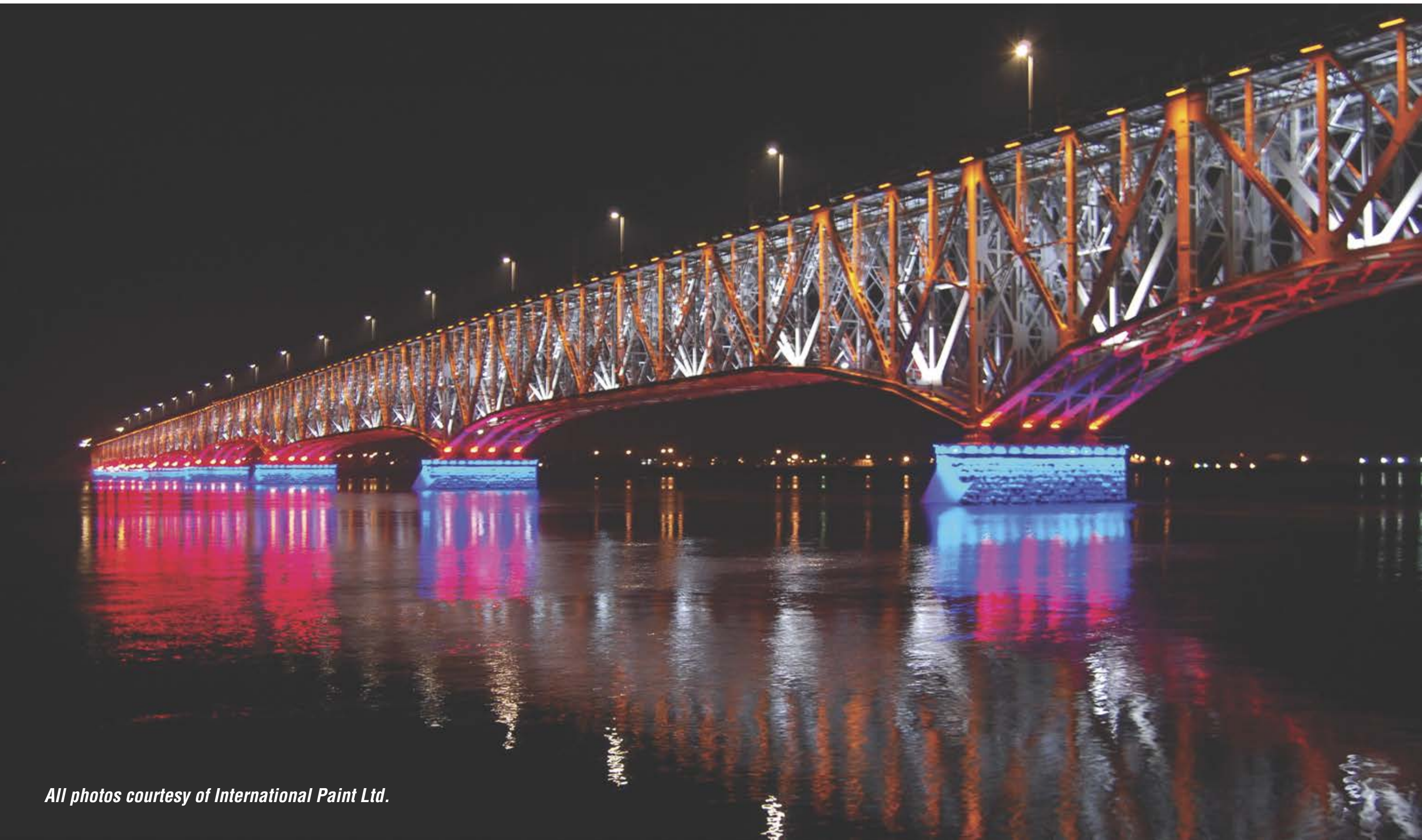
Editor's Note: This article apeared in JPCL *in August 2009.*

Massive changes have occurred in coating formulation for the heavy-duty market in the past 25 years. This article aims to explain the reasons for the changes and the results of them.

In the marine and protective coatings market, there have been two key drivers for change:

- increasing levels of legislation and regulation to protect the environment from air pollution by reducing volatile organic compound (VOC) emissions from coatings, and to remove from coatings any raw materials that may pose risks to worker health and safety and the environment (HSE); and
- higher customer expectations for coating performance and the need to increase the lifetime of the assets being coated.

Conforming to these drivers has led to advances in existing technologies and the introduction of new technologies such as polysiloxanes. Testing methodology for coating performance has also changed significantly over the past 25 years. For instance, the industry has moved from the use of constant hot salt spray to more meaningful cyclic tests that have much better correlation with real life conditions. Changes in testing have improved the ability to benchmark and accurately assess a product's performance in the field.



All photos courtesy of International Paint Ltd.

Direct-to metal polyaspartics can be formulated below 250 g/L and can give corrosion resistance in C3 environments similar to that of a combination of epoxy and polyurethane.

The Influence of Regulations on Product Development

In the mid-1980s, most coatings in the heavy-duty market were single-component products, with alkyds, vinyls, and chlorinated rubbers dominating. The main drawback of the thermoplastic coatings was their very high VOC levels, which meant that they were never going to be sustainable when VOC regulations started to be introduced. Also in the 1980s, formulators were starting to understand how two-pack products (for example, epoxies and polyurethanes) could be exploited and the potential improvements in performance they could offer. By the mid-1990s, two-component materials started to dominate the market purely on performance—at that time, VOC legislation was in only the early stages of development.

The major challenge to the coatings industry and particularly the formulating chemist has been to continue to improve and, at times, maintain the performance of the two-pack coatings, while reducing the level of VOCs—not an easy task.

Increasing the volume solids of most coatings leads to a range of problems, including slower drying with softer films, higher viscosity, and application challenges. Problems arise especially with finish coats where low dry film thickness (dft) is required but at decreasing wet film thicknesses (wft). In effect, the wft range decreases as the solids increase. For example, a polyurethane finish at 50% solids requires a closed film at a wft of 100 microns to obtain a dft of 50 microns (2 mils), which by spray is relatively easy to achieve. However, at 80% solids, the same 50-micron dft will require a 62.5-micron (2.5-mil) wft, which is considerably more difficult to achieve due to the reduction in solvent. Achieving desired dfts with higher solids coatings remains one of the key challenges for today's formulators.

A Brief History of VOC Regulations

- 1980s: There were very few VOC regulations. Some California air quality management districts in the U.S. began to introduce architectural and industrial maintenance (AIM) coatings rules. Because California has a climate that supports the build-up of low level ozone and smog from the state's many cars, industries, coatings, and other products, districts in California took actions to control the build-up of ozone precursors such as VOCs. [*Editor's note: See "Regulations and Coatings Work: Key Developments over 25 Years,"* JPCL *August 2009, pp. 72–77.*] In Europe, some countries had VOC rules that limited the VOC content of certain paint products, but the limits were high and certainly not restrictive.
- 1990s: In the U.S., the 1990 revision of the Clean Air Act (CAA) resulted in national VOC rules, one of which was a national rule for AIM protective coatings. As the 1990s progressed, revision of the VOC limits in the already established California districts' rules began.
- 2000 to the present: In 2006, California's South Coast Air Quality District set the strictest limit yet for industrial maintenance coatings—100 g/L.

In October 2005, the first restrictions of the European Union's (EU) solvent emissions directive (SED) began to apply, although the SED had been issued back in 1999 in the newly formed EU.

Since 2007, many other countries such as South Korea, Hong Kong, and Taiwan have started to develop their own VOC rules and regulations.

The Choice of Raw Materials

The second key driver for change has been the number of raw materials that have come under scrutiny due to HSE concerns. Typical examples include

- lead pigments,
- coal tars,
- chromate pigments,
- pthalate plasticizers from acrylic emulsions, and
- sensitizing epoxies.

Thankfully for the formulator, as any coatings publication shows, there is a constant stream of new products from the coatings industry. Some are replacements for current materials, and others are totally new technologies offering brand new solutions. The challenge to the formulator is to replace potentially toxic or hazardous raw materials while either matching or indeed improving the performance of the new or reformulated coating. The formulators' work is never done.

High Solids (>80% by Volume)

The biggest shift in the heavy-duty coatings industry was to fully explore epoxy amine chemistry. Twenty-five years ago, many epoxy amine products were on the market, but chemists were just starting to find out how to better exploit this technology with, for example, new curing agents. When formulators realized that the performance obtained from epoxies was significantly better than that of the majority of single-pack analogues, the 80s saw a rush of formulations to market. Anti-corrosive primers, high-build epoxy barrier coatings, and chemical-resistant finishes and tank linings were among the new formulations, and all demonstrated improved mechanical properties and corrosion resistance compared to single-component products. By the end of the 1990s in the heavy-duty market, the majority of single-pack products had been replaced by two-component coatings.

Epoxies have provided the bulk of the high-solids coatings. One key advance has been the move to faster curing systems. The lower solids products were mainly formulated with solid epoxy resins and had the added advantage of lacquer drying. As solids levels in coatings increased, it became more difficult to formulate with solid resins because of the higher application viscosities, so liquid resins, which have lower viscosities, had to be used. Liquid resins present their own problems, with reduced flexibility being one of the most important. Thermal cycling of epoxies to determine resistance to cracking, particularly at higher than standard dfts, has become a key test for the formulator.

Replacing standard three-coat systems with two-coat systems in aggressive environments has been done occasionally, but such a move must be taken with great care.

The introduction of new amine technologies has also seen big changes for the industry, and formulating chemists have been quick to exploit them. The use of phenalkamines has significantly improved the cure speed and dry times of high-solids epoxies and allowed them to be used down to 0 C (32 F) in many situations. Phenalkamine technology was a massive improvement over traditional polyamide curing agents and was used to speed production in new construction and in shipbuilding in emerging areas such as Korea.

The push for lower VOC finishes has continued, with polyurethanes being formulated below 420 g/L. New technologies that contain no free isocyanate emerged with new curing mechanisms. Acid epoxy systems have been formulated below 340 g/L. Higher solids polyurethanes can be formulated in the U.S. with the use of VOC-exempt solvents, but, in general, it has proved difficult to cost effectively reduce the VOC of polyurethanes to 250 g/L and below.

A recently developed technology that offers a route to coatings that are above 80% solids is polyurea chemistry. One specific type of the chemistry is polyaspartic. Polyaspartics are based on the reaction of an aliphatic polyisocyanate and a polyaspartic ester, which is a sterically hindered aliphatic diamine. The major advantages of this technology are that it can be formulated to be applied as a direct-to-metal (dtm) coating and that it offers fast cure, corrosion resistance, and durability in a single coat.

In an effort to reduce VOC levels and costs, there has been a move to use fewer coats in a specification. One way to reduce the number of coats is to use a coating that has both primer and finish properties, a primer/finish. This type of coating, which can be applied dtm, offers corrosion protection and aesthetics in a single formulation, often leading to the replacement of many two-coat systems in ISO 12944 (C3) environments of medium aggressiveness. Primer/finishes have been either epoxies, when toughness and resistance to mechanical damage are required, or polyurethanes, when better durability and color retention are needed.

In more aggressive environments, the move to reduce the number of coats must be taken with care, especially offshore, where the standard three-coat systems have occasionally been replaced with two coats. The problem with using two-coat systems in aggressive environments is that there is a lack of control of film thickness, and coatings on complex steel configurations can have many thin spots, leading to corrosion problems. Until the introduction of polyaspartics, no products have quite been able to provide good corrosion resistance and excellent aesthetics with gloss and color retention.

Research has shown that polyaspartics can be formulated below 250 g/L, which gives dtm corrosion resistance in C3 environments and properties similar to those of a combination of epoxy and polyurethane.

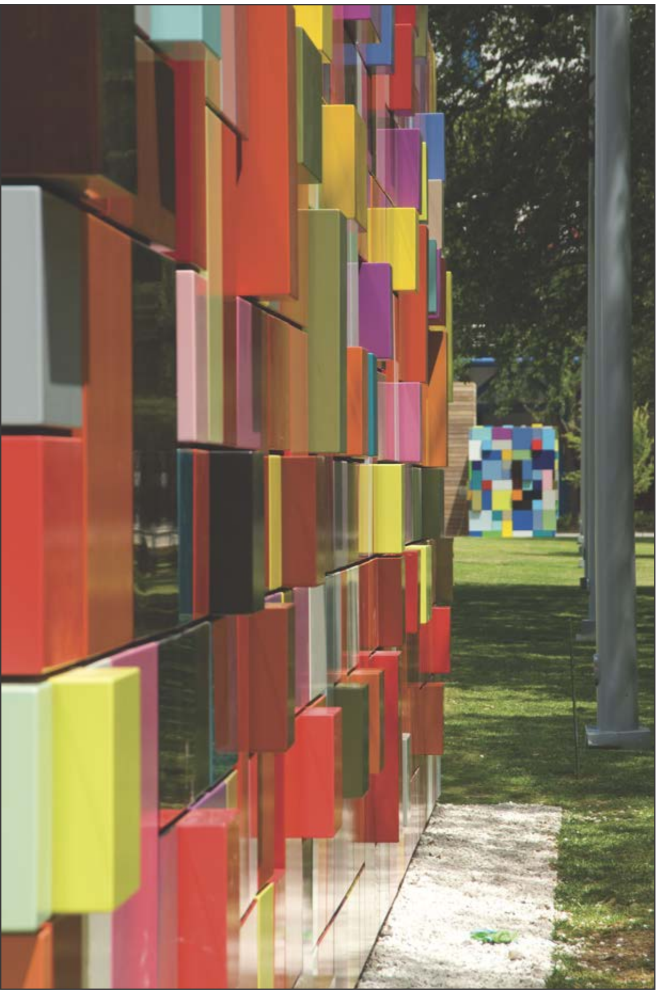
As the solids levels have increased, application equipment has also had to adapt over the years from standard airless spray to plural-component. Although at the time of this writing, the majority of high-solids coatings are still applied by airless spray, the use of plural-component spray is starting to rise and will become a more important application method over the next ten years.

Waterborne Coatings

One effective way to reduce VOCs is to use waterborne coatings. Twenty-five years ago, the main waterborne technologies available were largely limited to single-pack emulsions, which were not ideally suited to new construction situations, where fast drying, early hardness, and block resistance (so that items can be stacked on each other without distorting the coating) are key properties. Emulsions also had a low tolerance for film formation at low temperatures and adhered poorly to minimally or improperly prepared substrates. At first, the use of waterborne coatings was slow and restricted to customers with heated paint shops and good control of the substrate, such as in original equipment manufacturing (OEM). By the early 1990s, the number of waterborne technologies multiplied to include not only new single-pack materials but also a number of two-pack products, such as epoxies and polyurethanes. With an understanding of the key issues, such as minimum film forming temperature (MFFT) and tolerance to compromised substrates, formulators could more easily target the final product for an appropriate end use. The development of two-component epoxies with performance similar to their solvent-borne analogues is now a reality.

Solvent-borne zinc silicates can be formulated down to a VOC level of 340 g/L, but getting below that level has proved difficult because of stability issues with the binder. However, there is a waterborne solution, usually based on using metal alkali silicates such as potassium silicate, which can give zero-VOC coatings. The waterborne zinc silicates have the added advantage of excellent cure at low relative humidity (RH) compared to the solvent-borne analogues, which often have poor cure below 30% RH.

The technologies now available for waterborne coatings are constantly improving. Many two-component systems can now offer performance equivalent to, or better than, that of their solvent-borne counterparts. In the next 25 years, there is likely to be a more even split of waterborne versus high-solids in the heavy-duty market.



One major advance in technology and one of the most exciting areas for the formulating chemist is the emergence of polysiloxanes.

High-Performance Coatings

Zinc-rich primers are still among the top-performing heavy-duty coatings. The past 25 years have witnessed only the change between zinc silicates and zinc epoxies, with each coating type dominating the other at different times. Zinc silicates offer outstanding corrosion protection but are more difficult to use because they must usually be tie coated to prevent pinholing in a high-build topcoat. These three-coat systems are still the preferred option for extreme environments, so there has been little change in the types of specifications.

The emergence of polysiloxanes is one major advance in technology and one of the most exciting areas for the formulating chemist. This technology marked the introduction of inorganic hybrid formulations based on blends of inorganic polysiloxane polymers and a compatible organic constituent. The glass-like quality of the polysiloxane confers excellent UV durability due to the bond strength of the Si-O compared to C-C bonds. Polysiloxane technology can offer both corrosion resistance (barrier protection) and better performance than the traditional polyurethanes. Careful formulation of the blend of resins could significantly alter the resulting properties. By the end of the 1990s, there were a few products utilizing this technology on the market. Many of them were patent protected, which is unusual in the heavy-duty market.

Moisture-cured, single-pack polysiloxanes have now been developed and are available. They are ideal for the maintenance and repair sectors. They have shown durability far exceeding all of the conventional single-component technologies and most two-pack technologies.

In certain markets, fluoropolymers are also used as highly durable finishes, although their use is not as widespread as the polysiloxanes, generally because of the fluoropolymers' high raw material costs and the requirement of isocyanates for curing. The typical solids of these materials is 40%, but newer developments are allowing up to 60%, and there are waterborne options.

New Product Test Methods

The drive toward higher product performance and longer coating lifetime to improve the durability of owners' assets has led to improvements in how new products are tested. The standard tests for an anti-corrosive primer developed 25 years ago consisted mainly of simple constant exposure tests such as hot salt spray (ISO 7253, ASTM B117), cold salt spray (BS 3900:F4, ambient temperature), condensation (ISO 6270), and exterior exposure in the type of environment for which the coating was intended. As coatings moved to higher solids and waterborne technologies, it has been necessary to introduce new test methods because the mode of failure in high-solids and waterbornes is often not the same as that in traditional lower solids products.

With any new technology comes the development of new tests that are able to reproduce, as accurately as possible, the failure modes observed in the field. For example, high-solids epoxies based on liquid epoxy resins are not as crack resistant as the conventional lower solids alternatives based on solid epoxy resins. There was a need to develop tests such as a thermal cyclic method with temperatures ranging from -20 C to +60 C (-4 F to +140 F) to evaluate coatings for cracking on welds, especially on high film thickness applications. This test method has shown great benefits in selecting formulations, especially in ballast coating development.

In the late 1990s, a set of corrosion standards known as the Norsok cycle was developed by the Norwegian petroleum industry. This new corrosion test attempted to mimic real life exposure for marine environments on offshore platforms, with salt spray, ultraviolet light (UV) exposure, freeze, thaw, and dry-out phases. The correlation with real time exposure was found to be better than that of the 'old' salt spray tests, and the Norsok cycle readily became accepted as one of the cyclic corrosion standards. New cyclic tests such as ISO 20340 and ASTM D5894 (an onshore cyclic test) have changed the face of product testing and improved the selection of systems used.

It is interesting to note that the need to pass ‘external’ accelerated performance tests can now determine the path of product development. For example, a coating system that will withstand many years of exposure in a particular environment could be rejected because it does not ‘qualify’ with certain cyclic accelerated tests.

Test methods for waterborne coatings have been developed with many methods remaining ‘in-house.’ Often the old standard tests such as hot salt spray were not accurate predictors of service life. Single-component waterborne coatings generally perform quite badly in tests such as constant hot salt spray.

Conversely, there has been little change in the methodology used to determine the ‘durability’ of coatings. The standard durability tests of 25 years ago, such as accelerated UV weathering and exterior exposure, are still some of the key tests performed in product development. The only improvements have been the actual cabinets themselves, which are now capable of giving much more reproducible results. A test developed in the 1960s concentrated natural sunlight up to eight times the power of the sun with the use of mirrors that tracked the sun in the sky. This test can also be directly correlated with Florida external exposure, thus giving a ‘natural’ accelerated test for all coating types.

The Next 25 Years

What does the future hold? Where will we be in another 25 years? If current trends are to be believed, then zero VOCs will be the norm, whether the coatings are solvent-free (100% solids) or waterborne. For the formulator, the race is on to develop a range of coatings that will meet stringent VOC requirements, remain carbon neutral, and maintain or improve current levels of performance.

As natural resources diminish, there will be an increasingly important need to use environmentally sustainable raw materials. Already on the market are environmentally sustainable products based, for example, on castor oil and derivatives that could be used as polyols in high-performance finishes. Epoxies from natural plant sources are available.

‘Smart’ coatings will also make it to the market. A smart coating can be defined as one that detects and responds to changes in its environment in a functional and predictable manner. Truly smart coatings are those that are capable of dynamically adapting their properties to an external stimulus, such as self-healing systems that can self-repair scratches and cracks. Other smart coatings may be responsive to temperature, corrosion, light, stress, atmospheric pressure, and biological growth.

There are many new technologies on the horizon to challenge the formulator. One thing is certain: the next 25 years will be interesting and challenging times for formulators.

Michael Donkin is the senior technology manager for International Paint Ltd. in the UK.

Sea Changes: 25 Years of Development in Marine Coatings

By Brian Goldie, JPCL

As in the protective coatings market, there have been changes in the marine coatings market over the past 25 years. Although there have been far fewer developments, the changes have been major and have had a significant effect on the market.

The changes have been in antifouling hull coatings technology and in coatings for dedicated seawater ballast tanks. The drivers have been environmental and safety concerns, respectively.

Twenty-five years ago, hull antifouling coatings were based on the use of toxic biocides, in particular, tin compounds. However, the harmful effects of tin-containing biocides on the marine ecosystem were recognized, and the recognition led to the International Maritime Organization's (IMO) regulation banning the use of tin compounds in antifoulings. Paint companies had to look to alternative antifouling technologies utilizing copper compounds and to technologies for low energy coatings, as foul release systems.

Also during the past 25 years, several vessels were lost at sea due to structural failure that was identified as being (partly) the result of corrosion in dedicated seawater ballast tanks. The best corrosion protection of the steelwork in seawater ballast tanks had been afforded by epoxy coal tar coatings, but for the most part, protection was rudimentary, and epoxy coal tars were not always used. Many seawater ballast tanks in vessels were protected with "soft" coatings, which gave very basic protection, and many in fact had no coatings at all.

The classification societies slowly began to accept that the use of good corrosion protection systems could help to prevent these losses at sea, and, as a first step, the document, "Guidelines for the Selection, Application and Maintenance of Corrosion Protection Systems of Dedicated Seawater Ballast Tanks," was adopted in 1995 under the Solas Convention (Safety of Life at Sea) as Regulation II-1/14-1. The regulation took effect in 1998. The main recommendations in II-1/14-1 were that only hard (fully cured) systems, such as epoxies, should be used; stripe coats should be applied to give extra protection at edges; and coatings should be light colored to aid inspection.

Increased efforts have since been taken to encourage better surface preparation and better application to improve performance and service life. These efforts culminated in 2008 in the introduction of the "IMO Performance Standard for Protective Coatings for Dedicated Seawater Ballast Tanks in all Types of Ships and Double-Side Skin Spaces at Bulk Carriers" (IMO PSPC). The IMO PSPC is a detailed regulation on the selection and application of coatings, including, for the first time, a mandate that experienced coating inspectors must be used to monitor all aspects of coating ballast tanks.

JPCL

The Technology Pipeline: Performance, Durability Imperatives Drive Advances in Coatings Raw Materials

By Cynthia Challener, Ph.D.

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Coatings for the protective/marine and high-performance specialty commercial architectural markets, given these disparate end use applications, not surprisingly are considered to be quite different technologies. In significant ways they are, but in many aspects, they also have notable similarities, often as the result of the need to address common performance-related expectations. Development of new technologies in both of these markets—and, consequently, development of new raw materials—are therefore driven by similar factors, such as the expectation of increased durability, the need for compliance with ever-changing regulatory requirements, the growing interest in 'greener' alternatives, and the globalization of the customer base. And of course, coatings manufacturers in each of these markets are seeking cost-effective resin, additive, and pigment solutions that address their particular performance needs.

From Croda comes a novel, non-VOC, chromate-free corrosion inhibitor that maximizes the corrosion resistance of waterborne coatings. Photo courtesy of Croda

Extended Service Life

Raw material producers strive to create value through innovation that leads to improvement in performance capabilities. Increasingly, that means developing raw materials that increase durability and long-term performance, require less maintenance, and are easier to apply, according to Rebecca R. Daley, Technical Service Chemistry with Nubiola. "There is increased interest in the market and from our customers for raw materials that facilitate the development of solutions that last longer and offer more performance than existing coatings," adds Maria Nargiello, Technical Director for the Coatings, Silicone & Resins business of Evonik Inorganic Materials.

This increased durability is generally expected to be accompanied by an increased level of performance. Steven Reinstadtler, Construction Marketing Manager—Coatings and Sustainability Initiatives with Bayer MaterialScience LLC, finds that, because formulators are challenged to constantly innovate and improve their products, they rely on raw material suppliers to fill the pipeline with new and differentiated building blocks. Carl Angeloff, P.E., Market Development Manager for Corrosion Markets with Bayer MaterialScience LLC, has also seen that applicators are looking for robust coatings that maintain adhesion in multiple application and service environments, and he believes this expectation is being driven by a need for long-term durability.

Steven Reinstadtler, Bayer MaterialScience

Longer-lasting performance can be achieved in a number of ways. In addition to better adhesion, properties such as improved color fastness, enhanced corrosion protection, better chemical resistance, improved barrier capabilities, reduced heat loads, and self-cleaning capabilities are just some of the options pointed out by Mike Kaufman, Coatings Application Development Leader for Arkema Coating Resins, that raw material suppliers are addressing through continual improvements in resin, additive, and pigment technologies.

In some applications in both the protective/marine and specialty high-performance architectural coatings markets, the substrates being painted have a life expectancy of many decades. The fewer times a ship or roof needs to be coated, the better. "A lot of coatings customers are conducting life cycle analyses for coating applications and realizing that more durable, higher-performing coatings reduce the number of repaints, which ultimately reduces the overall cost," explains Jeff Dvorak, Marketing Manager for Industrial Coatings for the NAFTA region at Wacker. It is also important to realize, observes Gil Burkhart, North American Sales Manager for Pigments with Ferro Performance Pigments, that longer-lasting coatings that provide additional protections—such as reduced heat loads, which are derived directly from the nature and quality of the raw materials—also extend the life of the underlying substrate.

Carl Angeloff, P.E., Bayer MaterialScience

Regulatory Compliance

The need to meet continually moving regulatory compliance targets continues to be a major driver for raw material development in most segments of the coatings industry. "Chemicals-related regulations have had a significant impact on the development of raw materials of all types," comments Thomas N. Hall III, Senior Market Development Manager for Coatings with BASF in North America. "Whether the issue is VOCs, corrosion inhibitors or antimicrobial compounds, legislation is driving the move towards high-solids and waterborne systems and the use of less hazardous additive and pigment technologies."

At Cytec, the demand has been greatest for high-solids, solvent-free, and hybridized chemistry solutions. "Environmental regulations and social pressures are pushing resin and coating technology advancements to higher levels," notes Amy Geiger, Cytec's Global Marketing Manager for Protective Coatings. The challenge for raw material suppliers has been to develop products that meet these new requirements but still provide ever improving levels of performance. For example, waterborne coatings can present challenges in terms of application, especially in areas of high humidity, and also of adhesion. Raw material suppliers are taking on these challenges, though, and have made significant progress in developing lower-VOC products with performance attributes such as corrosion protection, weatherability, and durability that are equal to or better than traditional products, according to Raphael Crawford, Global Marketing Director for Dow Coating Materials.

Raphael Crawford, Dow Coating Materials

The regulatory demands are now global in scope, as well, and have implications for development of new coating raw materials. The EU Registration, Evaluation, and Authorization of Chemicals (REACH), similar REACH-like legislation in countries around the world, and labeling and packaging requirements of country-specific implementations of the UN's Globally Harmonized System (GHS) all must be met. "Product development processes must ensure that this array of regulatory requirements is considered early on, because they can place limitations on the choices of the substances that can be incorporated into new products," states Fabiana Requeijo, Nubiola's Global Market Manager for Coatings.

Greener Products and Processes

In addition to the need to meet regulatory requirements, coatings companies, and, in turn, their raw material suppliers, must respond to the growing end user desire in both the protective/marine and high-performance specialty architectural markets for more sustainable solutions. “These expectations are part of a larger trend toward improved occupational health, safety, and sustainability, from the factory to application in the field,” says Crawford.

Such efforts include the development of greener products that reduce applicator exposure risks while still meeting performance requirements, and often include elimination of potentially hazardous ingredients, according to Daniel Calimente, Technical Marketing Manager for Industrial Coatings at Wacker. Developing products with a reduced carbon footprint is also important.

Addressing all of these needs and expectations can be quite challenging. “Cytec’s approach is to first understand the unmet needs from an entire system perspective, including asset owners, contractors, formulators, and coating manufacturers, then consider whether the solution can be solved with existing technology or if a new resin is required, all the while putting an emphasis on health and safety,” Geiger comments. Arkema, meanwhile, has made a commitment via its EnVia™ program that all new latexes meet certain standards for GREEN, including reduced odor and elimination of formaldehyde, according to Kaufman.

Global Presence

The high-performance architectural and protective/marine coatings markets are increasingly global in scope. “This development poses some challenges for coatings raw material manufacturers,” says Angeloff. In addition to the need to satisfy international regulatory requirements, raw material suppliers must consider the availability of components in different regions, how different applications methods might affect performance requirements, and the impact of various local climates, according to Geiger. “Coating formulators, in turn, face all of the same issues, and are, not surprisingly, turning to raw material suppliers that can manage these issues and support them on a global basis,” concludes Crawford.

Cost-Effective Solutions

Underlying all of the above requirements and expectations for raw material suppliers is the need to provide products at the lowest possible cost. “In today’s uncertain economic climate, cost has become an even more prominent issue. Successful resin, additive, and pigment producers are able to keep their product costs under control while still maintaining quality and performance,” Daley comments. Geiger adds that there are many raw material technology options available that meet or exceed critical performance criteria, but attracting interest in them can be challenging because there are often coating cost thresholds that limit options, unless there are additional value-added benefits.

Fortunately, there has been a growing recognition that sustainable raw materials offering improved durability and performance and meeting more stringent regulatory requirements come at a higher cost, according to Reinstadtler. Nargiello explains further: “Often, these new coatings solutions are based on new raw material choices that come with a higher price per gallon, and there can be some hesitancy in the approval process due to the higher cost. In the end, however, we see these higher value solutions developed with higher value raw materials prevailing and being implemented, as they deliver an offering that is both better in appearance and performance.”

A new rust converter from Halox converts rust into a paintable protective black layer that seals out moisture and protects against corrosion. Courtesy of Halox

Focus on Corrosion Protection and Marine Coatings

The market for protective and marine coatings covers numerous different applications that dictate the choice of coating system out of a vast array of possibilities. The overall goal, however, is the same for all: protection of the underlying substrates, and, where possible, provision of added functionality. The ideal formulation of the future will be a one-coat system that behaves like a conventional solvent-borne coating in terms of ease of application, appearance, and faster dry times, but has the environmental impact of a waterborne coating. In addition, it will offer effective corrosion protection (or anti-fouling properties) without the use of hazardous additives, according to Hall.

One of the biggest issues for corrosion protection coatings is the replacement of the very effective inhibiting pigment strontium chromate, which currently requires blends of materials, generally at a greater cost. Alternatives include strontium and other polyphosphates, pyrophosphates, and calcium-based ion exchange materials. Other types of compounds being investigated include organo-modified metal salts such as zinc cyanurates, silica compounds, carbon nanotubes and nanoparticles of aluminum, zinc, and silicon, salts of cerium, praseodymium, and other rare earth elements, and electrically conductive polymers.

For marine coatings, one of the biggest issues is marine antifouling. Self-polishing silyl acrylates containing copper, copper-free antifoulants containing organic biocides, and completely biocide-free silicone- and fluoropolymer-based foul-release systems are effective technologies in use today. They have replaced tributyltin, which has been phased out due to its toxicity. Corrosion is also an issue for ship owners and operators, particularly in sea water ballast tanks. Coatings used in this application must also address the issue of transmigration of marine organisms through discharged ballast water.

Polysiloxane resin systems are helping address the demand for fewer coats. "With these silicone systems, only two coats are necessary, which reduces raw material and labor costs for the end user. They also require much less surface preparation when it is eventually time for re-coating, which provides further benefits," notes Dvorak. Their very low coefficient of friction also makes them effective hull coatings in marine applications, where they exhibit good anti-fouling properties and contribute to lower fuel costs, adds Calimente. And Wacker now offers more environmentally friendly alternatives, including solventless (SILRES® IC 368) and water-based (SILRES® MP 50 E) resins; its HP technology, which consists of epoxy (SILRES® HP 1250) and amine-functionalized (SILRES® HP 2000) siloxane resins that enable easier integration of this important chemistry into final formulations; and new α-silanes, which, due to their increased reactivity, offer the possibility of overcoming the emissions issues associated with the common γ-silanes.

BASF's R&D group looks to create synergies by using the different technologies developed across the company's various businesses, according to Gregory Turco, Technology Manager for Resins and Performance Additives. Its Joncryl® 1522 resin emulsion for low VOC (100 g/L) coatings is designed for direct-to-metal applications, and delivers high gloss and appearance, excellent corrosion protection, and good exterior durability, according to Hall. Joncryl® OH 8313 and Luhydran® S 938 T are two new hydroxyl (OH) functional emulsions for polyurethane coatings formulated to VOC levels less than 200 g/L without exempt solvents.

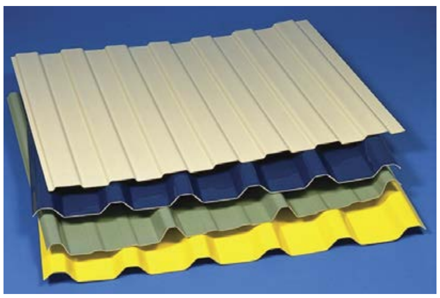
Bayer's expertise in polyurethane coatings has helped the company address many key issues for formulators of protective coatings. "Because the assets being coated are so valuable, this market tends to be risk adverse and specifies proven technologies like urethanes, and our new ultra-durable resins help satisfy the need for longer durability and risk reduction," Angeloff observes. The company has also developed user-friendly, next-generation, polyaspartic coating system technologies based on proprietary aliphatic isocyanate prepolymers that offer improved productivity and robustness in different application and service environments, formulation flexibility, and low VOCs.

To address the need for reduced system costs and increased productivity, Cytec focuses on pushing waterborne and UV resin technology that can bring the greatest value to the entire value chain. Products include low-VOC waterborne epoxy and hardener resins, including most recently a solvent-free epoxy resin with improved corrosion resistance, water-resistance, and hardness formation for protective concrete and metal applications. Its waterborne acrylic urethanes and alkyds are finding their way into applications where worker exposure to VOCs is a concern; moreover, the products allow for higher application film thicknesses and gloss retention than typical waterborne systems. Geiger notes that acceptance of these newer products can be slow because of the lack of the availability of long-term field testing data, an issue that Cytec and many other raw material suppliers are working hard to address.

Raw Material Highlights: Protective/Marine Coatings

- **Cardolite LITE 3000 Series Phenalkamides** are a new class of epoxy curing agents designed to provide coating formulators with the benefits of both polyamides and phenalkamines in one product. Phenalkamides offer the fast curing and corrosion protection properties of phenalkamines with the improved flexibility, overcoat window, and color stability that are typical of polyamides.
- **B-Tough™ C2** epoxy functionalized toughening agent from Croda, for epoxy coatings used in marine and protective heavy-duty applications such as flooring, cargo holds, and storage tanks, offers both flexibility and hardness with excellent impact resistance at lower temperatures and low viscosity for easy use.
- **AC 2403** self-crosslinking acrylate dispersion from Alberdingk Boley, for aqueous corrosion protection formulations for all metal substrates, provides excellent adhesion through the formation of a highly hydrophobic, steam-impervious film. It also offers very good UV resistance. It is well suited for high-gloss paints, metal coatings, and wood stains with good block resistance, good surface hardness, and quick dry times.
- Thin-film formers **Michem®Prime 6121** and **Michem®Lube 190** from Michelman show good adhesion to metal and aid corrosion protection. Michem®Lube 190, an anionic polyethylene wax emulsion, provides mar and scratch resistance as well as improved water resistance. Michem®Prime 6121, a functionalized polyolefin dispersion, provides outstanding adhesion to both metallic and cellulosic substrates and enhances the water, grease, oil, and solvent resistance of coatings.
- **CN9030** urethane acrylate oligomer from Sartomer, for UV/EB-, amine-, or peroxide-cured formulations, provides excellent weathering resistance and offers good corrosion protection to steel surfaces.
- **HALOX RC-980** is a cost-effective alternative to tannic acid for use in water- and solvent-based coatings as a rust-converting additive in rust-converting paints for industrial steel structures, shipyards, and numerous other rusted metal applications. With RC-980, rust is converted into a paintable, protective black layer that will seal out moisture and protect the part against future corrosion.
- **Crodacor OME FE** novel corrosion and flash-rust inhibitor from Croda is designed to maximize the corrosion defense of aqueous coatings. Crodacor OME FE is non-VOC and does not contain chromates or HAPS.
- **BYK-4511** adhesion promoter from BYK USA, for two-pack epoxy systems for industrial and protective coatings, provides improved adhesion on metal substrates along with greater surface tolerance and enhanced flexibility.
- **InhibiCor™ 1000**, a non-chromate corrosion inhibitor pigment technology optimized for aerospace aluminum protection, was developed by a joint venture between WPC Technologies, Inc., formerly Wayne Pigment Corporation, and Crosslink. InhibiCor™ 1000 displays performance characteristics and mechanistic similarities to those of the industry standard hexavalent chromium, but without the associated health, safety, and environmental concerns.
- **Bayferrox®** iron oxide pigments from Lanxess are for coloring of corrosion protection coatings. The low water-soluble salt content and low conductivity of the aqueous extract of Bayferrox® pigments are advantageous for the performance of corrosion protection systems.
- **Copper Omadine™**, a booster biocide for marine antifouling paints from Lonza Microbial Control (which acquired Arch Chemicals in 2011), is now available pre-dispersed in a self-polishing zinc acrylate copolymer. The product has non-agglomerated particles and offers safer handling, less settling, and better performance.

Dow Coating Materials is addressing unmet needs in the protective/marine market with advanced waterborne chemistries ranging from acrylics and epoxy dispersions to high-solids systems, including new resins for advanced, low-VOC, anti-fouling marine coatings and single-coat protective systems; high-temperature fusion-bonded epoxy resins that facilitate better long-term durability and performance; and resins with reduced curing times. The company will soon be launching new products for the American marine and protective coatings market that will include a series of water-based curing agents, a family of waterborne epoxies (liquid epoxy resin emulsions, a novolac resin epoxy dispersion, a solid epoxy dispersion, and high-temperature fusion-bonded epoxy resin systems). "All of these products are specifically designed to deliver innovative building blocks to facilitate the formulator's ability to develop high-performance coatings that can be tailored to suit their needs," says Crawford.



Urethane acrylate oligomer from Sartomer provides good weathering resistance and corrosion protection to substrates such as corrugated metal sheets.
Courtesy of Sartomer

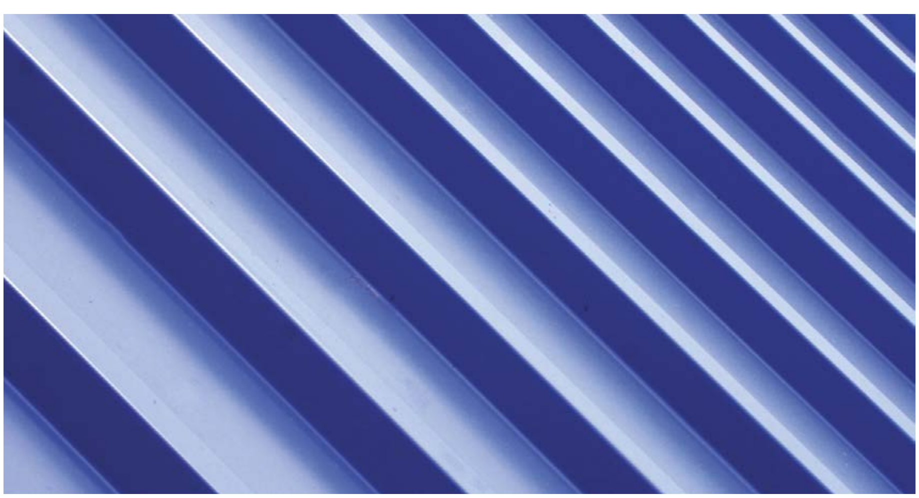
Spotlight on High-Performance Specialty Commercial Architectural Coatings

All segments of the building and construction industry have suffered during the recent recession. The lack of new construction has shifted the emphasis to reworking of existing structures. "There is greater activity in the areas of refurbishing, restoring, and repair, and raw material suppliers have had to modify their approach accordingly," observes Nargiello. "Demonstrating that a particular raw material can achieve a special appearance on an existing surface, can be applied in an easier and faster manner by contractors, and offer new and longer levels of environmental protection than the status quo technology are all performance areas being targeted," she adds.

Cool roof and wall coatings are good examples of specialty coatings that are experiencing strong growth. Such coatings help reduce the heat load of buildings, thus reducing energy consumption (and CO_2 emissions). They also prolong the life of the underlying substrate (metal, shingles, stucco, etc.) by minimizing expansion and contraction, according to Burkhart. White elastomeric coatings—the vast majority based on acrylics, but silicone and urethane systems are used as well—are used on commercial buildings with flat or low-sloped roofs. Coatings colored with infra-red (IR) reflective pigments and based on polyvinylidene fluoride (PVDF) or silicon-modified polyester resins (SMP) are used on sloped metal roofs. Shingles now are also being manufactured with granules that have been pre-coated. Burkhart adds that these coatings are also finding their way onto the walls of stucco buildings. "For the colored coatings, the challenge is for the pigment manufacturers to continually expand the range of colors (especially blacks and browns) while increasing the total solar reflectance."

The raw materials are also expected to be very long-lasting, making durability a significant performance issue. "There are well-established systems that have delivered consistent durability performance for many years, but innovative raw material suppliers are always seeking new ways to help paint producers raise the performance bar," notes Eric Kaiser, Global Marketing Director for Arkema Coating Resins. Lifetimes of reflective roof, curtain wall, and aluminum extrusion coatings depend largely on the resin type, with polyvinylidene fluoride (PVDF) -based coatings providing the best performance (~30 years), and SMPs, acrylics, and polyesters, which are less expensive, giving coatings that perform well, but are not as long-lasting (~15 years or less).

The biggest regulatory issue for specialty high-performance architectural coatings is VOCs, but many of these applications are on metal surfaces that require corrosion protection, so replacement of chromate corrosion inhibitors is also a factor for these formulations.



New pigments from Shepherd are designed for use in building products such as high-durability and IR-reflective coatings. Courtesy of Shepherd

Regarding VOCs, waterborne technologies are providing the answer, according to Reinstadtler. "Waterborne resins are becoming ubiquitous in every coating type as technology improves. In many cases such as polyurethanes, these resins have undergone many improvements over the first generation waterborne versions to become equal to or better in performance than their old solvent-borne analogs," he comments.

Arkema is one of the key suppliers of PVDF resins (Kynar 500). Until recently, its use has been limited to factory-applied applications. Today, however, the company offers Kynar Aquatec, a liquid latex version of Kynar PVDF that is suitable for field-applied architectural systems. Arkema has also introduced ENCOR™ Flex 187 and ENCOR™ Flex 3186, resins that offer improved dirt pickup resistance

Raw Material Highlights: High-Performance Specialty Commercial Architectural Coatings

• **Sporgard®** and **Azotech®** new generation fungicides from Lanxess are derived from modern crop protection products and show very specific and unique modes of action, thus providing excellent environmental, toxicological, as well as handling profiles.

• **HEUCODUR® IR 945** from Heubach is an IR-reflecting pigment that combines jetness and a neutral color shade in reductions and offers a high total solar reflectance.

• Two new pigments come from Shepherd Color: **Blue 10C595** cobalt blue pigment with a lower surface area for lower resin demand, high gloss, and high solar reflectivity; and **Orange 10C321**, a new color and color space that bridges the color space between conventional titanates and lead- and chrome-based pigments while also offering high solar reflectivity.

• Holliday Pigments' new red-shade orange high-performance grade **Solaplex® Bright Orange (34H1004)** is a mixed metal oxide pigment.

• **Dispersogen® ECS** from Clariant is a universal pigment dispersing agent for both waterborne and solvent-borne coatings that is effective for organic pigments, inorganic pigments, and carbon black, and it can help simplify the production process.

• Additives from Pflaumer Brothers include the following: **Zero-VOC hyperdispersants** for viscosity reduction in pigment dispersions and pigment treatments; water-based IR **Heat-Reflective pigment dispersions** for use on PVC window profiles; and **Terachem® 53-4368** and **Terachem® 53-2371** nano-aluminum oxide dispersions for epoxy and 2K polyaspartic coatings, respectively, that provide increased mar, scratch, scrubbing, and rub-off resistance.

• **TEGO® Foamex 823** emulsion for waterborne coatings with broad compatibility eliminates the need to maintain a large number of specialty defoamers for different formulations, thus reducing complexity.

• Several new products come from Dow Corning: **slip and leveling additives** provide good slip and hand feel performance without causing unwanted foam stabilization or decreasing recoatability; **superwetting agents** provide good spreading and wetting at low use levels, even on difficult-to-wet substrates such as wood, plastics, and metal; and **Dow Corning® 87 and 88** are low-VOC, solvent-free and APEO-free silicone resin emulsions that provide improved water resistance at low use levels.

• Products from OMNOVA Solutions include the following: **Mor-Flo WE 30** performance additive provides improved hardness, anti-mark, and block resistance to floor polishes without adding color; a new **Pliotec®** waterborne resin allows for the formulation of 2K institutional coatings that reach full performance after three days of cure and provide scratch resistance; and **Pliotec® SC55** self-crosslinking, low-VOC (<100 g/L VOC), APE- and formaldehyde-free, all-acrylic latex for the concrete sealer market has excellent UV stability and blush resistance.

• Pflaumer Brothers also offers polyaspartic technology: **Teraspartic® 277**, **Teraspartic® 292** and **Teraspartic® 230** polyaspartic amines for 100% solids polyaspartic coatings used in concrete floor coatings, fiberglass gel coats, and corrosion-resistant direct-to-metal coatings; **Tallicin® 4040** deaerator for polyurea polyaspartic coatings that helps minimize pinholes, craters, and orange peel in 100% solids coatings applied at up to 6-8 mils of film thickness; and a new line of **Terachem® 53-Color Concentrates**—polyaspartic amine-dispersed colorants offering a wide range of colors for use in polyurea/polyaspartic coatings.

• DSM and Partner Empresa Brasileira de Biotechnologia (Ebrabiotech) of Brazil recently launched of a new line of **DSM-branded bio-based castor oil materials** for the industrial concrete floor coatings market.

for white reflective roof and elastomeric wall coatings, which helps them stay whiter longer. Coatings formulated with these resins are also suitable for a variety of other end-use applications, such as cool wall coatings, insulating coatings, and vapor barriers.

Bayer MaterialScience has extensive expertise in urethane chemistries and is continually leveraging that expertise for the development of new solutions. The company recently launched several new products: a two-component (2K) polyaspartic coating technology used in waterslide refurbishment that provides fast return service coupled with outstanding weatherability; a low odor, ultra-low VOC (<15 g/L), two-component polyurethane waterborne technology for sealers designed to protect stained and polished flooring in commercial and retail spaces; a low-VOC, engineered polyisocyanate that, when used in conjunction with polyaspartic coatings raw materials, produces a topcoat for industrial and retail flooring that cures effectively in a wide range of humidity levels; and a low-VOC, waterborne polyurethane architectural wall paint technology for healthcare facilities that offers similar application properties to current acrylic wall paints but with much higher durability, nearly no odor, and resistance to harsh disinfection chemicals.

A new matting agent from Evonik provides higher transparency with lower viscosity in UV coatings. Photo courtesy of Evonik

Evonik's focus has been to expand its existing portfolio into water-based barrier protection systems. Many of Evonik's treated silica grades, whether fumed or precipitated, are well known for solvent-based coatings technology, but their efficacy is not as well known in waterborne chemistries. "Our efforts have been to demonstrate this efficacy and educate formulators that many of the same attributes that they have come to rely on in solvent-based systems hold true for water-based systems as well," says Nargiello. Toward that end, the company has commercially launched water-based dispersed solutions that offer both ease-of-use and increased coatings performance.

Ferro Performance Pigments is continually working to optimize the total solar reflectance of its IR-reflecting pigments and to expand the color range that provides effective reflectance. Recently it has added three products in the challenging black and brown color spaces. V-781 Cool Colors™ IR Black, V-785 Cool Colors™ IR Black, and V-760 Cool Colors™ IR Dark Brown are IR reflective pigments with very high solar reflectivity. V-781 is a Red-Shade black, V-785 is a Blue-Shade black, and V-760 is an Iron Chromite Brown Hematite dark brown pigment. "V-785 is a very interesting pigment with a unique dark, blue black hue compared to other IR pigments and provides a color closer in masstone color depth to carbon black," says Burkhart. The many IR reflective pigments from Ferro can be used by themselves, combined with each other, or even mixed with titanium dioxide to form a wide range of colors that can meet federal and/or state specifications and guidelines for cool roofing.

Nubiola manufactures a line of high-performance direct anodic corrosion inhibitors and an array of inorganic pigments, including ultramarine blue, iron oxide, zinc ferrite, chrome oxide green, and bismuth vanadate. "Our R&D efforts focus on developing unique products that enhance our product portfolio and address the needs for pigments and corrosion inhibitors that comply with ever increasing environmental constraints," Daley says.

Other Specialty High-Performance Architectural Coatings

- Insulating coatings are typically latex emulsions containing ceramic beads or silica particles that help prevent heat from passing through the walls.
- Anti-graffiti coatings are based on several different types of resins, including fluorinated silicones, fluorinated polyethers, epoxy silicones, aliphatic urethanes, and some polyesters. The resins are designed to provide low surface energy so that inks cannot adhere to the surface.
- Air/vapor and even water barriers are often membranes prepared from special forms of nonwoven polyethylene fibers that can let air and/or water vapor pass through but prevent water penetration. Depending on the product, they can be used in the foundation of a building or as an envelope around the structure.
- Thin-film intumescent coatings provide insulation to the substrate and work by expanding their volume from 10 to 75 times and generating an ash-like char. They provide an attractive way to protect exposed steel and other structures. Most thin-film intumescents are formulated with vinyl acrylic or epoxy resins and contain a promoter or catalyst (typically a phosphate salt such as ammonium polyphosphate), a char former (often pentaerythritol), and a blowing agent (usually a melamine derivative). Ablative coatings, or sacrificial coatings designed to reduce the rate of burn, usually contain fire-retardant chemicals such as aluminum trihydrate or antimony oxide.

Cynthia Challener has worked as a self-employed consultant since 2000, offering technical writing and editing services to the chemical and allied industries. She contributes regularly to several chemical industry publications, and her clients include leading specialty chemical, biochemical, and advanced materials companies, trade associations and public relations and market research firms. Cynthia received her BS in Chemistry from Stanford University and her Ph.D. in organic chemistry from the University of Chicago. She worked as a Principal Research Chemist at ARCO Chemical Company and Technical Services Director for flavor and fragrance producer Bedoukian Research prior to starting her own business.

JPCL

Raw Material Suppliers Answer Calls for Green and Smart Coatings

By Brian Goldie,
JPCL

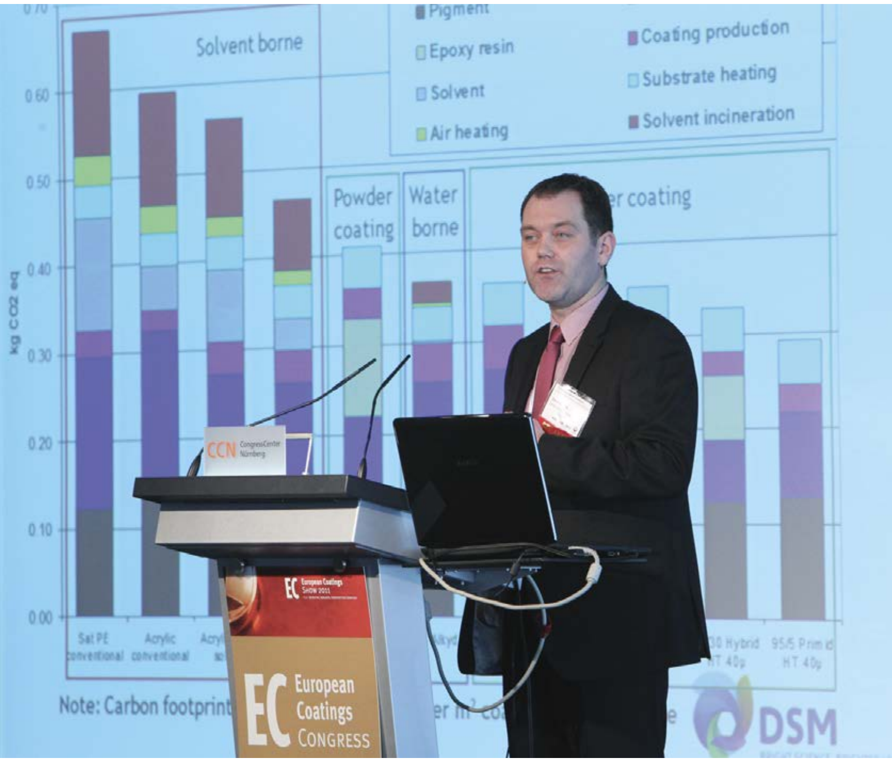
Editor's note: This article appeared in JPCL *in July 2011.*

At the end of March 2011, the world's paint raw material suppliers met at the European Coatings Show in Nuremberg, Germany.

The bienniel show, which is the largest coatings event in Europe, had a record 26,000 trade visitors this year. Some 890 suppliers to the paint industry from 45 countries displayed their new and traditional products. At the parallel European Coatings Congress, 650 participants from 40 countries heard some 150 papers of outstanding interest in the topical issues of this highly innovative sector.

This review of the exhibition and conference discusses what the developments in new products and technologies mean to users of protective coatings and what users can expect in new paints or improved performance. The properties described in the review are based on comments and data sheets from suppliers and have not been independently verified.

Photo courtesy of NuernbergMesse© and Thomas Geiger©



Approximately 150 papers were presented during the European Coatings Congress. Photos pages 18–21 courtesy of NuernbergMesse©.

Trends: Green, Waterborne, and Smart

Most new products from coating raw material suppliers at the show are based on ingredients from renewable or sustainable resources. The concept of "green" products, even the color theme, was carried over in a number of stand designs.

The reliance on fossil fuels as sources of raw materials for coatings is shifting to a reliance on natural products, with suppliers also being sensitive to the need to not affect the use of these materials in the human food chain. For example, suppliers that incorporate soya-based ingredients into their raw materials are aware of the effects on the supply of soya ingredients because they are a major source of nutrition for many countries.

Although new products for high-solids are still in demand, an underlying trend at the show was an increasing emphasis on waterborne systems rather than high(er) solids as a means of meeting the more stringent regulations on volatile organic compound (VOC) content in coatings.

A third trend was an increasing number of smart, or functional, coatings developments on display.

Resins and Curing Agents

The major raw material suppliers—BASF, Bayer, and Dow—all exhibited their comprehensive product ranges for a wide variety of industries.

The industrial coatings market is one of the most diverse that BASF serves, and it introduced two more products.

- Basonat® LR 9080, a waterborne, fast-drying polyisocyanate mainly for general industrial coatings, allows faster handling of the coated substrate.
- Acronal® PRO 80, a modified acrylic dispersion for metal primers, not only offers high-performance corrosion protection but it also is free of alkylphenol ethoxylates (APEO).

APEOs are non-ionic surfactants with an emulsifying and dispersing action that makes them suitable for a very large variety of applications; however, APEOs, especially nonyl phenol ethoxylates, are considered very toxic for aquatic life and, in Europe, are no longer allowed or wanted.

Polyurethane coatings formulated with Bayer raw materials are already found in a wide range of applications; however, the company's latest developments go even further as coatings increasingly take on new functions. Bayer's and other suppliers' new polyurethane products and developments will be detailed in the next chapter.

The Dow Chemical Company's five businesses combined to demonstrate the benefits of the company's latest technological advances in their industries. Dow Construction Chemicals introduced white reflective roof coatings, a new technology to reduce over-heating in buildings. At the top of most agendas in today's building industry is the drive to create products that are more sustainable and take maximum advantage of ways to save energy. To this end, one of the main areas promising significant progress is roof technology, specifically, the development of coatings aimed at lowering building temperatures caused by radiant sunlight.

After many years of study into the indoor temperature effects of direct sunlight, Dow Construction Chemicals developed and, at the show, highlighted its latest innovations in its "cool roof" technology program: reflective elastomeric coatings that are durable and efficient, with the potential of making the single largest contribution to reducing CO_2 emissions from domestic, commercial, and industrial buildings. In addition, the cool roof coatings are designed to play a significant role in extending the longevity of structural roofing materials.

A record 26,000 people attended the exhibition.

Another company promoting cool roofing was Arkema. It showcased its polyvinylidene fluoride (PVDF) resins for long-life coatings dedicated to cool roofing. The company also featured its very low VOC acrylic emulsions.

The Huntsman Performance Products division brought two new fast cycloaliphatic amine-curing agents to the market. XTA-801 and DCH-99, which offer low viscosity, low color, and high reactivity, are designed for use in coatings, flooring, and other applications. When combined with the company's Jeffamine® polyetheramine (PEA) hardeners, the new curing agents can enhance glass transition temperatures, modulus, and hardness, and can improve chemical resistance as well as low temperature curing properties. The company also introduced a PEA epoxy curing agent that offers low viscosity, low color, higher glass transition temperatures, and faster property development than other solutions typically available. Another new product from Huntsman is a cycloaliphatic amine chain extender for polyurea spray. The extender is designed to be easy to use and environmentally friendly.

From Wacker came product innovations and customized solutions for industrial coatings, construction, and adhesives and sealants. It also unveiled SILRES® IC 368, a liquid, solventless silicone resin intermediate for highly weatherable coatings. The new silicone resin is formulated so that an addition of just 15% increases the UV resistance and weatherability of the organic binder in the coating system without impairing the mechanical properties of the system.

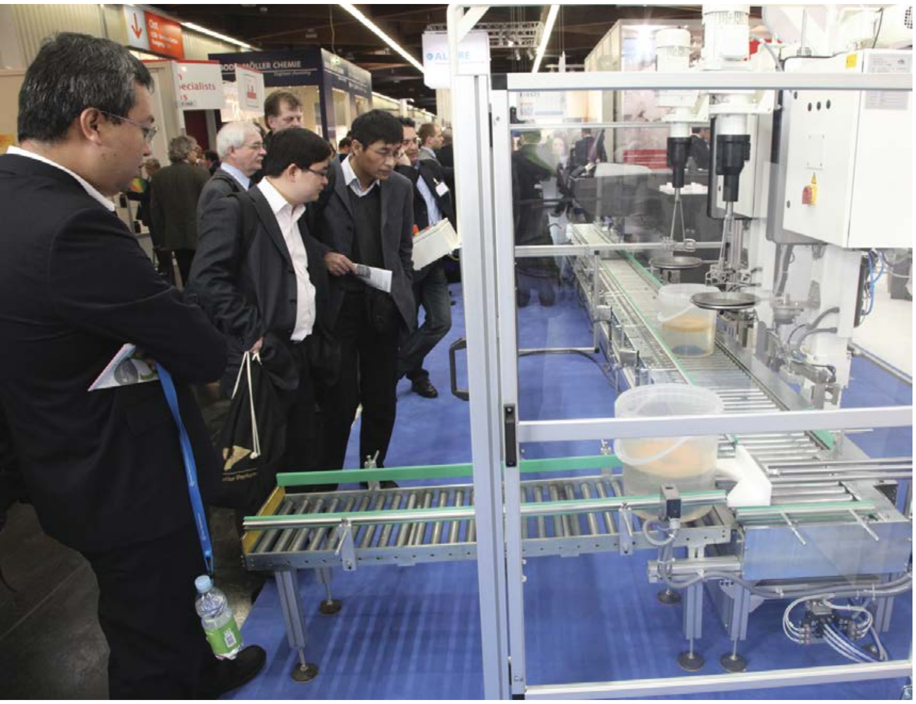
Lab and open-air weathering tests show that SILRES® IC 368 confers much better gloss retention, superior weatherability, better heat resistance, and a longer service life compared to similar products. Designed to be highly versatile, the new intermediate is suitable for modifying alkyd resins, hydroxy-functional acrylic resins, and hydroxy-functional polyesters commonly used in industrial coatings for metal, including coil coating.

Perstorp Holding AB's Voxtar™ is, according to the company, the world's only renewable pentaerythritol platform**.** Voxtar™ cuts a carbon footprint by up to 75% compared to that of conventional fossil-based penta and di-penta polyols while providing identical properties and performance. It is made from bio-based acetic aldehyde and formaldehyde. Combining the renewability of Voxtar™ with the latest waterborne technology significantly shrinks the carbon footprint of high-solid alkyd paints and alkyd emulsion paints compared to traditional petroleum-based latex paints.

The product also exemplifies the company's efforts to reduce emissions and energy consumption associated with raw material manufacturing—Perstorp uses renewable raw materials such as bio methanol to decrease the use of petrochemical raw materials. Moreover, renewable energy has been powering parts of the company's production sites since 1991, and more than 80% of its R&D work is focused on environmental innovation.

Perstorp's approach to innovation is driven by sustainability on three fronts: reducing emissions and energy consumption in raw material manufacturing; developing products that enable customers to formulate low-environmental impact solutions; and high-performance additives that enable more durable and long-lasting end products.

Omnova Solutions, together with its recently acquired Eliokem, is a significant supplier of styrene butadiene lattices, acrylic emulsions, bio-based polymers, and additives. The company presented a new range of hydrophobic acrylic emulsions under the Omnapel™ name. The emulsions exhibit exceptional water resistance, good exterior durability, and other resistance properties, making them useful in water-resistant coatings such as concrete sealers. In addition, they can be blended with other polymer systems to enhance water resistance and durability. Some of the products can be



Industry professionals check out new products from suppliers.

used to create coatings that, when cured above 135 C, are insoluble to acids, alkalis, and organic solvents.

Incorez introduced a waterborne epoxy curing agent—Incorez 148/604— to help companies comply with the requirements of the VOC Solvents Emissions Directive, the European Union's main policy instrument for reducing industrial emissions of VOCs.

Charles Lynch, Commercial Manager at Incorez, commented on the launch: "Our new waterborne epoxy curing agent is a water soluble polyamine curing agent that is APEO, formaldehyde and solvent free, and so does not contribute to the VOC levels of the coating formulation. It is designed to produce very tough and durable, high-gloss waterbased coatings with both liquid and solid epoxy resins. In particular, this hardener displays very good compatibility with neat Bisphenol A type liquid epoxies, such as Epikote 828, to provide excellent hardness and cure development."

Croda Coatings & Polymers brought out its latest "green" innovation, Priamine 1071, for marine and protective coatings. Priamine 1071 is a low viscosity curing agent for epoxy systems. It can be used as a main curative and co-hardener, and it addresses a growing demand for the development of high-solids, low-VOC formulations. Due to its high flexibility and chemical resistance, this novel dimer diamine, bio-based building block is suitable for interior and exterior coating applications that require durability under severe conditions. Its sealant and protective properties as well as its improved adhesion properties can extend the service life of a coating.

Air Products featured its next generation of epoxy curing agents aimed at helping formulators design coatings solutions that benefit the environment and that are effective over a range of coating applications. Using its "Total Reactive Technology" approach, the company developed a modified polyamine curing agent that is 100% reactive (to epoxy resins) and that eliminates the need for a plasticizer. With its high performance and fast curing at ambient and low temperatures, the technology has already been successfully used for indoor flooring applications. The plasticizer-free technology is also more sustainable and has near negligible emissions throughout the lifetime of the coating. According to experts at Air Products, the new generation technology complements the increasing popularity of water-based systems.

Additives

"Green" again was the word when it came to new additives, but, as stressed by Byk Chemie, no global standard precisely defines "green" in the context of the surface coating industry. Everyone has a perception of its meaning, and the demand for "green" products keeps growing, hence the number of new developments. "Green" is also a synonym for "environmentally friendly," but what does that phrase mean? According to Byk, the VOC content of products and raw materials is one important indicator of their impact on the environment; however, the deciding factors are often the various eco-labeling systems in existence and the percentage of renewable materials in a product. Formulators often have to balance the use and type of "green" materials against performance requirements. With this in mind, Byk has developed products and technologies that meet current environmental standards without sacrificing the quality of the products being replaced.

New products on show included Byk-1740, a green defoamer based on eco-friendly and sustainable raw materials—vegetable oil derivatives. It is VOC-free and completely sustainable while providing the same performance as the standard mineral oil-based defoamers. Especially suitable for waterborne emulsion paints, the new defoamer has no negative influence on color or odor.

Other new Byk products exhibited for waterborne systems included silicone-free defoamers, defoamers free of mineral oil as well as silicone, and wetting and dispersing agents.

According to Clariant, it was one of the first companies to offer a 100% APEO-free alternative for manufacturing binder emulsion polymers. In addition to its low VOC levels, Emulsogen® EPA 073 is now one of few anionic emulsifiers with FDA approval. When combined with nonionic emulsifiers like Emulsogen LCN 287 or Emulsogen LCN 407, these APEO-free emulsifiers offer increased latex stability and better shelf life. They increase the availability of more environmentally acceptable alternatives to solvent-borne paints and coatings in contact with foodstuffs.

Rhodia is also moving toward more sustainable coatings with its portfolio of breakthrough performance additives created to meet formulators' demands for specific solutions for creating the next generation of eco-friendly coatings. The company highlighted its new eco-friendly evaluation approach to designing sustainable coatings by spotlighting its growing line of zero-VOC, APEO-free performance additives and solvents for waterborne coating. Rhodoline® OTE is a novel zero-VOC, APEO-free range of additives for extended open time (workability) in waterborne coating formulations. It provides a two- to four-fold increase in open time without the addition of solvents, thus giving painters longer to work overlays seamlessly or to touch up paint to correct imperfections such as drips and brush marks.

Air Products launched a new range of defoamers and de-aerators based on organic, silicone, and molecular chemistry that will allow manufacturers to produce high-performance coatings that are more durable, efficient, and environmentally friendly. The defoamers and de-aerators are particularly useful for waterborne systems and can be used in floor coatings in combination with the company's epoxy curing agent technology.

BASF also featured Dehydran® SE 2, a high-performance silicone polymer emulsion defoamer for premium waterborne paints and clear coats. It offers good foam suppression and long-term persistency, is highly compatible and easy to handle, and minimizes gloss reduction. Because Dehydran® SE 2 is VOC-free and has an ultra-low semi-volatile organic compound (SVOC) content, it also helps manufacturers formulate paints and clear coats that meet the requirements of environmental standards and safety certifications, such as the German TÜV, Green Seal GS-11, the EU Ecolabel, and the Blue Angel.

In the range of rheology modifiers, BASF introduced DSX® 3801, a VOC-free, mid-shear rheology modifier with excellent ICI thickening. The ICI build of the thickener clearly exceeds that of benchmark waterborne products, even at lower dosages. Due to the high efficiency and improved performance of DSX® 3801, a smaller amount of it is needed in formulations—a "do more with less" approach that delivers sustainability benefits.

Dow Coating Materials announced the launch of its new EVOQUE™ Pre-Composite Polymer Technology—a revolutionary development for paints and coatings that promises to change the way formulators think about hiding and the use of titanium dioxide (TiO_2). The acrylic-based technology improves the particle distribution and light scattering efficiency of TiO_2, facilitating improvements in hiding efficiency and allowing for up to 20 percent less TiO_2 used in the formulation. Additional benefits include improved barrier properties such as stain and corrosion resistance.

Depending on their formulation goals, paint manufacturers can choose to reduce TiO_2 content or improve hiding while they improve paint performance. The Pre-Composite Polymer Technology may also help formulators reduce the carbon footprint of their end products by reducing the energy footprint that comes from mining, processing, and transporting TiO_2 to their formulation plants. Dow Coating Materials is conducting a life cycle analysis, which will be verified by a third party, to quantify the full spectrum of sustainability advantages that may result from using its new technology.

Pigments

The trend for "green" products also extended into the new pigments offered from the various suppliers. The developments were predominately in color pigments, although some new environmentally friendly anti-corrosion pigments were on show from companies such as Halox, Nubiola, SNCZ, Sachtleben, and Pigmentan.

Smart Coatings

One class of “smart coatings” is the self-healing systems that incorporate Bayer MaterialScience products. The systems are functionalized anti-corrosion coatings or topcoats that can “heal” damage autonomously, similar to the self-healing mechanism of the human skin.

Other products for smart coatings were for graffiti resistance.

New perspectives for smart coatings are being found in marine coatings with the use of carbon nanotubes, again from Bayer MaterialScience. The nanotubes allow another approach to providing different properties and additional functions, and their use as coating additives could open up even more intriguing perspectives. The high mechanical strength and electrical conductivity of the particles, in particular, promise novel possibilities for formulating coatings and for improving the strength of structural components while keeping their weight extremely low. Novel epoxy-gel coatings with nanotubes are already significantly improving the scratch-resistance of coatings for ship hulls.

Nanotechnology is also being used to give floor coatings with improved properties. The COL.9® nano-based binder from BASF, which has been used to produce “self-cleaning” wall coatings, can also be used to coat substrates such as concrete, stone, or tiles. This means that, for example, tire marks or oil stains on garage floors can be a thing of the past. The functional principle is the same for both facade and floor applications. The binder combines the benefits of synthetic resin dispersions with those of silicates. (COL.9 is a dispersion of organic polymer particles in which nanoscale particles of silica are incorporated.)

The organic part of the binder, i.e., the acrylic resin, ensures sufficient elasticity while the mineral part lends the colored coating the required rigidity. This makes coatings particularly resilient as well as resistant to dirt and chemicals.

Congress

The themes at the show were also prominent at the congress. In fact, the plenary lecture by Professor Matthias Beller, University of Rostock, Germany, was “Sustainable chemistry: A key technology for the 21st century,” which addressed the improvement of industrial chemicals production.

Approximately 150 papers were presented in 25 sessions covering a range of technologies and end uses, with specific sessions on sustainability and bio-based coatings, smart coatings, and nano-technology. The majority of new products on show were also the subject of detailed technical presentations.

Dr. Matthias Beller addressed sustainable chemistry in his keynote speech.

Summary

The emphasis of the products being exhibited and technologies presented was on their environmentally friendliness, with materials for waterborne systems predominating. Companies were also keen to explain their desire to use renewable ingredients as their raw material sources and their efforts in reducing the carbon footprint of their production facilities.

Brian Goldie, technical editor for JPCL, has worked with protective coatings for many years, including in the oil industry.

JPCL

Reducing VOCs in Polyurethanes Takes Two Routes

By Brian Goldie,
JPCL

Editor's Note: This article appeared in JPCL *in August 2011.*

Polyurethanes have become an increasingly important, versatile technology for protective coatings. The high solvent resistance, good mechanical properties, and excellent weathering properties of polyurethanes make them suitable as topcoats in a variety of applications. Current environmental regulations to restrict volatile organic compound (VOC) content has meant more challenges for the formulator in developing higher solids or waterborne polyurethane finishes. This article reviews developments in these areas as presented at recent European and U.S. conferences and exhibitions.

Waterborne or High Solids?

In deciding whether to take the high-solids, solvent-borne (or solvent-free) route or use waterborne technologies to meet VOC restrictions, North American and European formulators have tended to go separate ways. Since the 1970 U.S. Clean Air Act, American formulators turned more often to solvents exempt from U.S. VOC regulations to make high-solids systems, rather than adopting waterborne equivalents. European formulators, however, have not had the luxury of using exempt solvents; therefore, most developments in low VOC coatings have tended to be with waterborne systems.

(Left) ECS trade fair activity. ©NuernbergMesse

European Coatings Show

A report on the new products on display at the European Coatings Show (ECS, Nuremberg, March 2011), except for developments in polyurethane (PU) systems, was published in the July 2011 *JPCL*. The article noted that the general trend of products on display to meet the lower VOC regulations was related to waterborne technologies, not higher solids, solvent-borne systems. The new products for PU coating technology from a selection of the Show's exhibitors are no exception.

According to Bayer, PU coatings formulated with its raw materials have a wide range of applications, with the latest developments targeting new functions. For example, waterborne two-component (2K) PU clearcoats and topcoats formulated with the new generation of Bayhydrol® A acrylic dispersions feature outstanding chemical resistance, making graffiti removal easy. They also satisfy exacting requirements for gloss retention and for weathering, UV, and scratch resistance. The specially developed PU dispersions can also be used to formulate waterborne 2K primers with good anti-corrosion and rapid cure properties. Improving on their predecessors, the new products can also be used to formulate coatings with VOC content well below 250 g/L—in some cases even below 100 g/L.

With the introduction of Easaqua™ X L 600, a new modified polyisocyanate, Perstorp has answered coating producers' calls for waterborne PU technology that offers high humidity resistance. With the balance between low viscosity and high NCO content, it helps meet the market's need for low VOC systems. Further, it improves coating adhesion on a wide range of substrates. Thus, it is particularly suitable for direct-to-metal (DTM) applications.

Also to meet the rapidly growing market for aqueous PU dispersions, Croda Coatings & Polymers displayed its bio-based polyester polyols for high-performance waterbornes.

Incorez demonstrated the practical use of oxazolidines by case studies showing the enhanced performance of one-pack PU flooring systems and improved performance of aromatic PU sealant prepolymers using oxazolidine latent hardeners; and the benefits of oxazolidine moisture scavengers in wind turbine protective topcoats.

Trends Shifting

There are now, however, signs that, with some exceptions, the dominance of waterborne technologies in Europe is changing, as can be seen from the new studies presented at several important coatings conferences over the past nine months, including the European Coatings Congress that accompanies the ECS, the Advances in Coatings Technology Conference, and SSPC 2011 (SSPC: The Society for Protective Coatings). The main exception to this changing trend was at the FATIPEC Congress, held in conjunction with Eurocoat. The difference may be related to the fact that FATIPEC/Eurocoat targets the architectural market and coating producers in the Mediterranean, where the climate is generally more favorable to waterborne coatings.

European Coatings Congress

While the trend for products on display at the ECS was toward waterborne technology, the PU technical session at the ECS's accompanying European Coatings Congress was primarily focused on developments for high-solids, solvent-borne PU systems.

M. Mechtel et al., from Bayer MaterialScience, Germany, noted that in the current economic climate, the search for the effectiveness and efficiency of coatings that maintain quality and environmental compatibility is more important than ever ("Are high coatings performance, efficiency, and environmental compatibility still a contradiction?"). Highly functional aliphatic poly-isocyanates enable fast-drying 2K PU topcoats to be formulated. Due to their high cross-linked density, they have excellent durability; however, in many cases, the high viscosity of these poly-isocyanates has required high solvent levels and thus reduced their environmental compatibility. The author described a new high functionality, low viscosity aliphatic polyisocyanate (HDI-allophanate) for clear coats and 100% solids coatings.

The effect of the polyol/isocyanate combination in achieving the desired VOC level in high-solids, 2K PUs while keeping good drying and hardness properties was the subject of a study by F. Lucas et al., BASF SE, Germany (“Structure-property relationship of 2K aliphatic polyurethane systems”). The authors found from a study of the drying kinetics of combinations of acrylic/isocyanate that the composition was critical to achieve specifically desired mechanical properties. Although this presentation was biased to automotive topcoats, the reasoning is valid for high-performance protective topcoats.

V. G. Parcios, Universidad de Alicante, Spain, discussed the synthesis of PUs from polycarbonate polyols (“Performance of PU coatings obtained with polycarbonate diol, polyether & polyester polyols”). Parcios demonstrated that the polycarbonate polyols gave better hydrolytic stability, mechanical properties, and low-temperature behavior than coatings made from polyether or polyester polyols. The polycarbonate polyol reduced drying times and improved pencil hardness, gloss, and yellowness index.

Reduced VOC levels were also the subject of a presentation by R. Shain et al., King Industries, U.S. (“Novel polyol modifiers to achieve VOC compliance with improved performance”). The authors described a unique family of polyester reactive modifiers for high-solids, solvent-borne industrial coatings. Several formulations were described to show how other physical and resistance properties were also improved such as flexibility and exterior durability. Despite these reactive modifiers being hydrophobic, they can offer advantages to a waterborne 2K PU: increased impact resistance, good salt spray resistance, and high gloss.

Waterborne technology was not entirely absent from the PU technical session at the Congress. K. Woods et al., Arkema, U.S., described hydroxyl functional PVDF-acrylic hybrid emulsions cross- linked with water-dispersible polyisocyanates to produce coatings with good weather-ability and abrasion resistance for wind turbine blades (“Water-based fluoropolymer-urethane hybrid systems for wind turbine blade topcoats”). The authors reported their work on optimizing the binder’s fluoropolymer level and the parameters of the resultant coating. These new hybrids combine the excellent weather properties of PVDF resins with good solvent resistance, hardness, toughness, and abrasion resistance from the urethane component.

Waterborne 2K PUs were also the subject of a paper by M. C. Schrinner et al., Bayer MaterialScience, Germany (“Next generation acrylic dispersions for high performance water-borne 2K PU coatings”). Noting that these systems had been gaining success and now have some properties comparable to their solvent-borne counterparts, the authors described a new generation of acrylic polyol dispersions. They have a reduced concentration of organic solvent of the dispersion and a reduced demand for additional solvent in the finished coating formulation. Both properties resulted in lower VOC coatings with good film properties, hardness, and solvent resistance

In addition, two general presentations were also on reducing VOCs in coatings by replacing solvent-borne systems with their equivalent waterborne counterparts.

J. Stubbs et al., DSM NeoResins, U.S., described a range of urethane and other resin monomers that could be combined to give environmentally compliant coatings (“Eco challenge to reduce emissions in high performance coatings”). The authors illustrated the design concepts for zero or low VOC systems.

J. Roper, et al., The Dow Chemical Company, U.S., described the development of a proprietary mechanical dispersion technology for waterborne dispersions (“Waterborne mechanical dispersions to replace solventborne coating binders”). The technology does not need solvent to form the dispersion. The authors demonstrated how the waterborne mechanical dispersions could be used to replace solvent-borne coating binders with waterborne systems, including PUs, to overcome the performance gap.

ACT '10 Conference

At the ACT '10 Conference (Advances in Coatings Technology) held in Katowice, Poland, in November 2010, the following papers described problems in formulating high-solids and waterborne PUs.

How solvents affect the curing and properties of high-solids PU was reported by D. A. Vasilyev, et al., from the Yaroslavl State Technical University, Russia ("The Influence of Solvents on Curing and Properties of 2K-PUR High Solids Coatings"). The authors identified the effect of solvents as one of the challenges facing formulators trying to meet VOC requirements. The authors' work showed a significant difference in the amount of the different solvents needed to produce the required application viscosity for spray-applied PU coatings. They found that using more thermodynamically stable solvents such as MEK, MIBK, and butyl acetate allowed a coating to be formulated with VOC below 420 g/L. However, they also found it necessary to incorporate potentially higher VOC solvents, such as toluene, to maintain coating properties and ease of use.

The problem of increased viscosity of high-solids PUs was also discussed by M. Glennstål et al., of Perstorp, Sweden, who introduced the use of polycaprolactone as a reactive diluent in his paper ("Polycaprolactone as Reactive Diluent in 2K PU Coatings"). Polycaprolactones are liquid aliphatic polyols with low viscosity, which makes them ideal as co-binders in 2K PUs. The authors found that replacing 25% of a conventional acrylic polyol with polycaprolactone reduced VOC by 13% at the required spray application viscosity. Polycaprolactones also improved drying time, but at the expense of pot life. Other formulation parameters, however, could compensate for the effects on pot life.

S. Easthope, et al., from Incorez Ltd in the UK, discussed the use of oxazolidines as a means of dealing with moisture, which can easily be attracted by the hydroscopic polyols or other ingredients in the PU formulation ("Oxazolidines: A Useful Aid to Solving Polyurethane Formulation Problems"). A side reaction between the isocyanate curing agent and moisture to form CO_2 can affect full cure and cosmetic appearance. Oxazolidines preferentially react with moisture, thus preventing the side reaction with the isocyanate.

FATIPEC

The biennial FATIPEC Congress was held during the Eurocoat exhibition (Genoa, Italy, Nov. 2010). Although the Congress deals mainly with architectural coatings, a few presentations on water-borne PU technology addressed high-performance coatings.

A. Sanderse et al., Nuplex Resins BV, The Netherlands, described the development of a practical waterborne 2K PU that can be brush or roller applied ("New developments on water-borne resins for 2K coatings"). The coating depends on careful selection of binders, solvent, and thixotropic and defoaming additives. The results of the study gave rise to the required VOC-compliant coating with properties comparable to its solvent-borne counterpart. Also from Nuplex Resins, J. Akkermann et al. described the results of an R&D study of the open (workable) time of waterborne gloss topcoats, which resulted in the development of very low VOC paints ("New developments on open time resins for waterborne decorative coatings").

I. Amici-Kroutilova et al., Lamberti SpA, Italy, described a study into chemical modifications of the PU polymer backbone ("New hydrophobic modifications of polyurethane aqueous dispersions for hard substrates coating"). Introducing hydrophobicity to promote adhesion and chemical resistance, the authors identified a range of novel hydrophobic polyols for new PU aqueous dispersions with reduced VOC content.

A new waterborne technology that can produce low VOC coatings without sacrificing hardness, and that can maintain good corrosion resistance and weathering properties, was introduced by L. Procopio et al., The Dow Chemical Company, France ("Protection of Metal with a Novel

Waterborne Acrylic/Urethane Hybrid Technology”). Their hybrid technology couples a hard acrylic dominant phase with a soft polyurethane minor phase. The result is a self-crosslinking hybrid polymer with low VOC/fast hardness development and the required corrosion resistance and weatherability in a 1K waterborne system. Corrosion resistance is similar to that of a conventional acrylic.

SSPC 2011 Conference

In the U.S., again the monopoly of high-solids systems seems to be changing with more interest in waterborne technology. This change was in evidence at the SSPC GreenCOAT 2011 Conference. One of three presentations on new developments in PU covered waterborne technology. The other underlying trend was for green developments in raw materials, similar to the trend at Nuremberg.

H. B. Sunkara et al., Dupont, U.S., described a family of poly(trimethylene ether) polyols manufactured in a sustainable process using a raw material derived from agricultural feedstock—corn (“Polyether Polyols: A Renewably Sourced and High Performance Ingredient for Coatings”). These polyols have low viscosity, low melting point, high flexibility, and heat and acid resistance, which make them ideal for PU coatings. The presentation discussed the performance benefits possible in solvent-borne and waterborne PU coatings by using the polyol as a reactive diluent.

L. Ferrnando, Kemwerke Inc., The Philippines, described the performance properties of coconut-based polyol resin used in PU coatings and compared with commercially available PUs, both as primers and topcoats (“Application study on the performance of polyurethane paint as a green coat using biobased coconut polyol resin for protective and marine industrial coatings”). Generally, properties similar to conventional PU coatings were obtained, although the novel coating had better flexibility and a high level of adhesion.

R. Stewart of Bayer MaterialScience, Pittsburgh, U.S., discussed the challenges to the formulator of DTM PU coatings to meet changing market requirements (“One Component Waterborne Resins for Direct-to-Metal Applications”). Stewart focused on the use of oxidatively curing PU dispersions for these applications. He linked the coating performance requirements to the choice of the resin building blocks—polyol, isocyanate, chain extender, and solubilizing agent.

Conclusion

Obviously, there is a lot of interest in polyurethane technology for protective coatings, but whether high-solids or waterborne systems will dominate the low VOC products is anyone’s guess. JPCL

The Next Generation of High-Build, Aliphatic Moisture-Cure Coatings

By Ahren Olsen,
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Editor's Note: This article appeared in JPCL in February 2011, and is based on a paper the author presented at PACE 2010, a joint conference of SSPC: The Society for Protective Coatings and the Painting and Decorating Contractors of America, held February 7–10, 2010, in Phoenix, AZ.

Current commercial aliphatic moisture-cure urethane (MCU) topcoats have been limited by their film build and by the conditions in which they can typically be applied successfully. They are usually applied at dry film thicknesses (DFT) between 2 and 3 mils and generally in cool and damp climates. A new aliphatic prepolymer, engineered specifically for high-build MCU coatings, allows formulators to develop MCU topcoats that can be applied at 6–8 mils' DFT (72 F and 50% humidity) with 10–12 mils' sag resistance.

This article first reviews how conventional MCUs cure, four common ways of formulating them, and their strengths and limitations, including suitable application and exposure conditions. The article then describes the development and testing of a new aliphatic prepolymer for MCUs.

Basics of Current MCUs: Content, Curing, and Formulation

A moisture-cure urethane coating is a one-component paint that consists of a polyisocyanate functional resin along with solvents, pigments, catalyst, and additives. After being applied to the substrate, the paint cures as the isocyanate resin reacts with ambient moisture. Figure 1 describes this curing mechanism in more detail. When the paint is applied to the substrate, solvent begins to flash off, and the paint absorbs some of the ambient moisture. The isocyanate (R-NCO) reacts with that moisture to form an amine (R-NH_2) and release carbon dioxide gas. (R denotes the rest of the organic molecule, which is not involved in the reaction.) The isocyanate will then react with the amine to form a polyurea-cross linked network.

Aliphatic MCU topcoats have several advantages. They can cure at low temperatures as long as there is ambient moisture. They are very surface tolerant. And because they are a one-component paint system, there are no chances for mixing errors with multiple components in the field.

Manufacturing a MCU coating is not a trivial process. The water in the solvents and additives and on the pigments must be removed from the mill base before adding the isocyanate. If this process is not done correctly, the paint will begin to cure in the can, causing viscosity build, out-gassing, or even gelling. There are typically four ways to make a stable MCU paint. These four methods will be referred to as "conventional PTSI method," "vacuum method," "IPDI method," and "low functionality isocyanate drying."

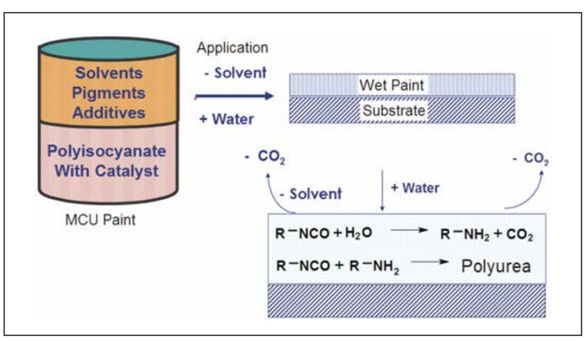

Fig. 1: Curing mechanism for MCU coating.

The conventional PTSI method uses the highly reactive monomer PTSI (p-toluenesulfonyl isocyanate). This monomer reacts very quickly with free water in the mill base to form a nonreactive byproduct, p-toluenesulfonamide (PTSA), which is kept soluble in the liquid paint through correct solvent choice.

The vacuum method uses heat and a vacuum to azeotrope out (to remove) up to 80% of the water from the mill base. The residual water is then removed using PTSI. This manufacturing method produces a higher quality of paint when compared to the conventional PTSI method. PTSI is an expensive raw material, and by removing a large portion of the water through the azeotrope step, a reduced amount of PTSI is required. The reduction in PTSI leads to considerable cost savings and creates less of the PTSA byproduct. PTSA is acidic and can cause issues with weathering and will slow the curing of the paint.

The IPDI method uses isophorone diisocyanate in large excess to overwhelm and react with the free water in the mill base. This is typically done under heat to expedite the process. The %NCO of the mill base is measured over time. Once the %NCO content stabilizes, the mill base is considered to be free of water, and the remaining free IPDI monomer is chain terminated using an OH-functional material.

The final method to make a stable MCU coating is to use a low functionality polymeric isocyanate, typically one functional to react with the free water in the mill base. The greatest benefit to using the low functionality isocyanate drying method is that it is a monomer free process with fewer handling concerns.

Current MCU Market Status

In the mid 1990s, aliphatic prepolymers for the North American region were developed specifically for aliphatic MCU topcoats. Several different prepolymers have been developed, which generally resulted in topcoat formulas that could be applied at thicknesses between 3–4 mils dry film thickness (DFT) before blistering resulted and with a sag resistance of 4 mils. The aliphatic MCU coatings on the market today are applied at 2–4 mils DFT and are typically used in the regions of the northeast and the northwest where there are cooler and damper conditions.

The North American MCU market has reached its full potential with the current technology. This is due to the technical limitations of this technology and application difficulties. MCU coatings that are applied beyond the manufacturer's recommended film thickness have a strong tendency to run and blister, which result in field repair and a generally poor perception of MCU topcoats.

To advance the MCU technology and coating market, drastic improvements were required in coating performance. A more robust technology is expected to renew interest in moisture cure coatings across the various sectors of the light- and heavy-duty protective coating markets and possibly open new markets within the construction sectors because of the improved film build.

New High-Build MCU Resin

After years of research, a new MCU resin has been developed. This resin is an HDI/IPDI prepolymer (referred to as HB resin) that was specifically engineered for high-build MCU topcoats. This resin is successful in making high-build MCU coatings because of its engineered reactivity towards moisture. The controlled reactivity is one of the keys to making high film-build MCU coatings. Table 1 gives data from three different MCU resins and a current commercial MCU. All three resins were formulated into the same base MCU formula, with the only variation being the substitution of the different resins.

The film-build-to-blister (FBTB), or maximum DFT before blisters, is measured on both a horizontal and vertically cured panel. The HB resin is able to produce much thicker coatings than either of the older technology resins or the commercial control MCU. The gloss of the HB resin-based MCU and its stability in the can are both acceptable when compared to the commercial control. The only drawback to using the new HB resin is the extended dry time. Extending this dry time is one of the keys to promoting high film build. Film build can be sped up through the use of more catalyst or by blending in some of the faster drying MCU resins at the cost of some film build.

Table 1: Two Old Technology MCU Resins vs. New HB Resin @ 72 F/50% Humidity*

Resin	FBTB[1] Horiz.	FBTB[1] Vert.	Gloss[2] 60°	Sag[3]	Initial Viscosity[4]	Viscosity[4] 2 Week @ 50 C	Gardner Hard Dry[5] @ 6 mils DFT
HDI Prepolymer A	2.1 mils	2.1 mils	61	12 mils	89 KU	> 140 KU	16.5 hr
HDI Prepolymer B	3.3 mils	2.3 mils	89	10 mils	80 KU	93 KU	18 hr
HB Resin	8.0 mils	7.1 mils	85	12 mils	83 KU	100 KU	32 hr
HB Resin (increased catalyst)	5.8 mils	5.0 mils	85	12 mils	82 KU	112 KU	24 hr
Commercial System	2.3 mils	2.1 mils	93	4 mils	70 KU	81 KU	9 hr

**All superscript information can be found under "References."*

Field Trial with High-Build MCU

In September 2008, a field trial was conducted to test the next generation aliphatic MCU topcoat in Baytown, TX. This high-build topcoat was based on the HB resin discussed earlier. A commercial control MCU topcoat (Table 1) was also sent to be tested with the high-build MCU topcoat. A third-party contractor applied the paints.

Older weathering steel beams were blasted to SSPC-SP 6 (Commercial Blast),[6] which resulted in a blast profile of 2.7–3.6 mils.[7] A commercial organic zinc-rich MCU primer was first used to prime the blasted beams. The following day, both the commercial and new HB resin-based MCU topcoats were applied. The conditions at the time of the MCU application were 97 F and 50% humidity, with a 101 F metal temperature and a 95 F paint temperature. These conditions are very severe for application of MCU topcoats, which are typically applied in damp and cooler environments. The face of each beam was sprayed at a gradient film thickness so the point at which the coatings were going to blister could be measured. Data from this trial is shown in Table 2.

The high-build MCU topcoat was applied up to 5 mils DFT before blistering was noticed, while the commercial control MCU could be applied up to only 1 mil DFT before blistering. Compared to current MCU technology, the new high-build coatings can be applied at significantly thicker film builds, even in more severe environmental conditions where MCU topcoats have not been used.

Table 2: Data from the Baytown, Texas, Field Trial in September 2008

Topcoat	Total DFT[1]	Blast Profile[4]	Primer DFT[1]	MCU DFT[1]	Dry Time	Sag[8]
Commercial MCU	3.2 mils	2.7 mils	2.2 mils	~ 1 mil	~ 20 hours*	5 mils
High Build MCU	6.2 mils	3.6 mils	1.2 mils	~ 5 mils	~ 20 hours*	12 mils

* The dry time was noted upon return to the paint site the next day, which happened to be ~ 20 hours after the application.

Summary

High-build aliphatic MCU topcoats have been developed with a new engineered aliphatic prepolymer. Compared to current MCU technology, which produces topcoats from 2–4 mils DFT, this new high-build MCU technology is able to produce aliphatic topcoats with DFTs of 6–8 mils (72 F and 50% humidity).

In a field trial, the new, high-build MCU topcoat was able to be applied at five times the coating thickness (5 mils versus 1 mil) before blistering, when compared to the commercial control, which was based on technology from the 1990s.

These advances in MCU resin technology will significantly advance aliphatic MCU coating technology in the maintenance coating market, possibly opening new markets within the construction sectors because of their improved film build. In short, it will allow specifiers and painters to use MCU technology in regions they never could before.

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Hybrid Coatings in the North Sea Offshore

By Anders Braekke,
Jotun A/S

Editor's note: This article appeared in JPCL *in December 2010, and is based on a presentation the author gave at PACE 2010, the joint conference of SSPC and PDCA, held February 7-10, in Phoenix, AZ.*

Polysiloxane products (often referred to as 'hybrid coatings') have been one of the major coating technologies in the European offshore sector, mainly because several customers have banned the use of coatings containing isocyanates. The potential long-term performance of polysiloxanes coatings has also been a strong argument for their being included as topcoats in NORSOK (501—rev 5) systems.

However, several failures have resulted in claim situations, with delamination, especially in two-coat systems, as the mode of failure, but similar problems have also been seen in traditional NORSOK (three-coat) systems.

The lack of adhesion and flexibility has been accepted as a major cause of failure, and multiple reasons have been discussed as the root cause of adhesion failure. As a result, polysiloxane products have been developed with a focus on long-term flexibility and predictable adhesion.

This article discusses some of the reasons for adhesion failure, and proposes a possible solution. The description of a new product with faster curing is also given.

Photos courtesy of Jotun A/S

The Situation Today

Specific Findings

The current situation is summarized in the extract from a report by my company on failures on facilities in the Grane Field. (See sidebar on p. 31.) We studied the problem of the failures and found that flaking could result at least in part from the topcoat's lack of adhesion and flexibility (Fig. 1). These factors seem to be especially relevant to two-coat systems on offshore platforms. But under certain conditions, we also have found failures in three-coat systems, including the NORSOK Standard M—501, rev. 5, system no. 1, which has been recommended for application to carbon steel when the temperature is below 120 C (~248 F).

Fig. 1: Flaking observed on Grane, resulting most likely from a combination of the use of only a two-coat system and the properties of the paint applied. Problems with the adhesion and flexibility of the topcoat over time could have contributed to flaking.

Market Situation

All major paint companies supplying the offshore sector offer polysiloxane systems, but their compositions have been designed differently. The polysiloxane topcoat market is one where the total patent situation is complicated. Formulating correctly in this area demands both creativity and technological insight.

Theoretical Explanation for Adhesion Failure in Offshore

Extensive Cross Linking Due to Silane Reaction with Water/Humidity

Traditionally the silane level has been approximately 15% of the formulation weight. But this high level of silane has been seen by some as a risk because of its potential reaction with water. The water reaction and extra cross linking give a harder coating with less flexibility, but the reaction also produces an alcohol (methanol or ethanol). Making a low silane product with approximately half of the silane level is one way to reduce risk, but the UV and gloss-retention level of the product will also be reduced accordingly. The technology challenge has been to increase the inorganic ratio in the product without increasing the risk of a build-up of methanol/ethanol.

This alcohol has been seen as one of the high-risk elements when it comes to polysiloxanes, because it represents a material loss from the film, and this will create additional stresses. We are always concerned about elements that could give rise to cracking. One other theory is that the alcohol migrates from the first coating and may cause total and unexpected delamination of a second coat. This is one of the main reasons why EU producers are very careful about the use of polysiloxanes in more than one coat. There will be situations when topcoating of polysiloxanes is necessary, and great care must be taken to obtain the best adhesion by cleaning or abrading.

Organic Modification Turns Brittle

Organic modification of hybrid coatings will increase flexibility, but the flexibility diminishes over time. Creating formulations that have an even distribution of organic/inorganic components has been seen as an objective. The increased brittleness of the product continues over years, so the measurement of flexibility over, say, the first three months, is not that relevant. Polysiloxanes are a long-term premium topcoat technology with an expected service life of 15 years or more. Adhesion and flexibility should be tested and monitored accordingly.

Possible Answer

There are several elements that may lead to system failure when using the product in the European offshore sector. The rainy, highly humid weather in the European offshore sector has been an argument for taking the flaking/delamination challenge seriously.

The weather is a more challenging environment, but the answer to delamination and flaking is probably more complex. There are probably multiple reasons for the problem and the instability of silane is only one reason. Increased hardness by cross linking will create stronger cohesion than adhesion (considered negative in any coating system), but even this is not a strong "reason why" argument alone.

Technology Development

One of the technology principles that has been used at my company is increased control of the curing process to ensure that the silane is fully reacted. One of the biggest differences in polysiloxane compared to other traditional technology platforms (for example, polyurethanes) is that this new polysiloxane technology is partly moisture cure—a certain level of humidity is needed for cure. This polysiloxane technology is also designed to have an alcohol produced in the curing reaction. As a result, for every cross linking reaction created in the coating, two alcohol molecules are released and one water molecule is consumed. This insight into the reaction is important when evaluating the curing mechanism since it can also create stress in the coating due to after-curing. This natural stress in the coating can, in extreme cases, give total delamination/flaking.

To compensate for this stress, one way of attempting to "tame" the hard and brittle siloxane components is with a soft organic modification. This technique works as long as the organic components stay intact in the coating. The problem is that organics components have a tendency to quickly become brittle, and the coating will be reduced in flexibility.

We have now developed a polysiloxane with a silane that gives the best possible control over the post-curing process and thereby maintains a better long-term flexibility and faster full curing. This makes a level reached where the coating is 'stable' and where the flexibility does not reduce further (due to extra cross linking). The formulators of the new polysiloxane are able to avoid the use of extra organic components in the coating because the need to 'absorb' stress is also reduced, resulting in a coating with somewhat lower initial flexibility but better and far more predictable long-term flexibility.

Figure 2 shows this new technology with some other polysiloxanes after undergoing the cupping test. The cupping test, e.g., ISO 1520, is a procedure for assessing the resistance of a coating to cracking and/or detachment when subjected to a gradual deformation by indentation. A coated metal panel is sandwiched between a hemispherical die and a hemispherical indenter. Pressure is applied such as to produce a "dome" shape in the panel, with the coating on the convex side. The pressure is increased until the coating cracks or disbonds from the surface.

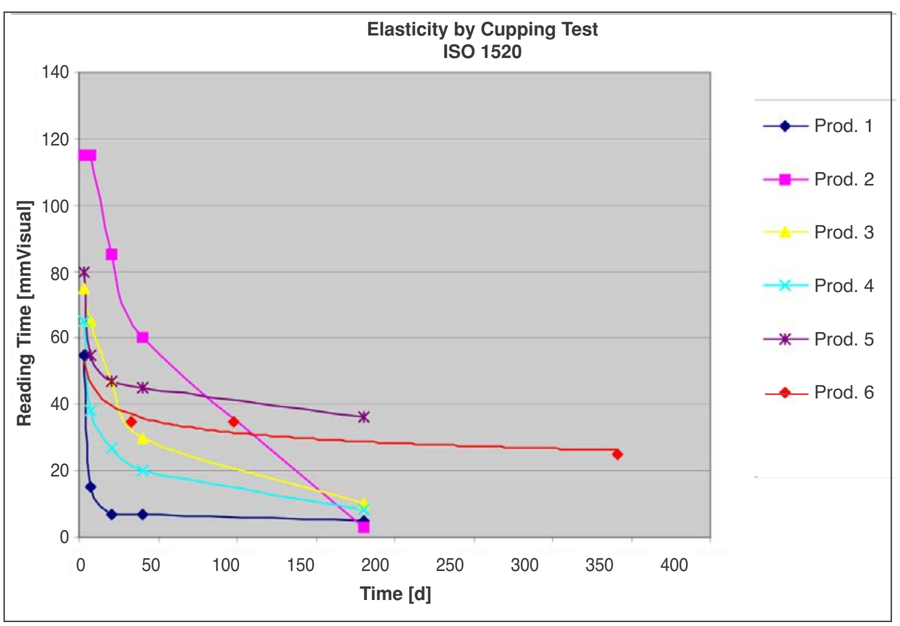

Fig. 2: Cupping test/days

As Fig. 2 indicates**,** Product 2 is highly flexible after 28 days, but the post-curing continues. Product 3 is better, but still not fully cured after 150 days. Product 1 is not very flexible, but still has a good control of the post curing. Product 4 is an example of a polysiloxane that has been developed but not launched due to lack of predictability in the post curing.

There is some uncertainty linked to this kind of test because, for example, relative humidity, temperature, and dry film thickness will all give some variations in post curing, and thus give different internal stress values. Adhesion to the substrate will of course also give varied results when using the cupping test.

This test and insight will, however, give an indication that great care should be taken when designing a polysiloxane for the high humidity in the European offshore environment.

Conclusion and Further Investigation

Using hybrid coatings has been popular in the European offshore sector due to their high performance and the absence of isocyanates. Challenges linked to the conventional hybrid coatings technology have mostly been associated with adhesion loss because of the reduction of flexibility. Reducing the after-curing of polysiloxane is widely accepted as a strategy for long-term flexibility and adhesion.

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Findings Reported

As noted in the text, a portion of the author's company's study, quoted below, summarizes causes for current and previous failures of polysiloxanes on offshore structures.

"Most of the paint applied on the main structure is based on a 2-coat system. There are some exceptions, since sometimes a red mid coat is observed under the flaking. In order to achieve a robust paint system it is well known to use a 3-coat paint system. The NORSOK Standard M-501, rev. 5, system no. 1 sets the standard for painting carbon steel structure for use below 120°C. The standard requires a zinc rich primer, a minimum of three coats and minimum total dry film thickness (DFT) of 280 μm. The zinc primer prevents the rust creep, the midcoat gives chemical and water resistance and the topcoat prevents UV-light [from] destroying the film, gives abrasion resistance and keeps the coating looking good. A satisfactory adhesion between the coats is of course very important.

A lot of flaking is observed on Grane. The reason for this is probably a combination of the use of only [a] 2-coat system and the properties of the paint applied. The frequency and the amount of flaking is so high over different types of undercoat that it is impossible not to look at the topcoat properties in order to find some of the reasons. The lack of adhesion and flexibility of the topcoat over time could therefore be a reason for the flaking.

3-coat system

The failed 2- and 3-coat systems of today should be replaced by the 3-coat system. The frequent failure in the existing topcoat indicates that the reason for this lies in the topcoat. We will therefore recommend that in overlap [overcoat] zones all topcoat is removed in order to just overlap with the midcoat and primer still left. It looks like the start of the flaking is somewhat unpredictable, starting with a "cracking rose" developing to areas with flaking. This failure sometimes starts on an edge, close to a welded stainless steel support and sometimes in the middle of a smooth surface. Therefore it seems impossible to predict future failures of the topcoat. Any coating system on top of another system will always also depend on the condition of the underlay [underlying coating] and not only the new system itself. Therefore it is important that in order to get a guaranteed good paint system, the old system has to be removed. In order to get a robust paint system on the above mentioned constructions is to use Norsok M-501, system no.1, with zinc epoxy + epoxy mastic + topcoat (polysiloxane or acrylic based). When a steel cleanliness of Sa 2 1/2 is impossible to achieve, [our company] recommend to use 2 x epoxy mastic + topcoat (2 x epoxy mastic3 + polysiloxane)."

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AGC Chemicals Americas;
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New Waterborne Fluoropolymer Resins for Ultra-Weatherable Coatings

Editor's note: This article appeared in JPCL *in December 2009, and is based on a presentation the authors gave at PACE 2009, the joint conference of SSPC and PDCA, held February 15-18, in New Orleans, LA.*

Fluoropolymers, introduced in the 1930s, are known for their excellent thermal, chemical, and weather resistance, along with surface properties like water and oil resistance, and optical properties. Because of their properties, fluoropolymers have been used in coatings on a variety of substrates. For example, fluoropolymers for coatings include aqueous dispersions of polytetrafluoroethylene (PTFE), tetrafluoroethylene/hexafluoroethylene copolymers (FEP), and TFE/perfluoroalkyl vinyl ether copolymers (PFA). These materials are used primarily in non-stick and anti-corrosion coatings.

Unfortunately, the use of fluoropolymers in coatings is limited due to their physical properties. Fluoropolymers have poor solubility in traditional solvents used in the coatings industry. Usually, fluoropolymer resins must be heated to temperatures greater than 200 C (392 F) to form a film. In addition, the low surface energy of the resins impedes acceptable adhesion to metals and other substrates, a property needed in primers and direct-to-metal coatings, for instance. Hence, fluoropolymers are not typically used as primers.

Among traditional fluoropolymers, only polyvinylidene fluoride (PVDF) is widely used in coatings. This resin is usually supplied as a dispersion in a high boiling solvent blend, and is used mainly in coil coatings, where it is processed at high temperatures. PVDF is employed primarily in architectural markets due to its exceptional weatherability.

A fluoropolymer resin was developed in the 1980s in an attempt to overcome the difficulties found in using traditional fluoropolymer resins in coatings, while still maintaining their advantages.

Tokyo Edo Museum, with FEVE coating
Photos courtesy of the authors

Institute for Global Environmental Strategies, with FEVE coating

These resins, known generically as fluoroethylene vinyl ether (FEVE) resins, are solvent soluble, and can be made compatible with water. This article describes solvent-borne as well as two types of waterborne FEVE resins—emulsions, which have been around for some time, and new dispersions—and the potential for uses of the new FEVE dispersion resins in coatings for field application where high weathering properties are needed.

FEVE Resins in Solvent-Borne Coatings

FEVE resins can be synthesized with reactive hydroxyl groups and can be cross-linked with standard aliphatic isocyanates to make fluorourethane coatings. FEVE resins can be used at high temperatures to make coil coatings, or at room temperature for field-applied coatings. This versatility in use substantially broadens the types of applications where FEVE-based fluorourethane coatings can be used.

Fluorourethanes have the same outstanding weatherability as traditional fluoropolymers but offer other advantages, as well. Fluorourethanes can be cured at either room temperature or elevated temperatures, so they can be used as maintenance coatings, applied in the field. Using appropriate additives, FEVE-based coatings can be manufactured in a wide range of gloss, unlike other fluoropolymers used for coatings. As solution polymers, FEVE resins have better compatibility with a wide range of pigments, enabling a broader color palette. And because fluorourethanes are cross-linked polymers, they tend to offer higher hardness and better corrosion resistance than some types of fluoropolymers commonly used in coatings. Yet, fluorourethanes retain enough flexibility and toughness for use as topcoats for military aircraft, where flexibility and adhesion are required at -40 C (-40 F) as well as at higher temperatures.

FEVE-based fluorourethane topcoats can be formulated and applied to yield a coating life exceeding 50 years. Based on work done by several Japanese transportation authorities, engineering organizations, and private parties, these topcoats are required to be used on all bridges in Japan, with an expected life of 100 years in some cases.

FEVE Emulsion Polymers for Coatings

The first waterborne FEVE polymers were aqueous emulsions, manufactured via emulsion polymerization. The resins were developed to enable coating manufacturers to meet VOC and HAPS regulations, which restrict the amount and type of solvents used to formulate coatings. Vinyl ether monomers substituted with polyoxyethylene (EO) units were copolymerized with the fluorinated monomer and other vinyl ethers to obtain stable emulsions and to maintain the structure of the FEVE copolymer. The resulting polymers are high in molecular weight, so they can be used in single-component coatings, or they can be cross-linked with aliphatic isocyanate dispersions. The emulsions have found use in blends with other waterborne resins to improve the weatherability of conventional coatings.

Unfortunately, coating properties obtained from these FEVE emulsions are generally inferior to those obtained from solvent-borne FEVE resins. This inferiority is believed to be due to residual emulsifier from the resin system in the cured FEVE coating, the presence of the EO units in the polymer, and the high molecular weight of the resins. In general, water sensitivity of FEVE emulsions is higher than that of solvent-borne FEVE resins, while weatherability is usually lower.

The shortcomings in performance of the FEVE water emulsions have limited their usefulness as low VOC and low HAPS coatings in the U.S. While solid FEVE resins provide a way to meet such regulations, the resins still require the use of solvents to produce coatings. There thus appears to be a need for a waterborne FEVE resin that offers the same performance as that of solvent-borne FEVE resins. FEVE water dispersion resins, as demonstrated below, yield properties in cross-linked coatings approaching those obtained with solvent-grade FEVE resins.

FEVE Water Dispersion Resins

Preparation of Resins

FEVE water dispersions are derived from FEVE solid resins of varying molecular weight, acid numbers, and hydroxyl numbers. To be useful as a coating raw material, a resin must first be stable enough in storage to impart a reasonable shelf life to the formulated coating. It was found that dispersion stability was influenced by several factors, including molecular weight, particle size, and acid value. The most stable products were derived from lower molecular weight, moderate particle size, moderate acid value polymers.

A FEVE water dispersion with properties shown in Table 1 was prepared and then formulated to make a fluorourethane topcoat.

Table 1: Properties of FEVE Water Dispersion

Property	Value
Appearance	Milky White Liquid
Solids, Wt. %	40% ±2%
pH	7–9
Particle Diameter, nm	50–300
Minimum Film Forming Temperature, °C	27
Acid Value, mg KOH/g-polymer	15
Hydroxyl Value, mg KOH/g-polymer	85
Hydroxyl Equivalent Weight (HEW)	660

Preparation of Fluorourethane Coatings for Testing

Coatings were prepared from the selected FEVE water dispersion, a two-part water emulsion FEVE resin, and a solvent-borne FEVE resin. Then, all three types of coatings were applied to chromate-treated steel panels, cured for 14 days, and subjected to a variety of tests.

Comparative Test Results for Physical Properties

The resulting fluorourethane coatings, along with an unreacted FEVE emulsion resin, were subjected to several standard tests for the coatings' physical properties. Of the results shown in Table 2, several are noteworthy. First, the gloss of the dispersion-based fluorourethane is close to that of the solvent-grade coating, and higher than that of the cross-linked emulsion coating. Hardness, impact resistance, and adhesion of the three coatings are about the same, although the cross-linked emulsion has slightly lower impact resistance. The FEVE emulsion that is not cross-linked has far lower hardness and impact resistance, and poor adhesion compared to the other three cross-linked coatings. While the emulsion is high enough in molecular weight to form a film using a coalescent, without the isocyanate cross-linker, film properties are poor.

The biggest difference in performance is in the water resistance of the three fluorourethane coatings. The water dispersion and solvent-grade fluorourethanes show excellent water resistance, while the cross-linked emulsion develops blisters during the test. In this battery of tests, the FEVE dispersion offered performance equivalent to that of the solvent-borne coating. This means that zero VOC fluorourethane coatings with excellent properties can be formulated using the FEVE dispersions.

Comparative Weathering

Fluorourethane coatings were tested in the ASTM D 53 accelerated weathering test. Accelerated weathering tests show that the dispersion-based fluorourethane weathers as well as the solvent-borne coating (Fig. 1).

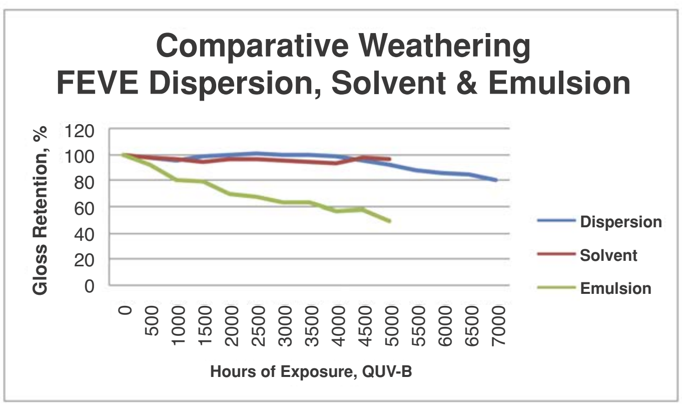
Table 2: Comparative Performance of Various FEVE Coatings

Property	Test	FEVE Dispersion (OHV=85)	FEVE Solvent-Based (OHV=52)	EVE Emulsion (OHV=55)	
Cross-linker (NCO/OH=1)	N/A	Water-dispersible isocyanate	HDI-Based polyisocyanate	Water-dispersible isocyanate	None
Gloss, 60°	ISO 2813	88	90	78	78
Pendulum Hardness	ASTM D 4366	79	80	75	19
DuPont Impact	ASTM D 2794 (D=0.5")	>1.0 m	>1.0 m	1.0 m	0.3 m
Cross-Cut Adhesion*	ASTM D 3359	5B	5B	5B	0B
Water Resistance ISO 2812 40 C, 24 hrs	Adhesion, ASTM D 3359	4B	5B	3B	0B
	Blistering, ASTM D 714	No Blistering	No Blistering	<8, Medium	2, Dense

Cross-cut adhesion test performed after soaking in hot water for 24 hours.

SEM Comparison: FEVE Dispersion and Emulsion

Scanning electron micrography (SEM) showed that the dispersion formed a uniform, dense film with no surface defects after cross-linking. Thus, water resistance in the dispersion was improved; water could not penetrate the film. In contrast, the cross-linked emulsion had surface defects thought to adversely affect physical properties such as gloss and water resistance. Also, the surface of the emulsion film was irregular, and the coalesced portions of the film could be seen. These imperfections could reduce the performance of the emulsion film.



UV/Condensation Cabinet Cycle
8 hours UV at 70 C (158 F) and 4 hours Condensation at 50 C (122 F)

Fig. 1: QUV-B weathering testing of FEVE-based coatings

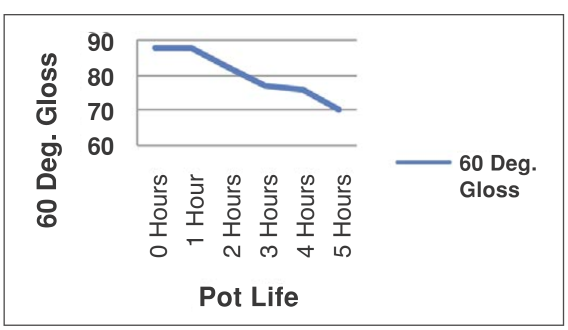


Fig. 2: Change in 60° gloss versus pot life

Application Characteristics of FEVE Dispersions

FEVE dispersions are formulated as two-component systems using water-dispersible isocyanates as cross-linkers. They are combined with pigments and additives for control of flow, gloss, foaming, and other application and physical properties. These systems can be applied with air or airless spray equipment, by roller, or by brush, depending on the environment at the job site.

As with other waterborne coatings, one of the difficulties in using FEVE dispersions is determination of the useful pot life of the blended coating system. Unlike solvent-borne coatings, the blended FEVE dispersion does not increase substantially in viscosity as the end of its pot life approaches. Other measures are used to determine the pot life, namely, a decrease in gloss during application, and a decline in physical properties of the finished coating after a certain pot life is achieved.

The FEVE dispersion was blended with a water-dispersible isocyanate at a NCO/OH ratio of 1.0. Coatings were then applied at one-hour intervals over the estimated pot life of the system. The gloss of the resulting coatings was examined. In addition, the solvent resistance of the cured coatings was examined.

Figure 2 shows the results of the gloss test for different pot lives. After 5 hours, the gloss of the cured coating measurably changed. After 6 hours, the cured coating showed extensive cracking, indicating that the pot life was exceeded. Solvent resistance of the cured coatings began to degrade at 4 hours' pot life. These results indicate that the expected pot life of the FEVE dispersion at 25 C (77 F) is a maximum of 4 hours. For use in the field, on-site testing should be performed, probably using gloss measurements, to ensure that the useful pot life is not exceeded.

Markets for FEVE Dispersions

It is possible to use FEVE dispersions for all applications where solvent-borne products are used today. Because FEVE dispersions can be used without coalescents, which may be considered VOCs, they can be used as industrial maintenance (IM) coatings for structures such as bridges, process plants, and water towers, even in California, where the current VOC limit for IM is 100 g/L. In addition, the dispersions can replace solvent-borne coatings in applications where the smell of solvents can affect occupants of a structure, such as office buildings. Other potential markets for FEVE dispersions include architectural, automotive, and aerospace.

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JPCL

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Self-healing Systems for Industrial and Marine Protective Coatings

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Self-healing polymers are a new class of smart materials that have the capability of autonomically repairing themselves after damage, without the need for detection or repair by manual intervention. Building on recent breakthrough technology in the design of microencapsulation-based self-healing systems, we are developing self-healing coating systems for extended corrosion protection of steel substrates (Fig. 1). A self-healing coating based on this technology would not only extend the lifetime of the corrosion protection system but would also reduce the cost of labor associated with corrective and preventive maintenance.

Fig. 1: Technical concept: Self-healing polymer coatings based on microencapsulation of healing agents.

The self-healing polymer system described by White et al. in 2001[1] was based on the Grubbs' catalyst-initiated ring opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD) in the site of damage, thus healing the damage and restoring structural continuity. While a successful demonstration of microcapsule-based self-healing technology, this approach was not deemed viable for commercial applications due to the chemical stability and cost of the catalyst. New chemistries have since been developed for applications in elastomers,[2] coatings,[3] and composites.[4] This article evaluates the application of polydimethylsiloxane (PDMS)-based chemistries in the development of self-healing coatings for heavy-duty industrial and marine applications.

Self-Healing System for Thermosetting Coatings

Thermosetting coatings such as epoxy and epoxy vinyl ester coatings are typically used in aggressive industrial and marine applications due to their chemical and corrosion resistance. However, when these coatings are eventually compromised by environmental factors and heavy usage, the substrate is exposed, leading to the rapid onset of corrosion. Significant corrosion ultimately leads to the need to take the equipment off line for maintenance. A PDMS-based self-healing system that gives a material the ability to autonomically repair mechanical damage has been demonstrated.[3]

The self-healing system, depicted in Fig. 2, is comprised of two varieties of microcapsules. The first type of microcapsule contains a mixture of hydroxyl-terminated PDMS and polydiethoxysiloxane (PDES) and an appropriate solvent, which was added for the purpose of viscosity modification. The second type of microcapsule contains a tin catalyst encapsulated in a solvent medium. Damage to the resulting coating ruptures the microcapsules, releasing their contents into the site of damage where they mix, react, and polymerize to repair the damage. Figure 3 exhibits the healing reaction that occurs in the site of damage.

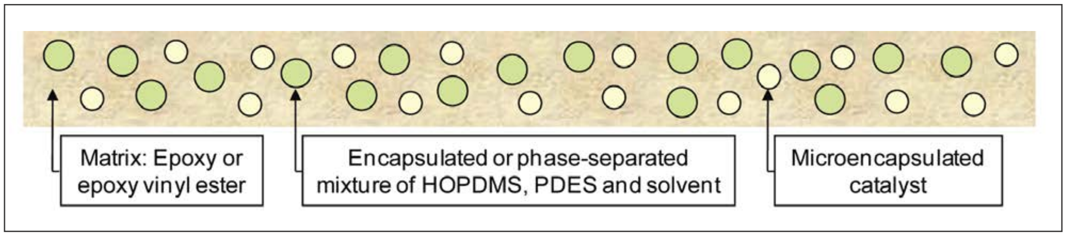

Fig. 2: Silanol condensation-based self-healing system. The mixture of HOPDMS, PDES and solvent is either encapsulated or phase-separated. The catalyst is encapsulated in polyurethane microcapsules. Damage through the matrix ruptures the microcapsules, and their contents mix in the crack plane, initiating a polymerization that seals the crack.

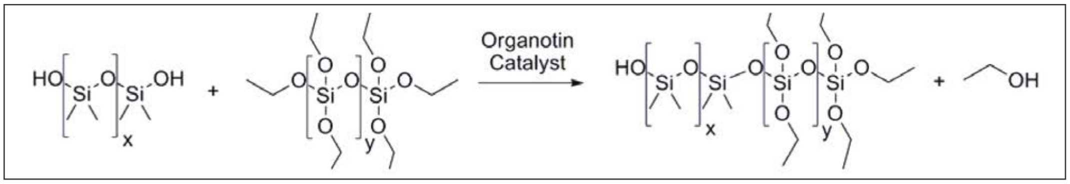

Fig. 3: Silanol polycondensation. A hydroxyl-terminated PDMS reacts with the ethoxy siloxane (PDES) in the presence of an organotin catalyst. The reaction results in a crosslinked network and releases ethanol as a condensation product.

A preliminary demonstration of the performance of this self-healing system is shown in Fig. 4. Four versions of the same epoxy vinyl ester coating were prepared and applied to cold-rolled steel substrates. The first version (Fig. 4a) was a basic control sample containing no self-healing additives. The second version (Fig. 4b) was a complete self-healing system with both the resin capsules (containing HOPDMS and PDES) and the catalyst capsules (containing the organotin catalyst). The third version (Fig. 4c) contained only the resin capsules, while the final version (Fig. 4d) contained only the catalyst capsules. All samples were scribed using a 50-micron scribe tool and allowed to heal at 50 C for 24 hours (h) before immersion in a salt solution for 120 h.

The resulting samples reveal two important observations. First, the addition of a complete self-healing system upgrades a basic traditional coating to a fully functional self-healing coating. Second, self-healing depends on restoring of barrier properties to the damage site as a result of the formation of new polymeric material due to the reaction of the contents of both varieties of microcapsules. Similar observations were made with commercial epoxy and epoxy vinyl ester coatings.

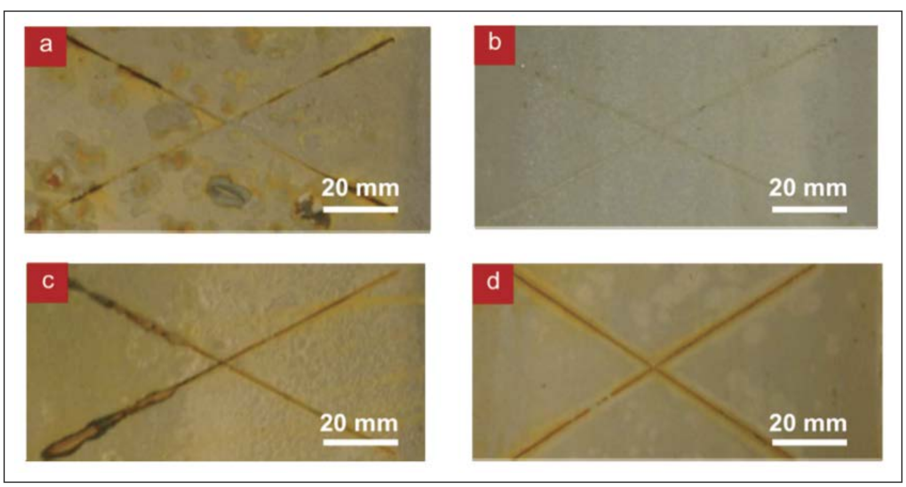

Fig. 4: Vinyl ester resin coating containing (a) only adhesion promoter (control sample); (b) the complete self-healing system including HOPDMS, PDES, catalyst microcapsules and adhesion promoter; (c) HOPDMS, PDES and adhesion promoter; (d) catalyst microcapsules and adhesion promoter. All samples were healed at 50 C (5).

Self-Healing System for Elastomeric Coatings

We have also demonstrated self-healing functionality in elastomeric coatings such as silicones. Building on the work of Keller et al.,[2] we have developed a different PDMS-based self-healing system for application in silicones and other soft coatings. This system is based on the Pt-catalyzed hydrosilylation of vinyl-terminated PDMS. As was the case for the system described in the section above, the resin and curing agent components of the polymer system were microencapsulated in two varieties of microcapsules and added to the coating before application on the substrate (Fig. 5). Damage to the resulting coating ruptures the microcapsules, releasing the contents to the site of damage where they mix, react, and polymerize. See Fig. 6 for a schematic of the reaction.

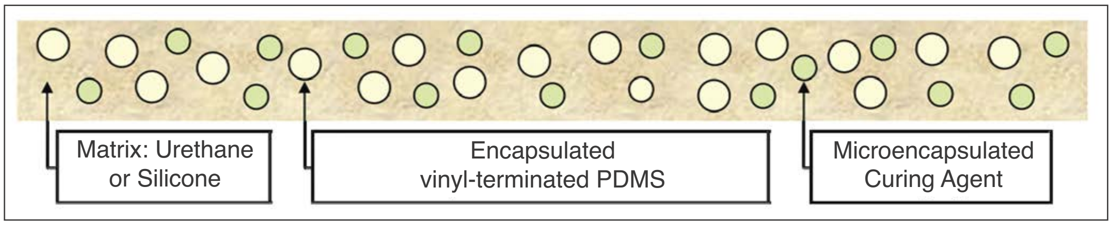

Fig. 5: Hydrosilylation-based self-healing system. The mixture of PDMS resin and solvent is encapsulated in one set of capsules while the curing agent/catalyst blend is encapsulated in a second set of microcapsules. Both varieties of microcapsules were prepared using polyoxymethylene urea microencapsulation procedure. Damage through the matrix ruptures the microcapsules, and their contents mix in the crack plane, initiating a polymerization that seals the crack.

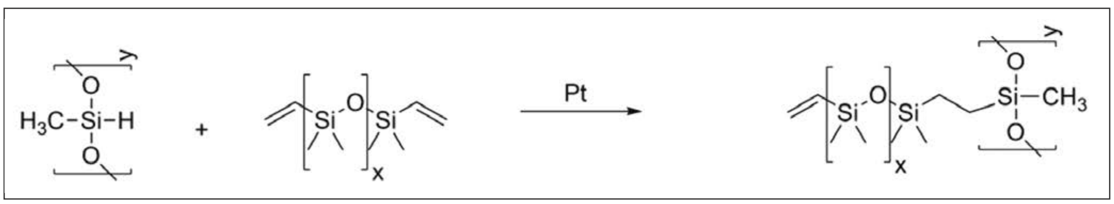

Fig. 6: Hydrosilylation of vinyl-terminated PDMS. The vinyl-terminated PDMS resin reacts with an active methylhydrosiloxane in the presence of a platinum catalyst to yield a crosslinked network.

This self-healing system was evaluated in a commercially available silicone coating, marketed as a corrosion-resistant coating. Two versions of the same coating were applied to cold-rolled steel substrates (Fig. 7). The control sample was applied as received from the manufacturer, while microcapsules containing the self-healing agents were added to the self-healing sample. Both samples were scribed using a 50-micron scribe tool, allowed to heal at room temperature for 24 h, and then exposed to salt fog (ASTM B117) for 120 h. As expected, the control sample was observed to rust within and around the scribed region. Blisters were also observed around the scribed region of the control sample. The scribe on the self-healing sample was observed to heal, extending the protection of the substrate. No rusting or blistering was observed anywhere on the sample (Fig. 7).

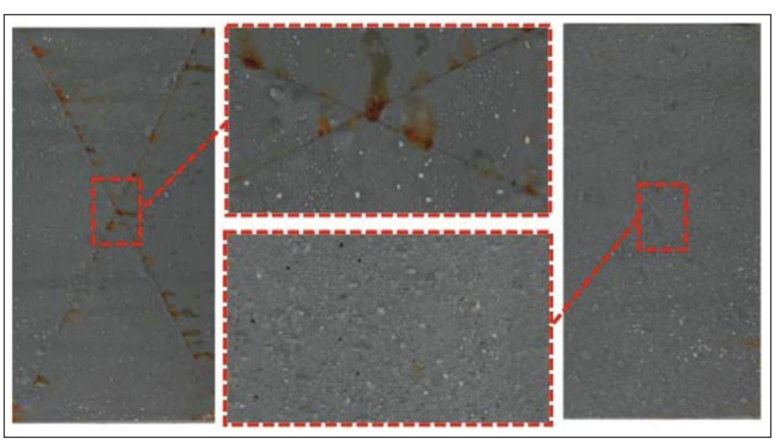

Fig. 7: Results from salt fog corrosion tests after 120 hours according to ASTM B117 of cold-rolled steel samples coated with a silicone coating containing no self-healing additives (control sample: left and top center) and with the self-healing additives included (self-healing sample: right and bottom center).

Conclusions

We have demonstrated the successful translation of self-healing technology originally designed for polymerized resins and reinforced polymer composites to coatings. Two different PDMS-based chemistries were used to achieve self-healing functionality in commercial thermosetting and elastomeric coatings. The samples exhibited in this article were prepared by drawing down coatings containing self-healing microcapsule additives. However, we have demonstrated the ability to apply similar coatings using siphon feed spray guns and high-solids static mixing spray systems, and we confirmed the survival of the microcapsules through this application process.

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