What defines a 'smart' coating and how clever have coatings really become? **Rosa Raskin**, Rosa S Raskin & Associates looks at the meaning of 'smart' in the coatings industry and its latest technological offerings, including influences from both the animal and plant kingdoms

Animal instincts: Cutting-edge coatings

Carbon nanotube technology is modelled on the gecko's adhesive properties

A feature that makes a coating 'smart' is its pre-determined response to a stimulus. A smart coating is a chameleon of sorts, modelled after nature (biomimicry), sometimes created via technology transfer, a metamaterial, or an idea from science fiction.

HOW SMART IS A SMART COATING?

According to research documented at various conferences, news reports and applied sciences literature, coatings are getting smarter. These 'smart' coatings offer more than a traditional coating, for instance the addition of biocides to self-cleaning properties and repairing capabilities. The most well-known model for self-cleaning, the 'lotus effect', gets its name from the leaves of the lotus growing in the waters of Asia. The surface of the leaves holds nature's secret to the plant's ability to keep itself clean. The carnivorous pitcher plant, genus Nepenthes, displays anti-adhesive properties, as its prey lose footing and adhesion capability and the insect falls deeper into the waxy walls of the plant to be digested.

A famous animal model, the gecko, whose name is believed to stem from the Indonesian/Javanese word 'Tokek', is a lizard of continued interest due to its adhesive abilities. The gecko's toes exhibit elastic qualities and attractive forces on an atomic level via the gecko's microscopic toe hairs. Researchers have surpassed nature's wonder by designing the first carbon nanotube material modelled after the gecko's adhesive properties. A recent design is several times better than previous models and has ten times greater resistance to perpendicular shear forces. Future efforts include the development of artificial gecko feet to grip vertical surfaces, which are easy to remove and function as adhesives that will not dry out in the vacuum present in outer space (Dirjish, 2008).

Australian researchers swam in waters to search for anti-fouling plant models to inhibit bacterial growth and control the formation of biofilms, a starting point of biofouling. The unique feature in their approach was not to kill bacteria and develop resistance, but to find compounds to inhibit the bacterial quorum-sensing mechanism (Rinaldi, 2007).

On land, smart paints and coatings may introduce novel architecture to extract pollutants from our environment.

According to Thomson Reuters Science Watch (http://sciencewatch.com/ana/fea/09janfebFea/) there are numerous scientific publications in Asia Pacific, along with international collaboration and co-authorship on scholarly papers, which account for Asia's increased presence in scientific research.

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As reported by Chemical Abstracts Service (CAS), China has experienced rapid growth, and now leads the world in producing patent applications in chemistry.

WHAT'S NEW IN LITERATURE?

Smart coatings research spans from underwater studies, including aquaculture, to outer space. Scirus is a scientific search engine that includes thousands of web sites as well as journal articles and other media. It is updated continuously. Articles on smart coatings appear in many fee-based databases, where unlimited synonyms and detailed query language allow searches in pre-determined formats. Databases citing smart coatings include Chemical Abstracts, Compendex, Engineered Materials Abstracts, Inspec, Metadex, World Surface Coating Abstracts, and many others.

Numerous professional, academic, and trade journals identify smart coatings including *Advanced Materials, Applied Surface Science, Materials Today, Nature, Nanotechnology, Science, Smart Materials and Structures* and over one hundred others, including ***APCJ***. A particularly interesting article on nano and smart coatings was featured in ***APCJ*** October, 2009 (Advincula, 2009).

A popular review of journal literature including state-of-the-art anticorrosive coatings systems is 'Anticorrosive coatings: a review,' (Sorensen, 2009), appearing on thefreelibrary.com website. Sorensen emphasises that the trend in lowering VOCs is the incentive for the industry to develop coatings with high-solid contents, powder coatings, or water-borne products with low amounts of organic solvents. Flaws in current anticorrosive coatings have prompted the study of new coating systems including self-healing coatings to prevent corrosion. A patent literature search for 'smart coatings' reveals intellectual property originating in the Asia Pacific region. A patent might indicate that the coating has memory, is a smart coating system, has intelligent skin, may self-repair, or is capable of self-assembly. Smart coatings may refer to paints, special polymers, and/or other materials.

INVISIBLE CLOAK

One notices more flaws on a glossy wall than on one painted in flat paint, but making an object invisible involves cutting-edge technology. Invisibility has moved from the science fiction tales of the Klingons in the TV series Star Trek, to reality. Invisible cloaking technology, common in the fictional adventures of Harry Potter, is included in research activities sponsored by science foundations as well as the military (AP, 2009).

In January 2009, the Associated Press (AP) stated in a news release 'They can't match Harry Potter yet but scientists are moving closer to creating a real cloak of invisibility.'

Blending into the background: modern coatings use advanced techniques to develop an 'invisible cloak'

Metamaterials deflect microwaves around a three-dimensional object, making it invisible to microwaves. The system is reported to be analogous to a mirage, where heat causes the bending of light rays and cloaks the road ahead behind an image of the sky.

As research continues, a wider spectrum of wavelengths to deflect objects will be identified. An invisibility cloak, consisting of more than 10,000 individual pieces of fibreglass arranged in parallel rows, is projected to scale to infrared and visible light.

Mathematical formulas determine the shape and placement of each piece to deflect the electromagnetic waves (AP, 2009). As evidenced by the news and documented in literature, interest in the research to conquer invisibility continues.

SMART DRIVING FORCES

The 2009 winners of the Thomas Alva Edison Award agree that the major driving forces in the development of smart coating systems are material degradation, corrosion and fatigue. The team received the award for inventing a smart coating system, patent number US 7244500. The coating is corrosion resistant and capable of collecting, analysing, managing and adapting to data and/or the environment in real time using a flexible sensor layer, a switch layer, and a visual display layer. The sensor layer senses environmental conditions and the visual display layer provides visual indication of the condition(s) sensed. The active coating senses temperature, conductivity, pressure, radiation, chemicals, substrate integrity, strain, scratches and corrosion.

Smart, cutting-edge coatings may display one or more of the following properties:

'Invisible cloaking technology, common in the fictional adventures of Harry Potter, is included in research activities sponsored by science foundations as well as the military (AP, 2009).'

Self-healing

A corrosion-inhibiting pigment of nanoreservoirs to protect metallic structures is included in a patent entitled Corrosion Inhibiting Pigment Comprising Nanorres (WO/2007/104457).

The invention involves active corrosion protection in a multi-layered coating including nanoscale inhibitors composed of a polymer or polyelectrolyte shell. The database, Metadex, reveals such titles as 'Nanoscale smart coatings can heal shallow pits, and fractures' (on metal, glass, silicone etc) in the journal *Advanced Materials & Processes*.

Self-cleaning

Many self-cleaning technologies are modelled after the lotus plant, which remains clean while growing in muddy waters. In 2009, a team from China published their re-creation of a 'lotus effect,' self-cleaning coating showing the same surface structure as the lotus leaf model in the journal *Applied Surface Science* (Su, 2009) via the *Science Direct* journal aggregator. Research on the 'lotus effect' has been transferred to coatings that de-ice roads and aircraft (Wray, 2009).

In space news, a lotus plant-inspired coating to protect NASA space gear consists of a transparent coating that prevents dirt from sticking to spaceflight gear and bacteria from growing inside astronauts' living quarters (NASA, 2009).

Self-assembly

Intelligent coatings can easily switch their properties as described in 'Intelligent polymeric surfaces through molecular self-assembly' (Goel, 2009) via thefreelibrary.com.

Amphiphilic surfaces, such as polyurethane coatings with hydrophobic and hydrophilic properties display intelligent behaviour, of interest in marine ecosystems, leading to the next property – anti-fouling.

Anti-fouling

Designing solutions for anti-fouling is of continued interest as the monetary and environmental costs of fouling continue to rise. Ongoing research includes the development of new materials and methods. Each new invention surpasses current state-of-the-art performance. The Asia Pacific region and The Netherlands are active in marine anti-fouling research. One approach to anti-fouling includes foul-release coatings systems to reduce the drag on ships and in aquaculture, to lower operating costs and adverse effects on the environment. Another approach identifies new anti-fouling chemicals in coatings to deter organisms, serve as safe biocides and/or prevent the formation of biofilms.

Anti-fouling compounds capable of being added to existing coatings continue to be identified in nature and nature provides the models for their creation.

Reflectivity and/or conductivity

New nanomaterials join metallics in the formation of conductive and reflective coatings. An entry from China cited on the World Intellectual Property Organization (WIPO) website identifies a smart coating that monitors a structure in real time. The coating includes a sensing layer composed of an electrically-conductive material.

The sensing layer, 10 nanometers to 100 micrometers thick, can sense damage to a complex structure, such as the formation of a crack, without disassembling the structure. (Zhigang, 2008).

Graphene is a potential material for new conductive coatings. Graphene is the one-molecule thick layer from the graphite of one's pencil. Graphene is invisible and is considered to be the strongest compound on earth. Whether it behaves as a metal or not it appears to depend upon its edge structure (Ritter, 2009). 'Spray painting' graphene with hydrogen atoms that attach to the carbon atoms, removes the property of conduction, turning graphene into graphane, an insulating material.

The amount of conduction and/or insulation is controlled by the extent of the saturation with hydrogen. Graphane is easier to work with and more versatile than graphene. The research conducted in Manchester, UK published in *Physics World,* and cited by the Institute of Physics, has much potential (Institute of Physics, 2009).

Nanoscale

Nanotechnology provides advances by depositing 'nanostructure films' on surfaces such as eyeglasses and solar cells. The products include more efficient solar cells per the reflectance of light and eyeglasses that capture more light, reduce glare and lower exposure to ultraviolet light. A convenient feature is that the coating for eyeglasses can be applied on-site at a lower cost than available coatings (Oregon State University News, 2009).

Metal objects such as cars, bridges, and aeroplanes begin to falter as they corrode. Using nanoscale materials for repair may save time, energy, materials and billions of dollars. Chemicals are attached to nanomaterials to create a coating that is placed between the primer and topcoat. The corrosion product fluoresces revealing the location of rust (Battelle, 2009).

Novelty

Metamaterials refer to speciality materials that have the ability to bend light around an object making it appear invisible. A 2008 patent application, 'System, method and apparatus for cloaking,' US 20080165442 A1, includes the use of a metamaterial cloak placed between the object and the observer. The object becomes invisible while the background appears unobstructed. The property of the metamaterial is not uniform, but varies by the distance from the cloak interfaces. (Cai, 2008).

Making a cloak from a metamaterial differs from the technology of covering up an object to make it look like something else in visible light. The European Patent Office includes a patent application for an 'Unmanned vehicle with a camouflage apparatus.' The text mentions that the cloaking device is a cover in the form of a bird of prey (Stelte, 2009). A rainbow is a beautiful optical effect in nature as water droplets reflect and refract light. When an object makes a light curve around it, it may become invisible. The challenge appears to be in bending multiple wavelengths of light around the object.

An October 2009 report in *Nature Photonics* describes a cloak concealing a deformation on a flat reflecting surface, operating in the near infrared wavelength, composed of nanometre-size silicon structures with spatially varying densities (Gabrielli, 2009).

CONCLUSION

The coatings industry provides more than materials for decorating or protecting substrates. Like the chameleon, a smart coating may change instantly in response to its substrate and beautify our world and/or identify and repair flaws or cracks, critical to safety. The smartest quality of smart coating materials is the property of variability. The coatings may not be uniformly designed per varying densities or spacial arrangement of nanoparticles, but developed with regard to utility and economic considerations.

Coatings are getting smarter as man's inventive spirit improves the models found in nature and science fiction. Cutting-edge coatings are intelligent in real time. They sense the environment, identify and respond to numerous stimuli, detect failure, self-assemble, self-clean, or anti-foul under the sea, on land, or in outer space. As documented in scientific literature and related media, although coatings are considered a mature industry, research is increasing per environmental and economic incentives, advances in technology and researcher interest.

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