The Intelligence Behind Smart Coatings

What makes smart coatings "smart" and why are they receiving so much attention? There are as many definitions of smart coatings as there are scientists conducting research in this very broad field. All agree, however, that intelligent coatings and materials will have significant impact on many aspects of our lives in the not too distant future. In this article, we present an overview of different classifications of smart coatings and discuss some of the new materials being developed by the government, academia, and industry.

Traditional coatings are designed to passively protect the substrate to which they are applied by providing a barrier between the surface and the environment. More advanced coatings contain a small percentage of a functional additive that enables the coating to provide some increased functionality. Other coatings have some functionality incorporated into the resin itself. The functionality in these materials is constant and is determined solely by the formulation of the coating.

Smart coatings go much further. In order for a coating to be considered intelligent, it must be able to sense a change in conditions in the environment and respond to that change in a predictable and noticeable manner. "Smart coatings combine functionality with design to provide a system that offers simultaneous multifunctional and multidimensional beneficial effects," says Bryan C.G. Glynson, chief executive officer of Alistagen Corporation. Janos Hajas, technical project support manager with BYK-Chemie GmbH, adds that smart coatings "offer over and above the normal functions of a coating, specifically protection and decoration, and also some unique, unusual functional properties which involve the intelligent selection between various types of responses to a given environmental stimulus."

by **Cynthia Challener**
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Response to the environment is not enough for some involved in the field. Smart coatings ideally provide an indication of their performance and can be remotely monitored, according to Peter Spellane, research scientist at Polymer Alloys LLC and assistant professor at New York City College of Technology—CUNY. These intelligent materials should also remain passive until prompted to perform a function, notes Brent St. John, CEO of Crosslink. For Dr. Robert F. Brady, a coatings industry consultant and retired coatings chemist, smart coatings also must initiate the desired response over and over again for thousands to millions of cycles over a period of years.

Intelligent coatings under development today can be categorized in many different ways—based on functional ingredients of the coatings, application, fabrication methods, etc. Stimuli/response materials include coatings acting as sensors; coatings that respond to changes in light, heat, or pressure; corrosion control coatings; command-destruct coatings; and color shifting coatings. Bioactive coatings include hygienic, antifouling, biodecontamination/detection, and biocatalytic coatings. Other smart coatings that are more difficult to classify include self-assembling polymers/coatings, electrically conducting coatings, super insulating coatings, self-repair and self-healing coatings, super hydrophobic coatings, self-lubricating coatings, molecular brushes, and optically active coatings.

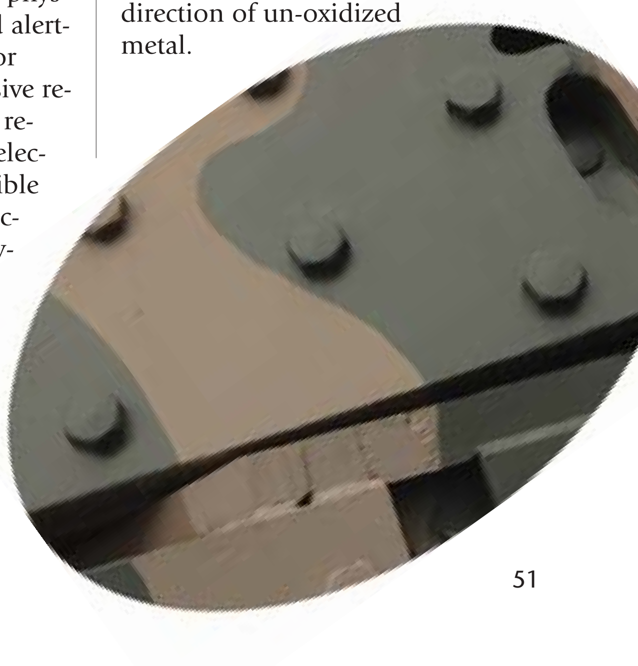
Stimuli for smart coatings can be any of a number of changes in environmental conditions. Intelligent materials under development can respond to heat, pressure, pH, impact, vibrations, pathogens and other organisms, certain chemicals such as corrosive materials, humidity, electronic and magnetic fields, sunlight and other radiation, and others. The functional ingredient within the intelligent coating can be the resin itself or a variety of additives including microencapsulated ingredients, pigments, antimicrobial agents, enzymes or other bioactive species, and nanoparticles and nanomaterials such as nanotubes, nanocapsules, microelectromechanical devices (MEMS), and radio frequency identification devices (RFIDs).

The potential applications for these numerous types of smart coatings are broad and varied. The U.S. government is interested in many types of smart coatings for corrosion control, camouflage, bioweapon detection and destruction, and other safety applications. The need for functional surfaces also exists in the aerospace, marine, automotive, construction, communication, textile, biomedical, electronics, energy, environmental protection, personal safety, and many other industries.

The U.S. government has active research programs within its own agencies and supports the efforts of a number of academic groups as well. The U.S. Army's Smart Coatings™ Materiel Program investigates smart coatings with the goal of reducing cost, equipment downtime, maintenance burdens, and the need for hazardous painting/depainting operations. Research efforts focus on development of intelligent materials with various capabilities including self-repair, selective removal, corrosion resistance, sensing, ability to modify the coatings' physical properties, colorizing, and alerting logistics staff when tanks or weaponry require more extensive repair. The program has already resulted in the development of electroactive polymers, micro-flexible electronics, nanoclays, and electrochromics useful for military-grade active sensing packages that detect damage of changes in environmental conditions. Integration and powering of these sensing packages into a multi-layered smart coatings system is now under investigation.

Researchers at the Industrial Ecology Center at Picatinny Arsenal and the New Jersey Institute of Technology, Wake Forest University, and Clemson University are collaborating with the Army to develop the next generation of smart coatings materiel via nanotechnology. Camouflage coatings with smart technology may be able to change color or even make a vehicle appear to be invisible by displaying an image of the vehicle's surroundings on its surface. Another alternative will be to have a rapidly changing pattern on the exterior of the vehicle.

The U.S. Navy also has an active smart coatings research and development program. Peter Zarras, a research chemist with the Polymer Science & Engineering Branch, Naval Air Warfare Center Weapons Division, is working on smart coatings as replacements for hexavalent chromium- and cadmium-based corrosion control coatings. "Environmentally friendly conductive polymers can respond to oxidants in a corrosive environment. These coatings can retard or inhibit corrosion through the formation of passivating metal oxide films that can protect the metal surface," says Dr. Zarras. The conductive polymers form a dense, adherent, low-porosity film that can maintain a basic environment on the metal surface, restricting access of oxidants and forcing the corrosion reaction in the direction of un-oxidized metal.



There are many examples of conductive polymers that can exhibit this behavior. Polyaniline is just one example. The Navy has developed a conductive polymer that is a derivative of polyparaphenylene vinylene and is a viable replacement for hexavalent chromium pretreatment on aluminum alloys.

Dudley A. Saville and Ilhan A. Aksay, of Princeton University, are taking cues from abalone shells, which are much stronger than any man-made ceramics and have the ability to repair cracks. These researchers are developing autonomic self-healing materials using a system that relies on electric-field induced colloidal aggregation of polystyrene or silica particles to repair defects. In this system, a small cylinder with a thin layer of insulating ceramic coating is placed inside a larger cylinder with the colloidal dispersion in between the two. A copper wire is placed in the middle of the cylinder and connected to a battery. When high stress is applied, a defect in the insulating coating occurs, exposing the metal underneath and creating a high current density at the damaged site. The colloidal particles then aggregate at the defect site. Copper ions from the wire then dissolve and stick onto the particles, essentially gluing them into place. This work is supported by NASA, which is looking for impact resistant coatings for various aerospace applications.

The U.S. Air Force is also interested in self-healing materials and provides funding for research being conducted at the University of Illinois at Urbana by Professor Scott White and his colleagues. Like Professor Aksay, Professor White is using biomimicry to develop a coating that can repair itself. This system imitates a rudimentary circulatory system and contains a complex network of "arteries" that direct the flow of liquid. The coating contains small amounts of a crystalline catalyst dispersed throughout. When the coating is cracked or punctured, the monomer flows through the channels to the damaged site and comes in contact with the catalyst, which causes polymerization and bonding of the crack faces. Professor White uses resins with broad commercial appeal such as epoxies, vinyl esters, and silicon rubber that typically find use in high-end applications. The percentage of catalyst incorporated into the coating depends on the application and expected damage, but is typically a 1% loading.

In a second approach, White and his colleagues have incorporated the monomer into the coating as a dispersed microencapsulated phase. In this case, the damage that occurs in the coating leads to localized rupture of microcapsules, releasing the healing agent into the damage site.

Self-healing coatings are attractive for both structural polymers and adhesives where even the presence of micro-cracks results in reduced performance. Outside of the military, these smart coatings have potential use wherever harsh environments are present, such as in marine, aerospace, and industrial applications. Currently Professor White is working with Intel to develop electronic packaging applications. "Our immediate goal is to create a commercially viable, cost-effective epoxy coating that prevents corrosion. In the future, we hope to develop a broad class of self-healing coatings for any number of applications. In general, we are interested in developing technology that imparts new functionality to coatings so that they can respond to a threat in the environment and repair or eliminate that problem," he explains.

Other academic researchers around the globe are focusing on the development of different technologies for self-healing and other types of smart coatings. One of the areas receiving the greatest attention is the development of intelligent coatings for corrosion control. Mark Soucek, associate professor at the University of Akron, is also developing coatings with encapsulated agents that are released within the coating in response to stimuli such as change of pH or fracture.

In a separate project, Dr. Soucek is investigating self-stratifying smart coatings that have components of a pretreatment, primer, and base coating. "The idea is that two to four separate coating processes can be replaced with one coating that stratifies to perform all the functions of the separate coatings," he explains. These coatings are typically inor-

ganic/organic hybrids—termed ceramers, by Dr. Soucek—that are part organic polymer coupled with an inorganic ceramic. More specifically, they are nanophase-separated metal-oxo clusters connected to a continuous organic polymer via a phase coupling agent. The ceramer coatings can self-assemble on metallic surfaces to create a passivating pre-ceramic phase which has been shown to inhibit corrosion even on surfaces in which corrosion has already begun. These coatings also have potential use as protective space coatings, where they may provide mechanical stiffness in combination with the ability to self-heal, deflect high-energy particles, protect against deep UV-light, and be optically transparent.

Sergiy Minko, the Egon Matijevic Chaired Professor at Clarkson University, investigates the wetting, permeability, adhesion, and friction properties of smart coatings with potential applications as sensors, membranes, textiles, protective cloth, controlled-release devices,

microactuators, and antifouling coatings. Dr. Minko is developing responsive polymer brushes formed when grafted chains of different polymers are tethered on one end to a solid substrate. These polymer brushes exhibit switching and self-adaptive properties and can switch their wettability, surface chemical composition, adhesive properties, and other characteristics in response to changes in solubility, temperature, pH, and other environmental factors.

In another project, Dr. Minko is developing coatings for textiles that provide adaptive surfaces that respond to changes in the biological environment. These smart coatings adapt their properties according to the presence of biological materials such as proteins and cells. These textile materials have potential biomedical applications, particularly in the area of implants. Switchable coatings sensitive to changes in temperature and humidity have potential application in the general textile industry.

Professor Michael C. Flickinger of the BioTechnology Institute at the University of Minnesota is actually incorporating biological materials—living but not growing microorganisms (bacteria, yeast)—into reactive coatings stabilized by nanoporous adhesive polymers. "Our biocatalytic coatings react to chemicals in the environment based on the selectivity of the enzymes contained in the embedded microorganisms," notes Dr. Flickinger. The microorganisms are stabilized at ambient temperature by the biomolecules that are concentrated around the microbes during film formation (coat drying) and rehydration prior to use. The technology relies on a multi-layer acrylate/vinyl acetate latex coating specifically designed to contain a high volume (up to 50%) of living organisms and form a thin film with a porous polymer sealant top layer that permanently entraps the cells.

These smart coatings can be used as industrial biocatalysts for stereo-specific oxidations and reductions, as biosensors, and as photo-reactive coatings. While it may take longer to get these types of smart coatings adopted by industry due to the presence of the microorganisms, Dr. Flickinger believes that these coatings could revolutionize how microorganisms are used in a stable, highly reactive form as industrial catalysts for the production of hydrogen gas as a fuel, in microbial fuel cells, and to utilize microbes in space.

The significant market potential for smart coatings has led many coating manufacturers to invest in R&D programs to develop intelligent materials. In fact, multifunctional smart coatings are providing coatings companies with an opportunity for growth through the development of value-added, high performance niche products. Companies are funding academic research efforts as well as actively pursing internal R&D programs to develop smart coatings technology.

Alistagen's Caliwel™ antimicrobial paints are a good example of a hygienic coating with significant potential. This smart coating is a waterborne, zero-VOC formulation based on a polyethylene resin and contains calcium hydroxide [$Ca(OH)_2$, also known as hydrated lime] encapsulated in a specially designed semi-permeable membrane. The Bi-Neutralizing Agent (BNA™) is based on a cellulosic membrane that prevents carbon dioxide from deactivating the calcium hydroxide, while allowing moisture and pathogens to come in contact with the antimicrobial agent. Caliwel paints have been shown to eliminate the growth of gram-positive and gram-negative odor-causing bacteria, mold, mildew, algae, fungi, and viruses on the coating surface. Alistagen has registered the product with the U.S. Environmental Protection Agency for surface applications and OEM applications in HVAC systems. It is safe to touch and can be washed without reducing its effectiveness, which lasts for six years.

Alistagen has outsourced manufacturing, and sells Caliwel through distributors. The company is actively pursuing licensing opportunities and is currently in discussions with two national paint companies. A large hospital in New York City has used Caliwel paint in a new wing and plans to expand its use throughout the rest of the facility. These antimicrobial smart coatings also find application in nursing homes and other healthcare facilities as well as in homes and office buildings for reduction of mold and mildew. Alistagen is expanding its chemistry base to grouts, sealers, and primers, and expects to launch three new products in 2006.

The company recently received the 2005 Technology Innovation Award for Caliwel™ from Frost & Sullivan. "We developed this product as a means for attacking the underlying cause of illnesses caused by allergens and pathogens," says Mr. Glynson. "Contact surfaces are a main transference mechanism for viruses and bacteria. Our goal is to help prevent the spread of disease, which is very timely today given concerns about potential viral pandemics. We believe that our smart coatings can offer a first line of defense in addition to providing a viable property protection system. We can provide a direct economic impact while helping people live healthier and better lives."

AK Coatings, a subsidiary of AK steel, offers silver-based AgION™ antimicrobial coatings for HVAC systems in hospitals, schools, and offices and in food handling and other industrial and consumer areas. The epoxy resin-based coatings are applied to stainless and galvanized steel through a coil coating process. Silver is a recognized nontoxic antimicrobial agent known to inhibit the growth of bacteria, mold, and mildew. The AgION antimicrobial agent is a zeolite, aluminum silicate ceramic containing 2.5% silver and 14% zinc ions. The silver is released when the temperature and moisture level in the air are appropriate for supporting pathogens. The AgION-coated steel is currently being manufactured and is readily available in standard 10 foot long sheets for most popular gauges.

Landec Corporation has commercialized smart coatings that adapt their permeability to different gases in response to changes in temperature. According to Dr. Stephen Bitler, these coatings are currently being used for food packaging applications within the U.S.

Crosslink has developed smart coatings based on electroactive polymers that sense a change in the environment and release an additive embedded in the polymer chain. The company's Senselink smart coating currently has applications in corrosion and decontamination for chemical and biological hazards for the military, according to Mr. St. John. Reactive Surfaces offers novel enzyme-based additives that, when mixed with paint and applied to surfaces, will detoxify neurotoxins, including nerve agents and pesticides. Microbiological Enzyme Technology (MET™) developed by the Clean Seas Company creates a biofilm on the bottom of boats that removes the food supply and secreted glues of unwanted organisms including barnacles, slime, and other soft growth. These organisms cannot attach strongly to the boat, and simply fall off as the craft moves through the water.

Self-cleaning smart coatings are also commercially available. **PPG** offers SunClean self-cleaning glass, which possesses photocatalytic and hydrophilic properties that make it possible to keep windows cleaner. A coating on the glass contains micronized titanium dioxide particles that act as a photocatalyst when energized by UV rays and loosen organic dirt. Hydrophilic properties of the coating cause water to sheet evenly over the glass surface, which helps to flush the surface clean and to accelerate drying. The use of nanoparticles makes it possible to create a transparent coating that does not interfere with the transmission of light through the glass.

Nano-X GmbH has also utilized nanotechnology to develop easy-to-clean and self-cleaning surfaces for interior and exterior applications. The company is also working on catalytically active surfaces that act as coatings to decompose odors, soot, or dirt, as well as corrosion and ant-fingerprint coatings for stainless steel surfaces. An additional area of interest is the development of nanoscale for conventional varnishes to enhance scratch resistance, UV stability, and/or to provide the work piece with easy-to-clean properties.

BYK-Chemie has launched several nanoparticle-based additives that are designed to increase the functionality of coatings, particularly in enhancing UV resistance and mechanical properties. "As an additive company, we focus in developing chemical specialties that can change the properties of coatings. It is a natural development of our business that we focus on additives for smart coatings," notes technical product manager John Du. The company offers additives for easy-to-clean and scratch resistance coatings. BYK-Silclean additives are designed to be used in coatings for easy cleaning of kitchen furniture, cell phones, audiovisual equipment, alloy wheels, motorbikes, mountain bikes, anti-graffiti coatings, and ice and snow release coatings. The NANOBYK series of additives find application in scratch-resistant furniture, and automotive and plastic coatings.

PEL Associates has developed smart coatings containing nano- and micro-sized layers that undergo removal on command. The coatings can be designed to respond to a wide variety of stimuli, including electrical signals and changes in various environmental conditions. As many layers as desired can be applied. The self-healing process is achieved through removal of the fouled or corroded layer, which only takes place when specified changes in the environment occur. Potential automotive applications include removal of corroded or damaged layers from bumpers, side paneling, etc. PEL's micro sensors also have potential as coating micro-crack detectors and light harvesting auto coatings to save on fuel.

Curran International offers CurraLon™, a self-healing, three-layer system based on polyphenylene sulfide that was developed in conjunction with the U.S. Department of Energy (DOE), Brookhaven National Laboratory, and the National Renewable Energy Laboratory. CurraLon is a unique coating that can have its properties changed and improved by addition of micro- or nano-additives. CurraLon properties can be altered for thermal conductivity, electrical conductivity, self-healing, abrasion resistance, release, flexibility or elongation, tensile strength, and tensile modulus, according to president Ed Curan.

Polymer Alloys LLC holds a number of patents that describe the use of polyphenylene ether and polyaniline in protective coatings for metals. These resins appear to react with substrate metal and with ambient oxygen to protect the substrate from corrosion, according to Dr. Spellane. Currently under development are corrosion-detecting sensor compounds with the potential to be embedded into coatings that can indicate incipient corrosion and allow for timely remediation of problems.

Cool Color™ pigments from **Ferro Corporation** are designed to reflect non-visible radiation. When pigments designed to reflect infrared radiation are incorporated into coatings, the coatings help keep surfaces cooler when exposed to sunlight. The infrared reflectance properties are independent of the color of the pigment, and therefore the pigments are available in many colors, according to Robert Blonski, research associate with Ferro. The technology utilized for infrared-reflecting colored pigments is an extension of Ferro's expertise in military camouflage pigments.

The wide range of research products and newly commercialized smart coatings products give a strong indication of the interest in intelligent materials by all facets of the coatings world. "These coatings will be a part of everyday life some day," says Mr. Zarras. It will not happen overnight, though. There are many challenges to overcome. Developing smart coatings that can be produced cost effectively is one of the main issues. "Smart coatings must possess exceptional performance attributes that justify the additional cost for their manufacture," notes Dr. Brady.

Technology transfer initiatives from both the government and academia to industry will also play a vital role in the future of smart coatings. "Companies developing smart coatings need to quickly move toward commercialization of their technologies. Research and scientific curiosity are important, but must be balanced with efforts to fill a need in the marketplace. Smart coatings must be brought out of the lab and into reality in the form of proven applications that are commercially viable," notes Crosslink's Mr. St. John. Professor Minko adds that, "The development of intelligent coatings will involve multidisciplinary research by materials scientists with different expertise: chemistry, polymers, physics, biology, medicine, and engineering. Very precise design, focused applications, and large investment are required for success."

Ultimately, increased demand for multifunctional, intelligent coatings that can sense and respond to the environment will lead to the development of materials that can be produced cheaply and safely, according to Mr. Zarras. "This new millennium will see rapid advances in these types of coatings, which will become the 'state-of-the-art.'" CT

For More Information on this topic:

Smart Coatings 2006 a three-day symposium on smart coatings, is being held on February 15-17, 2006 in Orlando, FL, sponsored by the Coatings Research Institute (CRI) in the College of Technology at Eastern Michigan University (EMU). The first symposium on this subject sponsored by the CRI at EMU was held in 2005. The current symposia covers the broad topic areas of bioactive coatings, stimulus and response coatings, nanotechnology based coatings and self-assembled intelligent layers. A complete list of paper titles and abstracts, and registration and housing information can be found at www.emich.edu/public/coatings_research/smartcoatings.