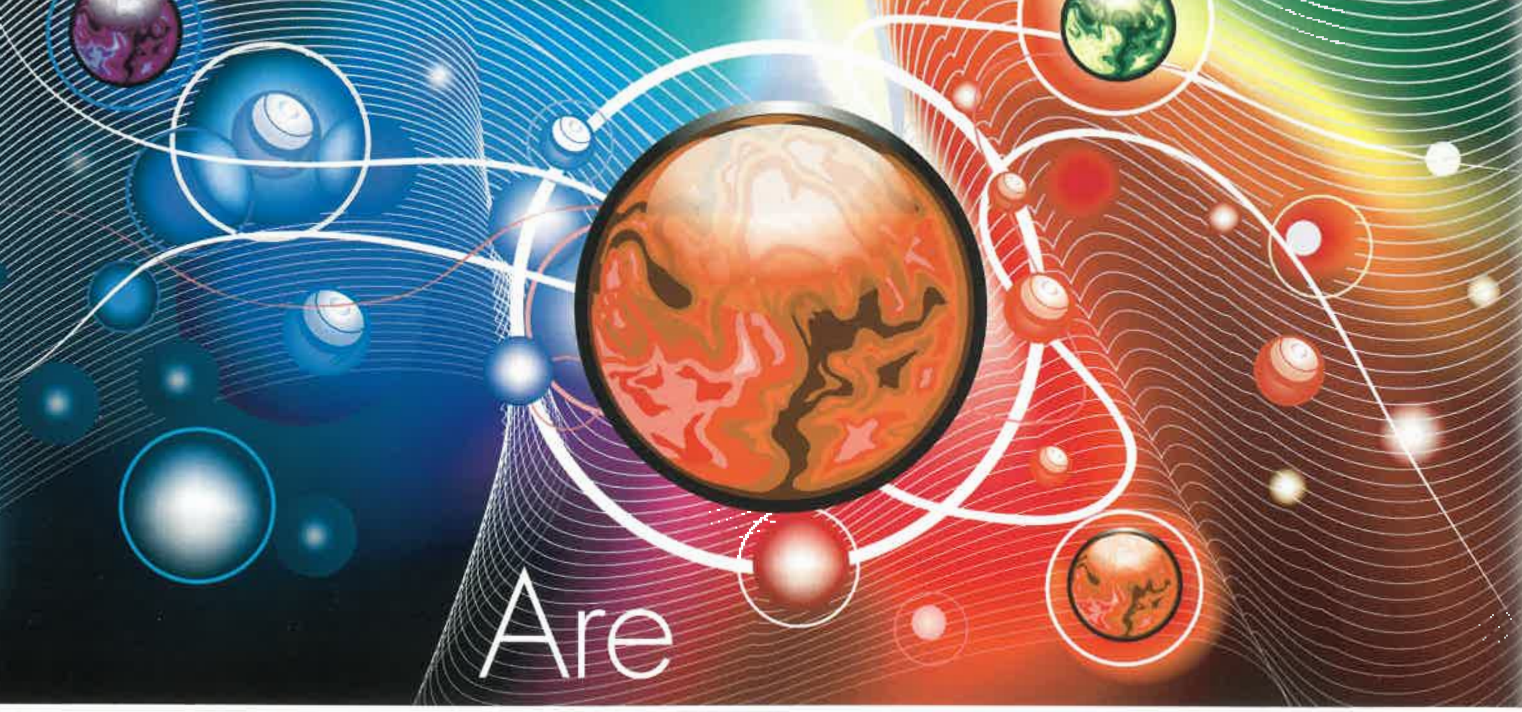

Are SMART COATINGS Getting Smarter?

By **Cynthia Challener**, CoatingsTech Contributing Writer

Interest in multifunctional coatings has grown in recent years as end users seek high performance surface protection combined with added features. Therefore, the idea of smart coatings that can respond to stimuli has become very attractive. Research groups continue to investigate novel coating systems that can self-heal, self-clean, and provide on-demand corrosion protection, among other functionalities. Some of these technologies have been commercialized on a small scale, while others are nearing commercialization and many more are in the early stages of discovery and development.

Even given the advances that have been made in this field, there still remains some debate about what defines a smart coating, and many also question the appropriateness of the "smart" label.

For purposes of this discussion, smart coatings are considered to be those that sense and respond to changes in the environment or within themselves, and preferably do so in a reversible manner. These changes include variations in light, temperature, pressure, air flow, surface tension, electrical current, acidity, chemical composition, bioactivity, surface contamination, etc. When a change in one of these conditions occurs, a smart coating responds by undergoing some further transformation—releasing a material, allowing a chemical reaction to take place, aligning polymer chains in a certain way—that addresses a problem. Once the stimulus is removed, the response is halted and ideally the coating returns to its original state.

While these capabilities dramatically improve the functionality of coatings, they do not make the coatings truly smart, according to many involved in the field. "Smart coatings is a sexy term that catches a lot of attention," notes Stuart Rowan of Case Western Reserve University (CWRU). "But these coatings do not undergo complex thought processes, so they aren't really smart." He and some other researchers like Victoria J. Gelling of North Dakota State University (NDSU) prefer terms such as responsive, adaptive, or active to describe these coatings.

Others believe that "smart" is indeed an appropriate term. "While these surfaces possess no ability to actually process information, the casual observer does see a stimulus-responsive process that appears to be a conscious activity . . . e.g., the coating appears to 'sense' a change in conditions and 'decide' to act in a certain way because of that change," says Steve McDaniel, chief innovation officer with Reactive Surfaces Ltd. (RSL). Others, such as Jamil Baghdachi of the Coatings Research Institute at Eastern Michigan University (EMU), consider "smart" to be a description that can be much better understood than more scientific terminology such as stimuli responsive or adaptive.

Whatever they are called, some of these responsive technologies have been advanced to the point where they can be effectively commercialized and applied as real solutions. "Three or four years ago, people involved in smart coatings research had just begun to develop responsive technologies after having gained an understanding of the fundamentals of the scientific concepts. Today, they have moved even further along the development cycle, with some products actually on the market," observes Baghdachi.

The smart coatings field is at about the midway point in its development, according to Timothy Long of Virginia Tech. "We are at the point now where we need to translate our fundamental understanding into new technologies. Given that these coatings are deriving their responses at the molecular level where the required chemistry is, for the most part, significantly different from today's technologies, moving towards commercialization will require the coatings industry to step outside of its normal comfort zone." The biggest issue will be adoption, agrees Jason Benkoski of the Johns Hopkins University Applied Physics Laboratory. "Innovation is really about user adoption and the practical application of new technology. Fortunately, there is a hunger for new technology across the board, with interest in smart coatings in the military, industrial, and consumer markets."

Advances in supporting technology and peripheral capabilities are also helping the smart coatings field advance more rapidly today, he adds. "Many newer technologies developed in other industries—particularly those related to production and manipulation of nanomaterials—are now becoming routine and commonplace, which will make it possible to cost-effectively manufacture smart coatings on the industrial scale."

Long expects that initial commercial successes will take place in industries that can support the higher costs of the first wave of new smart coatings technologies, such as the biomedical and electronics fields. One such example is catheters, which are coated with a hydrogel based coating that is self-lubricating when exposed to the higher temperatures and moisture inside the human body.

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proved, however, before a highly cost sensitive sector such as the adhesive industry will adopt them, maintains Long. Baghdachi adds that it is also important to realize that commercialization does not necessarily mean large volume production. Many of the high-technology, high-performance smart coatings will have applications in smaller, niche markets.

Companies large and small are focused on developing smart coating solutions. Examples include RSL; Toyota Research Institute of North America (TRINA), Inc.; and NEI Corporation (NEI).

RSL develops bio-based additive technology specifically for making conventional coatings dynamically functional, according to McDaniel, and is targeting development of drop-in technology for large scale end-use applications. The company's first technology up for auction is DeGreez™, an enzyme-based formula developed in conjunction with The University of Southern Mississippi that provides self-cleaning capabilities. Carefully selected lipases in the additive hydrolyze the long-chain triacylglycerols found in various oils and greases commonly deposited on surfaces, breaking them down into harmless substances that can be washed away with water. Tests confirmed that the additive does not have any measurable effect on coating performance at addition levels of 3–15%. When prepared surfaces were contaminated with a 2 µL per cm^2 layer of vegetable oil, a coating blended with DeGreez was clear of 90–95% of the oil within 12–24 hr. Furthermore, the degreasing activity is maintained after scrubbing with abrasion and detergents.

In a typical automobile, there are about 62.5 sq ft of surfaces that can be coated with a self-cleaning coating. RSL estimates that the hydrolysis rate (assuming 100% contact coverage of an evenly coated contamination) of a thin layer of cooking oil over the total surface area is about 26.9 oz/hr.

DeGreez has also been shown to be effective as a drop-in liquid additive containing 2 wt% enzyme in commercial laminates prepared from overlay paper treated with melamine resin. When properly conditioned, the lipolytic enzyme not only remains catalytically active after being pressed under typical manufacturing conditions (temperature and pressure) but also remains stable in pressed composites stored at room temperature.

The company is continuing to improve the DeGreez technology by increasing the additive's capability to withstand higher temperatures and pressures, creating quantitative assays for measuring cleanability and modifying the formulation for true anti-fingerprint coatings that actually remove oils and other residues that comprise the complex chemical composition of a fingerprint or smudge from the surface, according to McDaniel. In addition, the company will soon be commercializing enzyme-based additives for self-decontamination of phosphorus containing pesticides and chemical warfare agents (OPDtox) and nontoxic peptide-based antimicrobial additives (ProteCoat™) that should require no or only minimal cautionary labeling (as opposed to existing toxic biocides) based on a recent EPA determination. In fact, RSL is currently developing an industrial scale fermentation route to ProteCoat and will eventually be targeting the general biocides market.

Also in the pipeline are various bio-based additives (enzymes, peptides, cellular) for long-lasting self-healing coatings that could prevent natural embrittlement through molecular level healing as well as for anti-corrosive, anti-algae/fungi, anti-viral, and antifouling coatings. "At RSL, we are using a virtually untapped database of natural compounds that has 'giga bytes' of information critically useful to the coatings industry," McDaniel asserts. There are endless possibilities, and as importantly, many bio-based additives offer multiple functionalities, he adds. The company is actively using polymer engineering to design resin systems to specifically host novel functionalities and genetic engineering to tweak natural functionalities to fit unique specifications of particular polymers.

Scientists at the Materials Research Department of TRINA, collaborating with researchers at the University of Minnesota, are also exploring the use of enzymes in easy-to-clean coatings. Clearcoats on automobiles are often stained by tree sap, bugs, bird droppings, and other organic-based materials. Hongfei Jia and his colleagues thought that natural catalysts would be a better approach to degrading biological stains and preventing their accumulation on the surface of the coating. The targeted activity of hydrolytic enzymes was another attractive feature. Potentially useful enzyme classes include proteases, lipases, amylases, and cellulases, which target proteins, fats, starch, and cellulose, respectively.

To prove this idea, the enzymes were applied as thin coatings on testing substrates and then exposed to stains. Both protease and α-amylase were found to decompose the complex molecules in stains such as egg white and starch, respectively, as evidenced by the detection of low molecular weight products. By simply rinsing with water, many stains—barbecue sauce, light mayonnaise, ground crickets (bug bodies analogy), chicken blood, etc.—were visualized to be easy to clean on bioactive coatings compared to a control without enzymes.

As many coating processes require baking at high temperatures, one challenge was to develop a means of stabilizing the enzymes at elevated temperatures. "Enzyme reactivity is determined by the three-dimensional shape of the structure. Therefore, we needed to find a way to prevent the enzyme from changing its natural shape," explains Jia. One strategy was to incorporate the enzymes into a hydrogel. This approach was so successful that the enzymes retained most of their initial activity even when heated as high as 80°C for over 1000 hr.

The same methodology then was applied to the incorporation of enzymes into a 2K PU coating system with the anticipation that some covalent immobilization of the enzyme would take place through reaction of the enzyme's amine groups with the polyol. While the stability of amylase in the PU coating was adequately improved, the results obtained for this system were not as impressive as the hydrogel stabilized enzymes. Even so, the cleaning performance of amylase in the PU coating was still about 120 times greater than that of the native enzyme. "We found through analysis using fluorescent tags that in the PU coating the enzyme particles were dispersed at the micrometer level, while in the hydrogel they were present at the 10s of nanometers. Therefore, our next efforts are focused on improving the dispersion in order to improve the performance," says Jia. He does note, though, that their results to date clearly verify the concept.

Meanwhile, NEI is offering a platform of self-healing polymer nanocomposite coatings that heal both surface scratches and mesoscopic damage (e.g., micro-cracks and cavitation). Simultaneous crack closing and sealing is achieved by heating the surface of the coating using a simple device such as a heat gun. In addition, according to the company, the technology is applicable to a broad range of polymer systems, particularly those that require maintaining a clear glossy appearance. Nanomyte®

Mend-MW self-healing clearcoat technology is a zero-VOC self-healing polyurethane dispersion. Nanomyte Mend-W is designed to be a low-maintenance finish for wood.

The company's subsidiary American NanoMyte, Inc. (ANM), which was formed in 2010, also offers a chromate-free self healing system designed to prevent corrosion of lightweight metals including aluminum and magnesium alloys, as well as steel. ANM's development efforts are partly funded by the U.S. Army's Armaments Research, Development and Engineering Center (ARDEC) Corrosion Protection and Control Group located at Picatinny Arsenal, NJ. The goal of the project with ARDEC, according to the company, is to provide corrosion protection of armaments, ground vehicles, and helicopters, thereby reducing rework, decreasing maintenance costs, and extending useful life.

Several academic researchers also receive support from the military for their research, which is not surprising. "The military is very interested in making coatings multifunctional, and smart coatings are a very attractive approach because they have the potential to incorporate systems that otherwise would have to be carried in some way," remarks Peter Zarras of the U.S. Naval Air Warfare Center Weapons Division (NAWCWD) at China Lake, CA. For instance, smart coatings might be able to generate electricity and/or incorporate a means of communication as well as possess self healing and corrosion protection capabilities, adds Benkoski.

His group at the Applied Physics Laboratory is developing paint additives that impart self-healing capability and enhanced protection to off-the-shelf primers with funding from the Office of Naval Research (Grant No. N00014-09-1-0383). Like many other self healing technologies, Benkoski's approach relies on microcapsules containing liquid reservoirs of paint that are released when the capsule is broken as the result of damage to the coating. What is unique about his technology, however, is the use of a metal shell for the microcapsules.

The Polyfibroblast additive is a free-flowing powder comprised of liquid polyurethane droplets with an outer polymeric shell that is coated with nickel or zinc. "The metal not only makes the capsule much harder, and thus prevents degradation of coating properties through incorporation of the additive, it also aids in corrosion protection by acting as a sacrificial agent," Benkoski explains. The shelf life is also longer because the metal creates a hermetic seal, preventing degradation due to the passage of small molecules through it.

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Manufacturing the metal shell has been the most challenging and the most expensive part, and the group is working to improve the process so that it will be easily scalable and be as cost-effective as possible. Importantly, according to Benkoski, everything is done in water using inexpensive, commercially available raw materials. Initial lab tests have shown promising results, and the group is now looking for an industrial partner for production of larger quantities for field trials.

Zarras' approach to anti-corrosion coatings is based on the use of the electroactive polymer (EAP) poly(2,5-bis- (N-methyl-N-hexylamino) phenylene vinylene) (BAM-PPV) (*Figure* 1). The work was conducted at NAWCWD in conjunction with Wright Patterson Air Force Base (WPAFB) and the University of Dayton Research Institute (UDRI). The high molecular weight (60,000–80,000) chromate-free pretreatment was developed to be effective with qualified non Cr(VI) primer and standard topcoat for a total non-Cr(VI) paint system. When corrosion occurs, the polymer is oxidized rather than the metal surface being protected. This mechanism is effective, but also is a limiting factor for the performance, since once it is oxidized, the BAM-PPV can no longer provide protection.

Even so, Zarras has shown that the pretreatment when used in a full military coating is an effective new option, meeting the 2000 hr neutral salt fog exposure requirement for alternatives to Cr(VI) military coatings. The coating system also passed adhesion testing. A 12-month field test of the BAM-PPV pretreatment as part of a full military coating was conducted on the rear hatch door of a C-5 cargo plane. A 1 wt% solution of BAM-PPV dissolved in Oxsol 100 (4 chlorobenzotrifluoride) was applied as a 2 μm thick coating using HPLV.

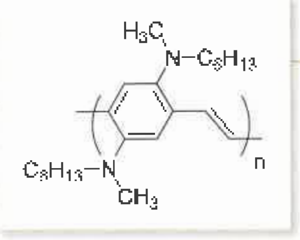

Figure 1—BAM PPV for use in corrosion protection coatings by Peter Zarras at NAWCWD at China Lake, CA.

The BAM PPV polymer has been produced in up to Kg quantities using straightforward organic synthetic techniques and commercially available raw materials. No significant change in dry film thickness was observed from 41.4 to 296.7 flight hours, and minor changes were attributed to dirt build-up.

At NDSU, Gelling is also tackling corrosion inhibition using a responsive coating based on electro-conducting polymers. Her approach is very different, though, and involves deposition of polypyrrole onto a carrier particle, typically aluminum flake, which is currently used as a special effect pigment by the coatings industry. She incorporates special dopant inhibitors—vanadates and/or molybdates have been shown to be the most effective—which have negative charges and are attracted to the positively charged polypyrrole backbone. When corrosion is detected, the dopants are released and move to the site of corrosion and halt its progression.

A second special aspect of Gelling's work centers around the advanced electrochemical measurement techniques she employs to evaluate the coatings. Through these studies she has been able to confirm the migration of the dopants through the coating, for example. "The ability to gather detailed electrochemical measurements helps us gain a much more in-depth understanding of these responsive materials and thus aids in the development of more effective coatings," she comments.

Currently her group is working on improving the polymer deposition process. Up to this point, catechol has been a necessary additive to get the dopant into the polymer. To be more commercially viable, a method for depositing the polymer onto the aluminum particles that does not require any additive needs to be identified.

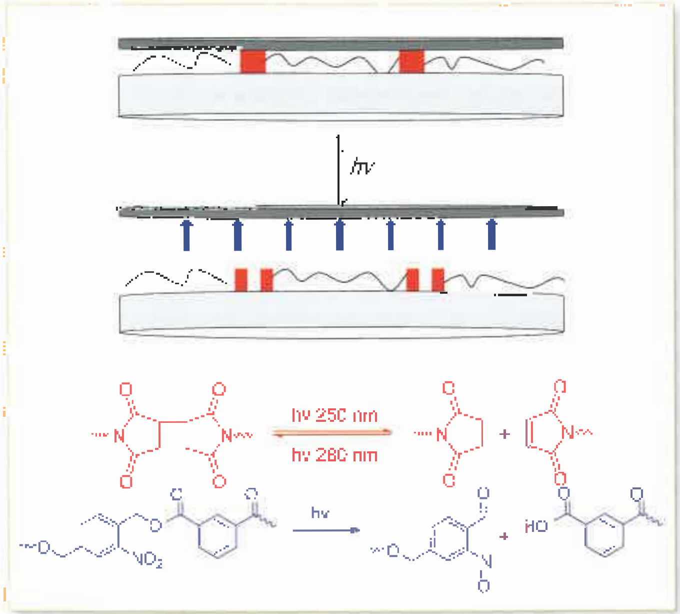

Figure 2—Light activated photoreversible adhesion for fabrication of microelectronics.

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While these scientists are looking at coatings that respond to the presence of corrosion conditions, several others are investigating the use of light as a stimulus. At CWRU, Rowan is collaborating with colleagues at the Adolphe Merkle Institute of the University of Fribourg and the U.S. Army Research Laboratory at Aberdeen Proving Ground to develop supramolecular assemblies for use in self-healing coatings. The telechelic polymers have a backbone of short (molecular weights <5,000) polyethylene butylene chains with terdentate ligands at each end. Upon addition of a coordinating metal ion such as zinc, these groups self-assemble into long polymeric chains to yield an elastomeric film. When the material is exposed to light of a specific wavelength, it depolymerizes and the low molecular weight segments can flow to fill in a void. When the light is turned off, the units repolymerize. In addition, only the area targeted with light is affected, so the change can be precisely controlled.

"At this point we have proved the concept that chromophores in supramolecular materials can be activated and respond with photo-healing behavior. The technology at this point is not commercializable, but we believe we will be able to develop an effective system with real world applications," Rowan observes. Polyethylene butylene was selected as the backbone material because of its low T_g, and the groups are now investigating higher T_g materials to see if they will work as efficiently. "The challenge is to make the coatings hard enough to be high-performance materials. One way we are trying to improve hardness and abrasion resistance is by making nanocomposites." He notes that initial results appear to be promising.

Photoreversible chemistry is also being explored by Long. His goal is to develop easily removable coatings for increased recyclability/recovery and other emerging electronics applications (*Figure 2*).

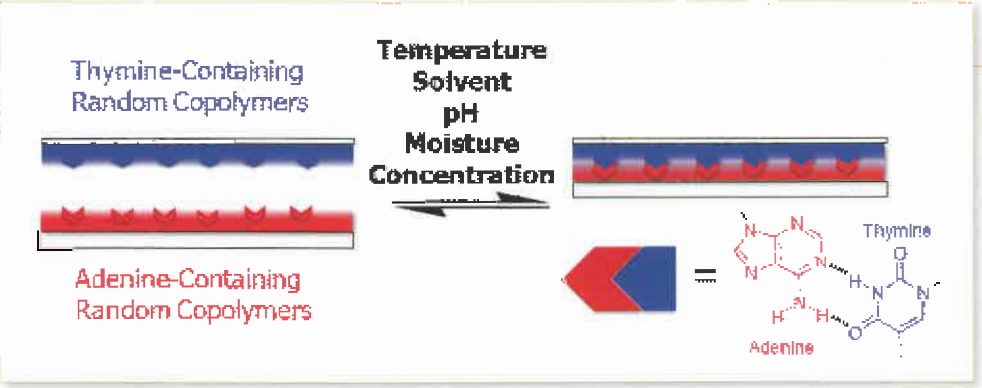

Figure 3—Scheme of nucleobase coatings with molecular recognition capability.

"Coatings are used extensively in the manufacturing of sophisticated electronics and it would be highly beneficial to be able to use reversible coatings and adhesives to facilitate these processes," Long notes. The adhesive wound care industry needs a smart adhesive technology that would provide a strongly adhering material that, when desired, could be readily removed in a triggered fashion.

Long's approach is to use light, which he views as a green reagent, to trigger changes at the interface between the coating and the surface. His design employs either polyesters (more sustainable due to access to bio-based raw materials) or polyimides (for high-temperature applications) that are functionalized with cyclobutane substrates through the photochemistry of maleic anhydrides, which undergo a [2+2] cycloaddition reaction to form cyclobutanes when exposed to one wavelength of light and the reverse when exposed to another. The properties of the surface of the coating are thus affected in the presence of light. This type of chemistry, often termed "click" chemistry, occurs in the absence of solvent at room temperature in high yields without formation of a by-product.

"One question we have to address when using light as the stimulus is whether or not certain wavelengths can penetrate deeply enough into the coating. That depth is dependent on the extinction coefficient of the coating. But for many applications, we only require a response at the interface of the coating and the surface, so we are able to tune the chemistry to overcome this apparent obstacle," Long remarks.

In a separate program, his research group is investigating the interface between biology and coatings. "Biological systems are continuously healing and refreshing themselves and responding to multiple stimuli, so it seems compelling to draw connections between biological concepts and smart coatings." His goal is to incorporate nucleic acids, or fragments of DNA, into systems in order to create coatings capable of molecular recognitions (*Figure* 3). If one nucleic acid heterocyclic base is bound to a resin, the coating should only recognize its complementary base pair (or functionalized derivatives) and thus react selectively. "The challenge here," Long says, "is to incorporate the fragments so that they retain their recognition ability."

If he is successful, Long envisions a coating system with molecular recognition capability that can be designed to react differently with different substances, and thus have properties that change depending on what comes in contact with it.

Michael Rubner at MIT is also focused on the molecular level, building coatings one layer at a time, allowing for careful placement of specific substances within the coating, and therefore providing a means for having precise control over coating functionality. The thickness of each layer (10 nm or less) is determined by thermodynamics and repulsive forces. Charged species are used to create each layer, and only so many charged molecules can be laid down at any one time. After a short rinse, a different oppositely charged substance is applied. The process is then repeated as many times as desired. The functionality of the coating is controlled by the selection of the various species used in each layer.

If layers of materials with different refractive indices (RI) are used to build the coating, the iridescent colors observed in insects, which are also achieved through structural design, can be created (the top layer has a higher RI). If a low RI material is used as the top layer, highly effective antireflective coatings can be produced. "We have been able to achieve an increase in light transmittance through

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glass from 92 to 99.9%. This enhancement is critical for improving the performance of solar cells," Rubner observes. Extremely uniform conformal coatings of minute dimensions that are not possible with existing processes can also be produced using this technology. Rubner can also control UV and IR reflectivity—key characteristics for optical coatings.

One of the challenges has been the development of a commercially practical production method. Originally each layer was created by dipping the substrate into an aqueous solution of the relevant material followed by a rinsing step, which was laborious and time consuming. Recently, Rubner and others have found that the layers will form if the solution is sprayed onto the substrate. It now only takes tens of seconds per layer compared to 5–10 min. "We are very excited about this development, because it means the technology is now commercially viable," Rubner asserts. The company Svaya Nanotechnologies is in fact building the processing equipment to enable production of these coatings on a large scale.

Optical coatings are by no means the only possible application for this molecular construction approach. Rubner has had promising results in the area of anti-fog coatings that remain clear even in high humidity conditions. In addition, he is also using the layering technology for biomedical applications. In this case, he has created a "backpack" for cells that can be loaded with drugs. The backpack binds to a cell programmed to go to a specific site in the body and, once there, responds by releasing the drug. The result is highly targeted delivery, enabling lower dosages and reducing the potential for negative side effects.

Optimization of polymeric thin films for energy generation is another area of study related to smart coatings. Rachel Segalman at the University of California at Berkeley is investigating the effects of the molecular structure on the electronic properties of semiconducting polymers, the crystal and grain structure on bulk conductivity, and the nanometer length scale on charge separation and recombination in photovoltaic and light emitting devices. Specifically, she and her group are studying block copolymers of semiconducting polymers and are trying to understand the effect of chain shape on polymer self-assembly and routes to control both self-assembly and crystallization on multiple dimensions.

Still others are exploring the potential of self-stratifying polymers. At EMU, Baghdachi is developing such coatings that exhibit multi-functionality such as sensory and on demand surface activity. "Through self-stratification, two-layer coatings can be produced with each layer possessing different functionality that complements or even modifies the properties of the other. The potential applications for such systems are extremely broad," he adds. For example, in the automotive sector, a coating that self-stratifies into a pigmented bottom layer and clear top layer could potentially enable elimination of one complete coating step.

In other areas, self-stratifying coatings would allow for incorporation of active ingredients only at the relevant surface of the coating—the top for antimicrobial, barrier, or self-cleaning coatings, for example, or in the bottom layer for anti-corrosion coatings. "In all of these cases, the active ingredient only needs to be at the surface of the coating," Baghdachi comments. "Current technologies require incorporation of such actives throughout the bulk of the coating. Self-stratifying systems therefore provide the opportunity to reduce resource consumption and lower cost."

Baghdachi's approach to creating these coatings is to rely on differentiated chemistry. More specifically, similar types of reagents (such as certain types of resins) with different rates of reaction allow for two different curing rates. As the faster reaction proceeds, the material becomes more viscous, while the reagents for the slower reaction remain more liquid. Mass transport rules then come into play, and the result is a two-layer coating with the faster curing system on the top and the slower system on the bottom. Incorporation of organosilicon and organofluorine groups allows for differentiation through surface tension as well. "In essence, we are relying on differentiating chemical and physical characteristics to drive the self-stratification mechanism," says Baghdachi.

Based on this survey of active smart coatings research programs, it certainly appears that significant progress has been made in the field. Whether or not the term smart coatings is a misnomer, it is clear that responsive coating technologies—including those that only a few years ago seemed farfetched—are indeed reaching the marketplace. And many of the projects underway are designed with ultimate commercialization in mind. "I won't be surprised at all if in a few years from now these projects have reached fruition and there will be all new smart coating concepts—perhaps those designed for true multi-functionality—that are already advancing through the concept verification stage," Baghdachi concludes.