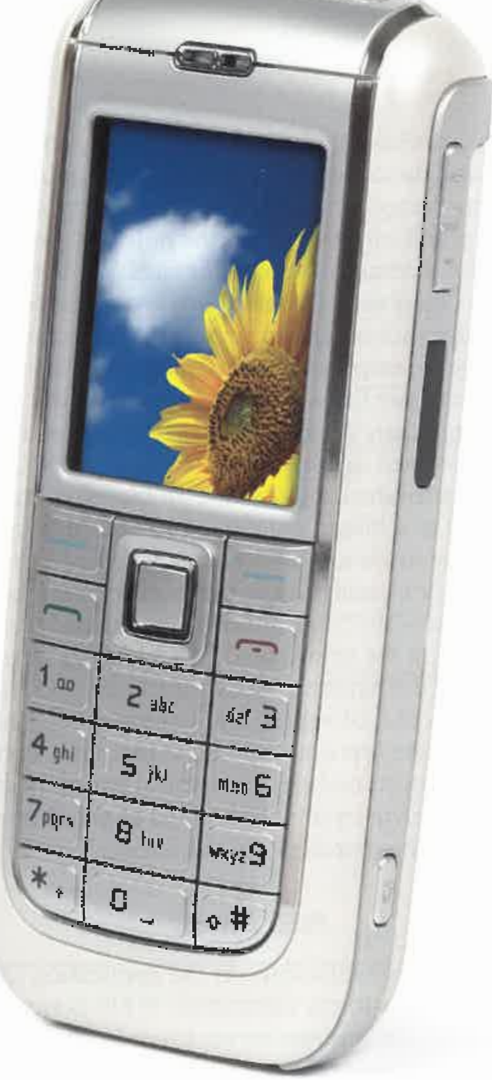
Smart Coatings Continue to Develop



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Since the topic of smart coatings was reviewed in CoatingsTech in 2005, the field has garnered much more interest and expectations have grown regarding the commercial potential of these important materials. Advances are being made by academic, government, and industrial research groups around the world. The excitement being generated by this work will continue to propel further gains in knowledge and increase the likelihood that smart coatings technology will eventually become a fundamental capability of the paint and coatings industry.

Even with all of the interest in smart coatings, it is still not obvious in some cases whether a coating is truly "intelligent." In part because of the attention the field is receiving, many high performance coatings are claimed to be smart materials, but they do not meet the proper criteria.

Smart coatings sense and respond to changes in the environment or within themselves, preferably in a reversible manner. Changes in light, temperature, pressure, air flow, surface tension, electrical current, acidity, chemical composition, and bioactivity, among others, cause the coating to undergo some sort of transformation. Once the stimulus is removed, the coating ideally returns to its original form.

Numerous types of coatings that do meet this definition are being developed. Much attention is being focused on coatings that provide some sort of sensing function. Self-healing coatings are being developed by a number of different groups. While they do not perform a reversible function, they do respond to the environment and are generally considered as smart coatings. Super hydrophobic and hydrophilic coatings that can control the wettability of surfaces have recently been the center of several research efforts.

The development of these smart materials is being made possible through advances in science and technology, particularly the development of nanotechnology and a better understanding of chemistry and physics of surface boundary layers; increasing environmental pressures and concerns; and a greater capacity and willingness to mimic naturally occurring coatings, according to Jo Lennartz, CTO of Akzo Nobel.

"One of the most notable changes that has taken place in the last two years is that people involved in smart coatings research are shifting from learning the science to developing technological solutions that can be applied to real world problems," notes Jamil Baghdachi, professor and program director of the

Coatings Research Institute at Eastern Michigan University.

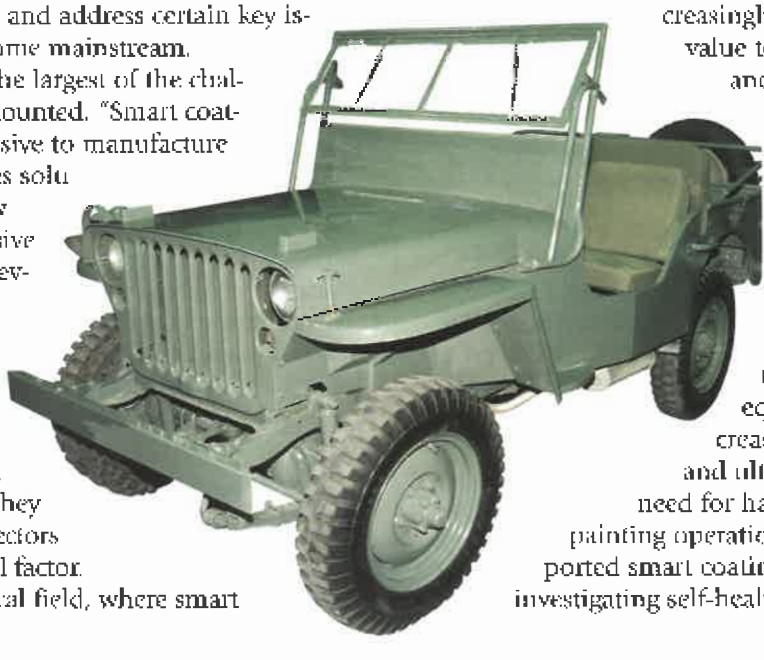
This shift does not mean that a flood of commercial smart coatings products will be available any time soon, though. "There is tremendous interest in smart coatings right now. The number of papers being published and the number of companies, both large and small, initiating R&D efforts is indicative of the health of the field," Baghdachi says. It will take time, though, to see results in terms of commercially available smart coatings products. "We are at the very early beginnings of the shift from academia to industry, and everyone involved in smart coatings is very excited about their future potential."

The Dow Chemical Company is a good example of a large supplier to the coatings industry that has a significant commitment to the development of smart coatings technology. As part of its newly formed Dow Coatings Solutions business, Dow will be focusing on four key technology areas including capabilities for reducing the environmental impact of coatings, enhancing durability, reducing system costs, and smart coatings.

"Our new market-facing coatings unit is bringing together 11 different businesses within Dow to provide a holistic approach to key issues in the coatings industry, and we see smart coatings as an important component of our strategy," says Wendy Hoenig, global R&D director for Dow Coatings Solutions. Her group is focused on three particular areas of smart coatings applications: novel functionality for release technologies, self healing materials, and intelligent self-assembly/self-stratification. "Our goal at Dow is to get some of these technologies commercialized within the next two years," she adds.

As with all new technology, smart coatings must overcome several hurdles and address certain key issues before they can become mainstream. Affordability is perhaps the largest of the challenges that must be surmounted. "Smart coatings today are very expensive to manufacture but provide in many cases solutions that can replace low cost but very labor intensive current methods for achieving certain functions," notes Baghdachi.

Today, high cost smart coatings can only be successful if they are providing an unmet need in the marketplace, or if they are targeted to industry sectors where cost is not a critical factor. Applications in the medical field, where smart coatings could be part of a life-saving diagnostic test or drug therapy, are one such example.



"The many R&D successes will only reach their full potential when smart coatings become economically marketable," asserts Stephen Lapitka, a consultant with Kline & Company, a research and consulting firm. "As various smart coatings take their respective markets by storm, R&D will be heavier focused on these coatings, further fueling the growth of this sector of the paint and coatings industry."

The manufacturing processes for smart coatings will also help determine their success in the marketplace. Those new coatings that can be readily produced using existing production equipment will be far more likely to lead to a viable commercial product. Processability is also an issue that must be considered.

Performance, particularly with respect to repeatability, will also be necessary before any smart coating can be commercialized. "Smart coatings, in order to be truly valuable, must have a minimum acceptable performance lifetime," explains Baghdachi. Whether the coating is responding to changes in light, the presence of water, or an electric current, it must respond to those changes thousands of times without fail."

One of the attractive features of smart coatings is their potential to not only improve upon the performance of traditional coatings or other materials, but to provide functionality that cannot be achieved with current technology. "The emergence of smart and other types of modern coatings means that the defining functions of a coating—protection and aesthetics—will be supplemented by a wide variety of new functionalities," states Lennartz. "At a fundamental level, these additional functionalities mean that the coatings themselves, as opposed to the structures they coat, will increasingly become the source of value to both the business world and society."

Military-related opportunities include corrosion control, camouflage, bioweapon detection and destruction, and other safety applications. Smart coatings have the potential to reduce costs and equipment downtime, decrease maintenance burdens, and ultimately eliminate the need for hazardous painting/depainting operations. Government-supported smart coatings research programs are investigating self-healing, corrosion control, photochromic and thermochromic, selective removal, and various sensing technologies.

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.

Self-healing coatings repair damages caused by various environmental conditions. A number of different approaches are being taken to develop such smart coatings.

Wenyan Li and Luz M. Calle of the NASA Corrosion Technology Laboratory at the Kennedy Space Center are using microcapsules formed through an interfacial polymerization; both size and pH sensitivity of the capsules can be controlled by adjusting the emulsion formula and reaction time. Both pH indicators that show a visible color change and corrosion inhibitors are placed in the microcapsules and then incorporated into paint systems. Determination of compatibility between the microcapsule system and various paint formulations is underway, as are long-term exposure studies to evaluate performance of the coatings.

At the University of Akron, associate professor Mark Soucek continues to study self-stratifying smart coatings that have the components of a pretreatment, primer, and base coating. The idea is to have one coating that stratifies to perform all of the functions of the various separate coatings currently required. The coatings, called "ceramers" by Soucek, are a part organic polymer coupled with an inorganic ceramic and are based on nanophase separated metal-oxo clusters connected to a continuous organic polymer via a phase coupling agent.

Professor Scott White and colleagues at the University of Illinois, Urbana, have made significant progress towards commercially viable and cost effective self-healing chemistries in the past two years. "These self-healing chemistries can be envisioned to have a wide variety of applications including self-healing coatings for anticorrosion applications," White notes.

In one of his approaches, two different polydimethylsiloxane (PDMS)-based healing chemistries (polycondensation and hydrosilylation) are used. Reactants or starting materials are embedded in the coating matrix in separate microcapsules. When these microcapsules are ruptured by some form of damage, their contents are released to the site of damage where they mix and initiate polymerization, thereby repairing the damage. The microcapsules were tested by adding them to a commercial epoxy coating and applying the modified coating to a metal substrate. No rusting was detected after the coated metal was scribed, allowed to heal, and then submerged in salt water for several days.

A second approach of White's group involves the microencapsulation of an epoxy/solvent mixture. Damage to a coating containing these microcapsules results in their rupture and the release of the epoxy/solvent mixture. At the site of damage, the solvent promotes the reaction of the epoxy with residual amine curing agents present in the coating matrix. "In addition to being cost effective, these chemistries offer broad chemical compatibility and the ability to be incorporated into a wide variety of coatings including common epoxy, polyurethane, and silicon-based coatings," says White.

Tamara Dikic at Eindhoven University of Technology in The Netherlands is applying the concept of self-healing to low-adherence coatings. She has developed coatings that have uniformly distributed throughout the bulk of the film fluorinated species that contain long polymer spacers. The polymers reorient themselves or move from sub-layers in response to changes in the surface tension of the film/air interface. Key properties that affect the ability of the polymers to self-replenish include miscibility, mobility, and spacer length of network precursors (dangling chains that are fluorine end-capped) plus mobility of the bulk polymer.

Because smart coatings technologies can sense a change in the surrounding environment or within the coatings themselves, they ideally can be applied in sensing devices. These technologies have potential as sensors in many industry sectors and are attractive because the coatings can cover a large surface area and are not restricted to a given shape. They also have no moving parts and do not require an external source of energy.

Piezoelectric paints prepared using lead zirconate titanate (PZT) ceramic powder as a pigment and epoxy resin as a binder have been shown to serve as vibration and acoustic emission sensors. Once a thin film has been deposited, a high electric field is applied to align the particles in the coating. Vibrations stretch the film, creating an electric charge that can be converted to voltage which can be read using a number of common instruments. These smart coatings are useful for measuring shock and vibration damage on large structures such as bridges, off-shore platforms, and pipelines where conventional instruments are difficult to install, require too much energy, or would be vulnerable.

Topasol LLC is a nanotechnology-based company that focuses on multifunctional coatings for the aerospace and solar industries. The company has developed a patent-pending in-situ nanoparticle technology that in a smart coating formulation provides a special mechanism that recognizes external force and allows the detection of impact and/or thermal damage on aircraft structural composite components. The nanoparticles can be dispersed in coatings and provide a color change upon exposure to heat or impact, according to the company. The first commercial application is anticipated to be aircraft surfaces, followed by natural gas and/or hydrogen fuel tanks for commercial vehicles.

Thermochromic and photochromic pigments and polymers that change color or exhibit some other characteristic in response to changes in heat or light, respectively, have been widely used in a number of coatings. Reversible temperature indicators are valuable safety devices for applications where high temperatures are possible. Low temperature indicators have potential uses as well. Thermally responsive inks and coatings may have application in the packaging industry, where they could indicate, for example, if required storage temperatures have been exceeded.

Professor Robert A. Weiss at the University of Connecticut is employing intrinsically conducting polymers (ICPs) in chemical sensors that detect the presence of volatile organic compounds (VOCs). Changes in the extrinsic conductivity of the polymers due to swelling by the VOCs, or changes in the intrinsic conductivity in response to charge-transfer interactions between the polymer and the VOCs, can be easily detected. Polypyrrole/polymer composites prepared by in-situ polymerization of pyrrole in the polymer matrix have been incorporated as a micro-layer of conductive material in polystyrene (a glassy polymer surface) and in open-cell polyurethane foam composites.

Landec Intelligent Materials has commercialized its Intelimer® polymers for a number of food packaging applications. These materials can abruptly change their permeability, adhesion, viscosity, or volume when heated or cooled by just a few degrees above or below a pre-set temperature switch, according to the company. The reversible changes are triggered by a built-in temperature switch that can be set within temperature ranges compatible with most biological applications.

Fighting viruses and bacteria has become a critical issue as the possibility of a pandemic looms. Various types of antimicrobial coatings have been available and others are being developed.

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 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.

Alistagen's Caliwel™ antimicrobial water-based, zero-VOC paints are based on a polyethylene resin and contain calcium hydroxide ($Ca(OH)_2$ encapsulated in a specially designed semi-permeable membrane. The membrane of the microcapsule prevents carbon dioxide from deactivating the calcium hydroxide while allowing moisture and pathogens to come in contact with the antimicrobial agent.

Several groups are working to develop smart coatings containing titanium dioxide nanoparticles that are photocatalytic and oxidize microbes when activated by certain wavelengths of light. Generally, titanium requires UV light for the desired photo-transition to occur. Means of doping the titanium with other metals and elements so that the catalytic reaction can be triggered by visible light is the focus of various research teams.

Professor Michael Rubner at the Massachusetts Institute of Technology is developing thin coatings created using controlled layer-by-layer assembly techniques to create surface texture and chemistry with nanoparticle/polymer or nanoparticle/nanoparticle assemblies. Using appropriate chemistries, textured surfaces that can slough off the biofilm that forms when bacteria attach to the coating can be created. These stimuli-response coatings will eject the biofilm based on a pH change. "We have achieved initial results and have shown that the coatings can cause the release of the biofilm," Rubner says. Currently, additional tests are underway to confirm these initial results and further explore the chemistry.

In addition to antimicrobial coatings, self-cleaning systems based on ultrahydrophobic or ultrahydrophilic coatings offer significant potential for commercial success with smart coatings.

Luna Innovations is investigating water-repelling coatings for use as corrosion inhibitors for metal components, for stain-resistant clothing, and as antifouling coatings for marine vessels. The company has developed a class of biomimetic ultrahydrophobic coatings that are simple to apply using conventional techniques and are cost effective for widespread use in various commercial applications.

For More Information on This Topic:

Smart Coatings 2008

A three-day symposium on smart coatings is being held on February 27–29, 2008, 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 was held in 2005. The conference will focus on bioactive coatings, nano-technology-based coatings, self-assembled intelligent layers, and stimulus and response coatings. A complete list of paper titles and abstracts, and registration and housing information can be found at www.emich.edu/public/coatings_research/smartcoatings.

Professor Eva Malmström of the Royal Institute of Technology in Sweden is using controlled radical polymerization to create superhydrophobic and self-cleaning biobased smart coatings. Chemelic Limited in Leeds, UK, is also using controlled radical polymerization to produce pH-responsive copolymers that self-assemble into micelles that have a reversible morphology once adsorbed onto a surface. The technology has been incorporated into an easy-clean coating for use on a wide range of surfaces including metals, glass, and plastics.

Certain types of polymer brushes have been shown by Rigoberto Advincula, an associate professor at the University of Houston, to conduct electricity and emit light very efficiently. Polymer brushes are formed by bonding polymer chains only at one end, forcing the chain to extend away from the substrates in a brush-like structure. Polymer coatings based on these materials could lead to brighter and clearer cell phone display screens. The coatings can be applied simply by dipping the screen into the polymer solutions or through electrodeposition methods similar to metal plating.

As can be seen from the few examples discussed here, smart coatings have the potential to impact every aspect of daily life. Our health will be improved through antimicrobial paints for hospitals and medical diagnostic devices based on sensing coatings. The safety of travel will be enhanced with smart coatings that detect corrosion or defects in bridges and airplanes. Our food supply will be better protected with smart coatings that indicate storage temperatures. Even our cell phone screens will be easier to read because of smart coatings.

With all of this commercial potential, it is not surprising that increasing numbers of companies and academic groups are becoming involved in some aspect of smart coatings R&D. "Like any boom and bust cycle, some technology will stay, but most will not. We are still early enough in the cycle that the winners and losers have not separated yet, so it is still very exciting," Soucek notes.

Dow's Hoenig expects several of the more basic smart, or perhaps what should be considered "smarter," coatings technologies to be commercialized over the next few years. "In the medium and longer term," she asserts, "the more challenging technologies will be developed in a way that makes them suitable for commercialization. Over time, coatings will become increasingly intelligent and provide materials with longer life spans and advanced functionalities at a reasonable price, while being produced in a sustainable manner."

The innate nature of coatings makes the idea of smart coatings all the more attractive. "Coatings present a simple avenue for improving the functionality of a material," says White. "Smart coatings can extend the lifetime of the substrates they protect, increase the range of applications for which the substrates can be used, and impart additional extrinsic functionality. Since coatings typically augment a materials' ability to be used in a particular application, the trend towards smarter coatings will continue as new applications for existing materials as well as new materials are developed."