Chapter 1

Twenty-First Century Materials: Coatings That Interact with Their Environment

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"Smart Coatings" represent the state-of-the-art of coatings technology. This technology has evolved through three principal stages. In the first, an ingredient with valuable properties is added to a coatings formulation, and all the unique properties of the coating are attributable to this additive. In the second, a specialized resin, pigment, or other material imparts to a coating properties that cannot be realized in any other way. "Smart Coatings," which represent the third and current stage of development, sense their environment and react to it. This paper will use this model of evolution to develop a framework for discussion at this meeting. Principles and examples of coatings at each stage of development will be given, and the way forward to unique coatings will be explored.

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We've come a long way since coatings were first used some 15-25,000 years ago by Cro-Magnon people to paint figures of animals on the walls of caves in Lascaux, France. Protein binders from animal or vegetable sources were mixed with native clays and used to record the animals upon which much of life depended. As coatings became more sophisticated, they evolved from purely decorative and aesthetic applications and became essential materials for the protection and preservation of surfaces. But even as recently as 60 years ago, house painters purchased powdered white lead (lead carbonate), vegetable oil, and a drier (catalyst) of some sort, mixed them on the job site, and brushed on a protective coating that would be expected to give 3 years of service in moderate weather.

Advances in the chemical industry after World War II produced a wide variety of synthetic resins, pigments, solvents, and additives that were rapidly used to improve protective and decorative coatings. New substrate materials were also commercialized, and coatings were formulated to protect all of them. Mechanisms of protection were identified and improved. *Inhibitive coatings* such as the red lead alkyds protect steel by slowly releasing ions which passivate the metal surface. *Barrier coatings* such as epoxies and urethanes interpose a barrier between the surface and corroding species such as oxygen and water, isolating the surface from attack. *Conversion coatings* are made by phosphating or chromating a metal surface in a treatment bath. A few atomic layers of metal on the surface of the substrate are thereby converted to a hard, durable corrosion-resistant layer. *Sacrificial coatings* such as the organic or inorganic zinc coatings maintain electrical contact between a metallic substrate and the zinc metal, so that a demand for electrons will oxidize the zinc in preference to the metal of the substrate. But, basically, these coatings just sat on the surface. They were like offensive linemen on a football team: "Go ahead and give me your best shot, but you're not getting through to my quarterback!"

Now at the turn of the millennium, a coating that just "sits there" is no longer the state-of-the-art. Coatings that sense their environment and make an appropriate response are needed for forward-looking applications in medicine, aerospace, environmental protection, battlefield awareness, and personal safety, among others. So how are we to create such coatings? What principles determine their performance? How can we design a coating that perceives its environment with sufficient sensitivity, produces an acceptable response, and continues to do so during thousands, if not millions of cycles during a lifetime that must be measured in years? All the while, none of the usual restrictions are waived: the coating must be safe for workers and the environment, and – in our dreams, at least – cost no more than the material it replaces.

The name usually used to describe this new class is "Smart Coatings," and that is also the name chosen for this Symposium. "Smart" can mean many things: intelligence or mental capability, clever or witty, brash or vigorous, and trendy or fashionable. All of these features can be seen in the coatings that will be described during this Symposium.

We might consider that Smart Coatings have evolved in three stages. In the first, something that modifies coating properties all by itself is simply added to the formulation. An example of this approach would be a silicone resin, which migrates to the coating–air interface and influences the adhesion, cleanability, and/or gloss of the coating. This approach is applicable to coatings containing just about every type of resin and pigment, and the response is solely attributable to the additive itself.

A second generation of these coatings uses specialized but relatively inert ingredients to produce properties not found in more conventional coatings. Examples would include silicone or heavily fluorinated polymers, which diminish the surface energy of a coating and allow it to resist adhesion. Usually the coating has to be reformulated from scratch, for the suspension and wetting properties as well as the application and curing properties are strongly affected by the specialized ingredient.

The third stage, now a Smart Coating, is characterized by a material which truly senses and responds to its environment. The sensing element might include a pigment sensitive to light, a polymer sensitive to pH or heat, or a polymer or polymer blend which induces a patterned surface that directs wetting and spreading of liquids on its surface. The entire coating must be formulated around this unique material to ensure that it may most effectively perceive environmental stimuli and exert its characteristic response. More and more examples of this type of coating are being devised. For example, "command-destruct" coatings contain sites in the polymer backbone, which cleave in response to a stimulus, effectively destroying and removing the coating. This and other examples are given in Table I.

It is instructive to review how smart coatings technology has advanced in various applications through these three stages. Let us do this now for two dissimilar applications.

Antimicrobial and Hygenic Coatings

Health and safety issues are constantly in the public eye. People require clean food and water and are always seeking to maintain a safe and healthful living environment. Therefore facilities that supply these needs must be kept clean and sanitary at all times. Examples are waste and wastewater management plants, hospitals and clinics, industrial facilities for manufacturing and packaging pharmaceuticals and food, commercial food preparation facilities, and restaurants.

Stage one coatings are formulated by adding a nonreactive fluorinated or silicone additive to any of the epoxy, acrylic, or polyurethane coatings used for this purpose. The additive migrates to the air–coating interface and reduces the surface energy of the coating, thus impeding the attachment of bacteria and also facilitating cleaning of the surface. Alternatively, a bactericide might be simply

Table 1. Examples of "Stage Three" Smart Coatings

Coating Type	*Operating Principle*	*Example*	
		Stimulus	*Response*
Ablative	Outer layers of the coating surface are slowly removed by chemical (*e.g.*, hydrolysis) or physical action	Shear of water flowing across the surface; temperature of water	"Self-cleaning:" Dirt, biofilm, etc. is removed with outer layer of polymer
Command-Destruct	Chemical bonds in the polymer backbone cleave in response to a stimulus	Heat	Depolymerization and removal of the coating
Corrosion Detection	Corrosion produces OH^-; acid-base indicators change color at different pH	pH	Color reports on the site and extent of corrosion
Hygenic	Capsules contain bactericide; capsule walls are destroyed by products (*e.g.*, acids, amines) of bacterial action	Bacteria	Release of toxin kills bacteria
Impact Sensitive	Capsules of different wall strengths contain dyes of different colors	Impact	Color reports on the site and strength of impact
Low Solar Absorption	Color pigments are transparent to UV light and allow it to be scattered by TiO_2	Sunshine	Failure to absorb UV, convert it to heat, and radiate the heat; cooler substrate
Piezoelectric	Lead–Zirconium–Titanate pigment generates an electrical current when stressed	Vibration	Proportional current; lifetime current reflects sum of stress
Pressure Sensitive	Paint contains a fluorescent pigment which is quenched by oxygen	Pressure (increased oxygen availability)	Fluorescence decreases as pressure increases
Self-Healing	Capsules containing uncured resin are broken	Impact	Replacement of damaged resin
Temperature Sensitive	Paint contains a fluorescent pigment which is quenched by heat	Temperature	Fluorescence decreases as heat increases

stirred into the coating. These "free association" coatings usually release excess active agent (*e.g.,* silicone additive or bactericide) early in their life, and fail when the amount released is too low to be effective.

Stage two coatings are based on a silicone resin or heavily fluorinated resin. These also impart low surface energy to the coating and, as the surface of the coating wears, a fresh surface of the same material is exposed and the desirable low surface energy is never lost.

A stage three smart coating contains a toxin encapsulated within various shell materials. The toxic agent is released when the shell of the capsule is destroyed. Capsules in such a coating would be made with shells sensitive to, for instance, enzymes secreted by bacteria or decomposition products (e.g., acids, amines, or ammonia) produced by bacterial action, and the rate of destruction is controlled by the chemical composition or the thickness of the shell. Capsules containing different toxins can be combined in a coating to give it broad-spectrum antimicrobial activity. The coating releases a toxin only in the presence of bacteria, preserving the active ingredient and extending its service life.

Another example of a stage three antimicrobial coating contains zeolites, an inorganic silicate which contains pores sufficiently large to hold metal ions. Silver ions can be absorbed into zeolites and then released at a controlled rate. Coatings containing silver-filled zeolites may be suitable for preventing contagion of cooking and eating surfaces and utensils, although once the silver is exhausted it may be impossible to reactivate the coating.

Antifouling Coatings

Antifouling coatings prevent the growth of marine life on the underwater surfaces of ships. This growth, or fouling, decreases the speed, range and maneuverability of a ship and raises fuel consumption by as much as 30%. Ultimately the ship must be removed from the water and mechanically cleaned to remove the fouling, and the time the ship spends out of service is also quite costly.

Early antifouling coatings were made by adding creosote or copper metal to coatings designed for other purposes. Toxic coatings representative of the second stage contained salts of arsenic, beryllium, cobalt, copper or mercury, organic biocides, or other toxins. Nontoxic second stage coatings have been created from fluorinated or silicone resins, which impart their low surface energy to the coating.

"Smart" antifouling coatings are based on an acrylic resin containing hydrolyzable esters in the side chains. The esters are transformed to alcohols at a rate, which depends on the temperature of the water and the shear imposed when water flows across the surface. The resulting polymer is water soluble and slowly washes away, taking with it biofilms and juvenile fouling organisms. These coatings usually contain toxins as well; a fresh layer of toxin is exposed as the older layers of coating dissolve away. These "ablative" antifouling coatings have been used on ships' hulls for about ten years.

Other Coatings that Interact with Their Environment

The stage three antimicrobial and antifouling coatings are good examples of smart coatings. They sense their environment and take no action until necessary. The antimicrobial coating senses bacterial degradation products and releases toxins to destroy the pathogen that produced them. The antifouling coating senses water temperature (which correlates with biological growth) and reacts with seawater, producing a water-soluble coating. What are other examples of coatings that truly sense and respond to their environment?

Lead–zirconium–titanate is a piezoelectric pigment that generates an electrical current when stressed. A coating pigmented with this material is used as a strain gauge on a pedestrian bridge. The paint is applied 50 microns (2 mils) thick directly to steel and coated with a thin conductive film. The electrodes (substrate and top film) are connected to off-site monitoring equipment, which measures the current generated by vibration and impact loads between 1Hz and 1kHz. The total current produced is a measure of the total stress experienced during the life of the structure; a sudden and sharp rise in the current may indicate a weakened structure that is less able to resist stress. The principal challenge was formulating the paint with a pigment loading high enough for the paint to function as a piezoelectric yet low enough for it to be readily applied by spray.

Self-healing coatings contain reservoirs of uncured resin within capsules. Corrosion, crack growth, mechanical damage, or chemical attack ruptures the capsules, releasing their ingredients where and when needed. The ingredients then react and become part of the film. For example, epoxies and amines (from separate capsules) react with each other; or liberated alkyd resins react with ambient air.

Medical implants are coated with a polymer, which resists adhesion to proteins, polysaccharides, fats, and cells. The polymer contains long side-chains of polyethylene oxide (PEO). The density and length of the PEO chains are tailored to function in the environment in which the implant will be used. The goal is to produce elongated, hydrated PEO chains that, in the dynamic environment of the human body, sweep across the surface of the implant and prevent settlement. The density of PEO chains on the surface is chosen so that the chains do not interfere with the motions of other chains.

Pressure-sensitive paints contain a pigment that fluoresces under ultraviolet light. Oxygen quenches this fluorescence. As air pressure on the coating increases, more oxygen is available to interfere with the output of visible light, and the intensity of fluorescence can be correlated with the pressure on the surface. This coating is used in the study of models of commercial and military aircraft in wind tunnels.

A coating that detects and reports on corrosion can be made by dispersing a number of pH indicators in a clear coating. Corrosion of metals produces hydroxide ions and raises the pH only at the site of corrosion. An acid-base indicator reacts with alkali and changes color within a specific pH range. The coating contains a selection of indicators that produce different colors and undergo their color change in different pH ranges; thus, the hue and location of color signal the extent of corrosion. Coatings can be tailored to specific substrates and to change color at a predetermined extent of corrosion.

The Future of Smart Coatings

Materials potentially useful in smart coatings are being produced in ever increasing variety and quantity. Some materials on the horizon of coatings technology are:

- Microelectromechanical devices (MEMs) are micromachined assemblies embedded below the surface of a silicon wafer. Pumps, motors, switches and other machines with dimensions of few millimeters are made by conventional photoresist technologies.
- Radio frequency identification devices (RFIDs) are millimeter-size silicon chips bearing a circuit, which oscillates in response to an external signal and responds at a chosen frequency. The signal is used to open a door, count inventory, or track parcels.
- Polymers and polymer blends form patterned surfaces. The wetting and spreading of liquids can be quite dissimilar on different polymers, and a surface patterned with polymer channels (think of a printed circuit board) can be used to direct the aggregation and flow of liquids on the surface of the coating.
- Specialized lipids self-assemble to form tubules. These tubules are plated with copper, and the lipids are removed and reused. In this way copper tubules approximately 500 nanometers in diameter and 5 micrometers long are formed. Various substances can be placed within these tubules and then slowly released from the tubules.
- Carbon nanotubes may be used as if they were nanofibers to strengthen a coating. In sufficiently high loadings, the nanotubes touch and the coating becomes conducting.

- Self-assembling nanocapsules are kept together by hydrogen bonds. Capsules in which other molecules are encapsulated may be destroyed by such strong hydrogen-bonding agents as amines and alcohols, and the internal molecule is released to exert its intended effect.
- Nanomaterials offer different chemical and physical properties than bulk materials. Although the distinction is not always precise, old nanotechnology usually describes nanoscale materials such as carbon black, fumed silica, and titanium dioxide produced for coatings for decades but getting the "nano" designer label only recently. New nanotechnology typically encompasses novel material structures, such as carbon nanotubes and quantum dots, with unprecedented properties.
- Sturdy enzymes able to resist denaturing and to function in a variety of solvents are being produced. New antimicrobial and hygenic coatings might be made by deploying these enzymes on the surface of a coating where they may breakdown bacteria or waste products.
- Polyaniline and other polymers that may be repeatedly oxidized and reduced may find a use in direct-to-metal applications such as sacrificial primers. Reducing the polymer so that it may be oxidized again may prove to be a challenge.

The way forward to produce organic surface coatings containing these radical new materials and devices is anything but certain. Some of these things must be on the surface of the cured coating, and some must be at the coating–substrate interface to ensure that they most effectively receive environmental inputs and exert their characteristic response. The coatings must be manufactured without destroying its unique properties, and must drive the device to its optimal position within the film before curing.

It's a big job, but we can dream, can't we? Coatings chemists have not yet failed any challenge, and we may look to the future with anticipation of the marvelous coatings yet to be invented.

Further Reading

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