Smart Coatings

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Smart coatings do not have any innate "intelligence," but they can, and do respond in predictable ways to changes in the environment, providing functionality that is "*well beyond simple protection or decoration*." In fact, the definition used in this reference[1] is that "*materials, which are capable of adapting dynamically their properties to an external stimulus, are called responsive, or smart*." Figure 1 depicts schematically some different types of smart coatings.

Some types of smart coatings

The first type includes: (a) linear chemical "chains" attached to the substrate at one end; and with functional groups at the other that react in a desired way in specific environments and (b) the so-called "polymer brushes" that can be engineered to change their surface properties, such as hydrophobicity and hydrophilicity.[2,3] The third type includes embedded strain gages or conducting or optical fibers[4] that when stretched, strained or broken can be used to detect incipient or actual damage or failure (*i.e.*, can be used to predict useful life of components and/or structures).

One example of a "passive" response is an additive (*e.g.*, pH indicator[5,6]) in a pipeline coating that changes color when there is a change in acidity. Such a change could be caused by localized corrosion, and the color change would indicate that some further action should be taken to mitigate substrate degradation in order to prevent the possibility of catastrophic failure occurring at some time in the future. Another example is a chelating agent added to a ship coating.[6] When the steel underneath rusts, the additive chelates the iron compound formed and converts it to a colorless compound. Appearance of the ship is maintained and repainting for aesthetic reasons is required less frequently. An example of an "active" response is a protective coating containing additives that, when the coating is damaged, releases chemicals - such as corrosion inhibitors[7] - to protect the exposed substrate surface. Another example would be a coating that contains micro-encapsulated monomers and a catalyst that, when the capsules are broken, polymerize to repair the coating *in situ*.[8]

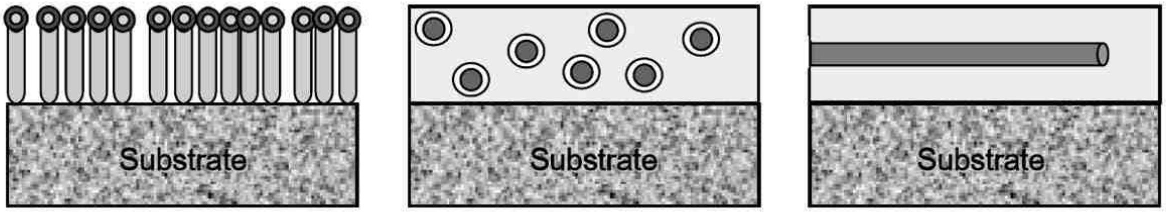
The following paragraphs provide a brief overview of some of the research and development work that is being conducted on smart inorganic and organic coatings for buildings and construction, corrosion prevention, biological, environmental and medical applications, clothing, transportation and electrical and optical devices. Many of the approaches described also are being evaluated or adapted for use by the defense industrial base.

Bio, medical equipment

Coatings incorporating treated "polymer brushes" briefly were mentioned above. Reference (3) mentions uses such as "controllable biointerfaces," and surfaces that can "actively modulate cellular microenvironments." Directed cell responses, including "growth, adhesion, proliferation, differentiation and migration," are discussed in another study.[9]

Nanofibers grown on surfaces and chemically treated can be tailored for use in a wide range of applications according to a news release from the Ohio State University.[10] Treatments have been identified that attract oil or water, while others repel oil or water. These fibrous coatings could be used for windows in construction, or in vehicles, such as automobiles and aircraft. Another coating has the property of uncoiling and suspending DNA strands in an aqueous solution on the fibers. It is said that this phenomenon could be used "to study how DNA interacts with other molecules" or "to build new nanostructures."

Military coating systems can come into contact with biological warfare agents. Decontamination is now accomplished with super tropical bleach, but more environmentally acceptable alternatives are desired. Research is being conducted on topcoats that contain nanoparticles with biocidal activity (*e.g.*, silver or quaternary



(a) Attached sensing or functional chemical groups **(b) Incorporated additives** **(c) Embedded sensors**

Figure 1—Three types of smart/responsive coatings.

ammonium salts) that can diffuse to the surface during preparation and application, and "interact with and kill microorganisms" or "catalytically degrade chemical agents."[11] Organic coatings such as polyethylene oxide, containing nanoparticles of silver can supply anti-bacterial and antifouling surfaces in their operating environments. Similar coatings, based on acrylic acid based polymers, can combine the anti-bacterial property with enhanced wound healing.[12] Similar, commercially available anti-bacterial and anti-fouling paints are described in Reference 8.

Buildings, construction and the environment

Smart coatings for use on or in buildings usually fall into one of two main categories. The first is self-cleaning surfaces that rely on photocatalytic reactions, and the second is glazing with controllable transmission and/or color to control light and heat transfer.[13] To a lesser extent, there has been some interest, especially in Japan and to some extent in Europe, to develop coatings that prevent the transmission of diseases (*e.g.*, "antimicrobial" surfaces as discussed above for handrails, door knobs, etc.) or to improve interior air quality.

A consortium in Europe is exploring the use of innovative construction materials to "help in the fight against air pollution." Plaster, mortar and concrete materials are being tested with coatings containing titanium dioxide, a photocatalyst, which in the presence of UV or sunlight can convert contaminants that stick on its surfaces to innocuous chemicals (such as carbon dioxide and water).[14] On exterior surfaces, these reaction products can be washed away by rain water. This PICADA Project initially is focusing on nitrogen oxides that cause smog and toxic substances such as benzene. At the University of Texas, strippable, water-based coatings that can detect and remove "hazardous nuclear contaminants" are being investigated.[15] These coatings react with contaminants on the surface to produce a color change. Over time the contaminants are leached into the coating and immobilized. Subsequent stripping of the coating then removes these contaminants, which then can be disposed of safely.

Electrochromic additives, such as tungsten oxide, have been added to electrochemically controlled films on glass to provide controlled light transmission and, as a result, also heat transfer.[16] A small applied voltage can change these films from almost totally transparent to opaque in very short times (less than equivalent photochromic coatings) so they have found use in windows in energy efficient homes and office buildings.[17] Nanofibers grown on surfaces and chemically treated to repel oil and/or water can be used in antifogging and self-cleaning windows.[9]

Corrosion prevention and control

Smart coatings have been devised for corrosion prevention, detection and control. In the area of detection, agar-based gels containing pH indicators, such as phenolphthalein, have been used as temporary coatings to identify areas of corrosion on the surfaces of original components and equipment, and on the surfaces of components or equipment that have been prepared for maintenance, overhaul or repair.[4] Such indicators also have been proposed for use in paints, wherein the indicating chemicals are microencapsulated and react with the change in chemistry when localized corrosion occurs.[4,8]

With respect to control and prevention, smart coatings include those that contain phosphate or chelating chemicals to convert the rust formed on steel structures, especially cruise ships, to control the amount of rust formation and provide an opaque film that "aids in color retention." This technology has been adapted by the U.S. Navy for use on their ships.[18] Other examples include the previously mentioned use of microencapsulated inhibitors,[6] and the use of "release-on-demand" inhibitors attached to nanoparticles, or in nanoporous additives to form stable barrier films in damaged coatings.[19] Both approaches were reported as being promising. Other researchers have tried a similar approach by incorporating silicon or cerium oxide nanoparticles into silane coatings on galvanized steel substrates.[20] The results obtained with CeO_2 particles were the most encouraging. Filiform corrosion on aluminum alloy substrates can be controlled with the use of hydrotalcite-like anion exchange additives[21] because they are effective halogen scavengers and also neutralize the aqueous acid formed at the head of the filiform structures. Conductive polymers, such as polyanilene, containing anionic inhibitors also have been investigated to prevent corrosion on AA2024-T3 aluminum alloy surfaces.[22] Here the mechanism is different in that damage exposing the substrate metal polarizes the polyanilene film and releases the inhibitor, allowing a protective film to form. Similar work has been done at the University of Sao Paulo for copper, silver and iron substrate materials.[23] The effectiveness of the passivating film that is formed depends on the relative galvanic activity (driving force) of the substrate metal.

Electrical, optical devices

The treated nanofiber coatings described above, if based on conducting polymers with an appropriate organic additive, can be used in light emitting devices, "transparent electrodes" and other "plastic electronic" components.[9,24]

It has been found that the optical properties of Mg_yNi thin films are very susceptible to hydrogen content[25] and, as a result, this behavior has been investigated for use as "switchable" mirrors and coatings for solar collectors. As deposited, the coating appears metallic and reflects about 60% of the incident solar irradiation. However, with only a small amount of hydrogen present in the film, the surface appears black and absorbs about 84% of the irradiation. Other researchers have investigated nanocoatings that permit reflected color changes by modifying the reflection coefficient[26] of a coating. Porous silicon is used as the matrix, which is infiltrated with active nanocompounds that respond to stimuli, such as an electric voltage, direct current or illumination. These coatings might be useful for thin film displays.

Energy

Components of industrial and marine turbines are subjected to high temperatures in service and are susceptible to oxidation and property degradation. One approach to controlling this form of corrosion is the use of multilayer of gradient coatings in which the compositions vary to provide different responses to the working environment.[27] For example, one embodiment is a high-temperature (MCrAlY) alloy base with a layer "enriched first in chromium, then aluminum to provide a chemically graded structure." Chromium in the first layer provides a self-healing function (protection) at lower temperatures, while above 900°C a protective alumina film is formed.

Fabrics, clothing

An effort has been made to mimic the "lotus" self-cleaning effect for use on textiles. Organic nanoparticles have been developed that, when attached to cotton fibers, provide improved water and oil repellence that is resistant to repeated washing.[28] Other work has focused on controlling water permeability of "breathable" waterproof fabrics with smart coatings.[29] Various formulations based on polyurethane films were investigated with the goal of permitting a desired change in water vapor permeability with temperature and relative humidity, while retaining acceptable tensile and tear strengths.

Transportation

A smart coating system for gas turbine engines is described[30] in which a protective coating on the turbine blades consists of several discrete layers containing different "taggants" (*e.g.*, chemical elements such as Ru, Pd, Pt). As the hot gases passing through the engine erode the surface of this coating, the taggant in that layer can be detected in the collected exhaust. When the detected taggant changes, this indicates that a layer of known thickness has been eroded away. Keeping a record of the time dependence of the changes in detected taggant can be used in a non-destructive, preventative maintenance schedule. A different approach, said to be useful for monitoring metal debris in engine cooling oil or ice build up on aluminum alloy aircraft surfaces, is based on incorporating piezoelectric ultrasonic transducers in sol-gel based coatings.[31]

Fatigue failure in aircraft structures and engines can lead to catastrophic failures. Two smart coating approaches are among the preventative technologies that could help to detect and mitigate this problem. One is the use of planar sensors between insulating, tough coatings.[32] One sensor consists of an array of thin wires of known resistivity. If strain (deformation) is sufficient to break one or more of these wires, the difference in resistivity can be detected.

The other sensor is a capacitance device that can detect contaminants on the surface of the coating. The combination of the two can be used to monitor the health of the engine. The other approach can be used to arrest fatigue cracking once it occurs.[33] In this smart coating, one component (*e.g.*, a tin alloy) melts at an appropriate temperature during the operating cycle and fills cracks that have just formed. This material solidifies and plugs the crack during the lower temperature parts of the cycle.

Electrochromic additives in coatings have been used in automobile rearview mirrors for some time, but improvements in the technology are making it more feasible to use them for automobile glazing that automatically adjusts transmission depending on driving conditions (sun glare in the daytime, and headlight glare at night). Similarly, nanofibers grown on surfaces and chemically treated to repel oil and/or water can be used in anti-fogging and self-cleaning windows and mirrors,[9] and nanoparticles of photocatalytic additives can be used to prevent permanent soiling of automotive interior surfaces.[34]

Technology drivers

As always, the drivers for smart coatings R&D are real or perceived needs; lack of an adequate solution; understanding the failure mode(s) and mechanism(s) involved; the availability of a broad, up to date, and accessible technology and/or knowledge base; and the ability to attack the problem as a system (*e.g.*, pretreatment(s), coating(s) and additive(s), and post-treatment(s), if necessary). For the user, a benefit could be the ability to preserve surfaces without the need for regular inspections or monitoring equipment, which often has to be accessed remotely, the data analyzed and a decision then made about taking any action. By having a smart coating available, inspection and monitoring can be eliminated in most cases, thus saving the costs associated with these. While the coating materials themselves may be more expensive because of the added functionality, and sometimes the need to modify application methods, this cost is more than offset by the savings in equipment, labor, travel and so on, associated with having to take remedial actions on-site. This can be especially important for large, remote or difficult-to-access structures such as oil and gas pipelines, oil rigs, bridges, utility pylons and the like. Other benefits have been mentioned for some of the other possible applications briefly described above.

Summary

In summary, smart/responsive coatings are receiving much more attention than previously because of the variety and different functionalities of coating additives, micro- and nanoscale sensors now available, and the opportunity to formulate coatings and apply them in novel ways for existing and proposed special (and usually high value added) applications. If the reader is interested, a further introduction to the current status of such coatings is given in the paper by C. Challener,[8] and a good general overview in the paper by W. Feng, *et al*.[35] Table 1 tries to capture some of these technologies and applications as a quick reference for you.

The above review has only scratched the surface, if you pardon the pun, but I hope you will be stimulated by the vast array of developments embracing a wide range of technologies to provide smart, responsive and functional coatings. Each of the general topic areas warrants a separate, critical review, but these are outside the scope of this column. *P&SF*

References

1. J. Baghdachi, "General Introduction/Overview," Smart Coatings 2006, February 15-17, 2006, Orlando, FL; Coatings Research Institute of Eastern Michigan University, Ypsilanti, MI, 2006.
2. K.B. Walters, "Tethered Stimuli-Responsive Polymer Films," Smart Coatings 2006, February 15-17, 2006, Orlando, FL; Coatings Research Institute of Eastern Michigan University, Ypsilanti, MI, 2006.
3. J. Lahann, "Designer Biomaterials: Engineering Diointerfaces with Controlled Properties," Smart Coatings 2006, February 15-17, 2006, Orlando, FL; Coatings Research Institute of Eastern Michigan University, Ypsilanti, MI, 2006.
4. S.-H. Her, *et al*., "Stress Analysis of Composite material Embedded with Optical Fiber," *Key Engineering Materials*, **326-328** (1), 59 (2006).
5. G. Frankel, *et al*., "Corrosion-sensing Composition and Method of Use," U.S. Patent 20030068824 (April 10, 2003).
6. R. Parks, "Coatings Put to Test to Keep Ships Cool," August 20, 1999; http://www.marinelink.com/Story/SearchAdvance.aspx?search=%22anti-stain+coating%22.
7. L. Calle, "A Smart Coating for the Early Detection and Inhibition of Corrosion," Smart Coatings 2006, (February 15-17, 2006), Orlando, FL, USA; Coatings Research Institute of Eastern Michigan University, Ypsilanti, MI, 2006.
8. C. Challener, "The Intelligence Behind Smart Coatings," *JCT CoatingsTech*, **3** (1), 50 (January 2006).
9. N. Gohad, "Bioactive Coatings for Directing Site-specific Cellular Responses," Smart Coatings 2006, (February 15-17, 2006), Orlando, FL, USA; Coatings Research Institute of Eastern Michigan University, Ypsilanti, MI, 2006.
10. News Release, The Ohio State University, "New, Invisible Nanofibers Conduct Electricity, Repel Dirt," (June 29, 2007).
11. J. La Scala, "Biocidal Coatings for the Military," Smart Coatings 2006, (February 15-17, 2006), Orlando, FL, USA; Coatings Research Institute of Eastern Michigan University, Ypsilanti, MI, 2006.

12. D.J. Balazs, "Functional Plasma Coatings Enabling New Applications," Session III, European Coatings Conference (May 15-16, 2006) Berlin, Germany.
13. G. Bräuer, *et al.*, "Smart Coatings for Intelligent Surfaces," *Vakuum in Forschung und Praxis*, **18** (6), 25 (2006).
14. News Alert, "EU Smart Construction Materials Absorb and Wash Away Pollution," European Commission, Brussels (March 4, 2004).
15. H.N. Gray & D.E. Bergbreiter, "Applications of Polymeric Smart Materials to Environmental Problems," *Environmental Health Perspectives Supplements*, **105** (S1), 55 (1997).
16. C.M. Lampert, "Advances in Smart Materials Technologies - Windows," *Proc. 48th Annual SVC Technical Conference*, Society of Vacuum Coaters, Albuquerque, NM, 2005; pp 675-690.
17. C.-G. Granqvist, "Electrochromic materials: Out of a Niche," *Nature Materials*, **5** (2), 89 (2006).
18. "U.S. Navy Freeboard and Superstructure Coatings," National Surface Treatment Center at http://nstcenter.com.
19. R. Cook & J. Elliott, "Smart Coatings through Emergent Nano-Technologies," Mega Rust 2007, (June 4-7, 2007), San Diego, CA, Paper MR-2007-18, National Surface Treatment Center, Louisville, KY, 2007.
20. M.F. Montemor & M.G.S. Ferreria, "Cerium Salt Activated Nanoparticles as Fillers for Silane Films: Evaluation of the Corrosion Inhibition Performance on Galvanised Steel Substrates," *Electrochimica Acta*, **52** (24), 6976 (2007).
21. G. Williams & H.N. McMurray, "Inhibition of Filiform Corrosion on Polymer Coated AA2024-T3 by Hydrotalcite-like Pigments Incorporating Organic Anions," *Electrochemical & Solid State Letters*, **7** (5), B13 (2004).
22. M. Kendig, *et al.*, "Smart Corrosion Inhibiting Coatings," *Progress in Organic Coatings*, **47** (3-4), 183 (2003).
23. S. de Souza, "Smart Coating Based on Polyanilene Acrylic Blend for Corrosion Protection of Different Metals," *Surface & Coatings Technology*, **201** (16-17), 7574 (2007).
24. N.-R. Chiou, *et al.*, "Growth and Alignment of Polyanilene Nanofibers with Superhydrophobic, Superhydrophilic and Other Properties," *Nature Nanotechnology*, **2** (6), 354 (2006).
25. J.L.M. van Mechelen, *et al.*, "Mg-Ni-H Films as Selective Coatings: Tunable Reflectance by layered Hydrogenation," *Applied Physics Letters*, **84** (18), 3651 (2004).
26. T.V. Murzina, *et al.*, "Nano-coating with Controllable Reflectance Spectrum," *Smart Structures and Materials 2005: Active Materials; Behavior and Mechanics*, W.D. Armstrong, Ed., *Proc. SPIE*, **5761**, 23 (2005).
27. J.R. Nicholls, *et al.*, "Smart Overlay Coatings - Concept and Practice," *Surface & Coatings Technology*, **149** (2-3), 236 (2002).
28. M. Schmitt, "Wash-permanent Nano-structured Surface Protection of Textiles by Bio-mimicking Lotus Leaves," Smart Coatings 2006, (15-17 February, 2006), Orlando, FL; Coatings Research Institute of Eastern Michigan University, Ypsilanti, MI, 2006.
29. C.-Y. Lin, *et al.*, "Smart Temperature-controlled Water Vapor Permeable Polyurethane Film," *J. Membrane Science*, **299** (1-2), 91 (2007).
30. J.-C. Cheng, *et al.*, "Smart Coating System with Chemical Taggants for Coating Condition Assessment, U.S. Patent 6,644,917 (November 11, 2003).
31. M. Kobayashi, *et al.*, "Integrated Ultrasonic Transducers made by Sol-gel Spray Technique for Structural Health Monitoring," *Smart Materials & Structures*, **16** (2), 317 (2007).
32. B. McKee, *et al.*, "Smart Coatings for In-situ Monitoring of Engine Components," *SPIE Conf. on Industrial and Commercial Applications of Smart Structures Technologies*, (March, 1999) *Proc. SPIE*, **3674**, 461 (1999).
33. H. Toda, *et al.*, "Feasibility Study on Smart Coating for Failure Prevention Under Thermo-mechanical Fatigue Loading," *J. Intelligent Material Systems & Structures*, **17** (12), 1099 (2006).
34. M. Mönkemeyer, "Photocatalytic Coatings for Automotive Application," Session I, European Coatings Conference (May 15-16, 2006) Berlin, Germany.
35. W. Feng, *et al.*, "Smart Polymeric Coatings - Recent Advances," *Advances in Polymer Technology*, **26** (1), 1 (2007).

Table 1
Some smart coating approaches and their possible applications

General Area of Applicability	Smart Coating Approach	Existing and Possible Applications	Industrial & Commercial Uses	Federal Gov. Uses (incl. DoD)
Bio, Medical Equipment	* Nano-fibers with chemical additives * Nanoparticle biocidal agents	* Cell modulation, implants, new DNA structures * Anti-bacterial/fouling coatings, chemical agent decontamination	Yes Yes	Not Yet Yes
Buildings, Construction, & Environment	* Nanoparticle inhibitors * Electrochromic additive * Photocatalyst additives * Nano-fibers with chemical additives	* Corrosion protection * Windows and architectural glazing * Walls, floors, ceilings -air pollution control * Self-cleaning, anti-fogging surfaces	Yes Yes Yes Yes	Yes Not Yet Not Yet Not Yet

Table 1 (cont.)
Some smart coating approaches and their possible applications

Corrosion Prevention & Control (General)	* Chelating & other additives	* Rust stain elimination on ships, etc.	Yes	Yes
	* Microencapsulated indicators	* Corrosion detection	Yes	Yes
	* Microencapsulated inhibitors	* Corrosion protection	Yes	Yes
	* Anion exchange additives	* Corrosion prevention	Yes	Yes
	* Inhibitors attached to nanoparticles	* Corrosion protection	Yes	Yes
	* Inhibitors in nano-porous particles	* Corrosion protection	Yes	Yes
	* Inhibitors in conducting polymers	* Corrosion protection	Yes	Yes
Electrical, Electronic, & Optical Devices	* Microencapsulated monomer and catalyst additives	* Corrosion protection (self-healing of polymer coatings on composites and metals)	Yes	Yes
	* Inhibitors in conducting polymers	* Corrosion protection	Yes	Yes
	* Nano-fibers with chemical additives	* Transparent electrodes, thin film displays	Yes	Yes
	* Hydride formation in Mg alloys	* Controllable mirrors	Yes	Not Yet
	* Nanoparticles in porous Si	* Controlled color reflectance, displays	Yes	Not Yet
Energy	* Inorganic “gradient” layers	* Medium/high temperature oxidation protection for pipes, burners, engines, exhausts, etc.	Yes	Yes
	* Microencapsulated indicators	* Corrosion detection in pipelines	Yes	Not Yet
Fabrics, Clothing	* Organic nanoparticle additives	* Stain resistance, waterproofing	Yes	Yes
Transportation	* Microencapsulated inhibitors	* Corrosion detection on aircraft, vehicles & ships	Yes	Yes
	* Inorganic “gradient” layers	* Med. & high temperature oxidation protection for pipes, engines, exhausts, etc.	Yes	Yes
	* Nanoparticle inhibitors	* Corrosion protection	Yes	Yes
	* Inhibitors in conducting polymers	* Corrosion protection	Yes	Yes
	* Electrochromic additives	* Vehicle windows and mirrors	Yes	Not Yet
	* Nanoparticle biocidal agents	* Anti-bacterial/fouling coatings, chemical agent decontamination	Yes	Yes
	* Nano-fibers with chemical additives	* Self-cleaning, anti-fogging surfaces	Yes	Not Yet
	* Nanoparticle taggants	* Turbine blade erosion detection	Yes	No
	* Piezoelectric transducers	* Engine wear monitoring, ice build up on aircraft	Yes	Yes
	* Embedded planar sensors	* Engine health monitoring	Yes	Not Yet