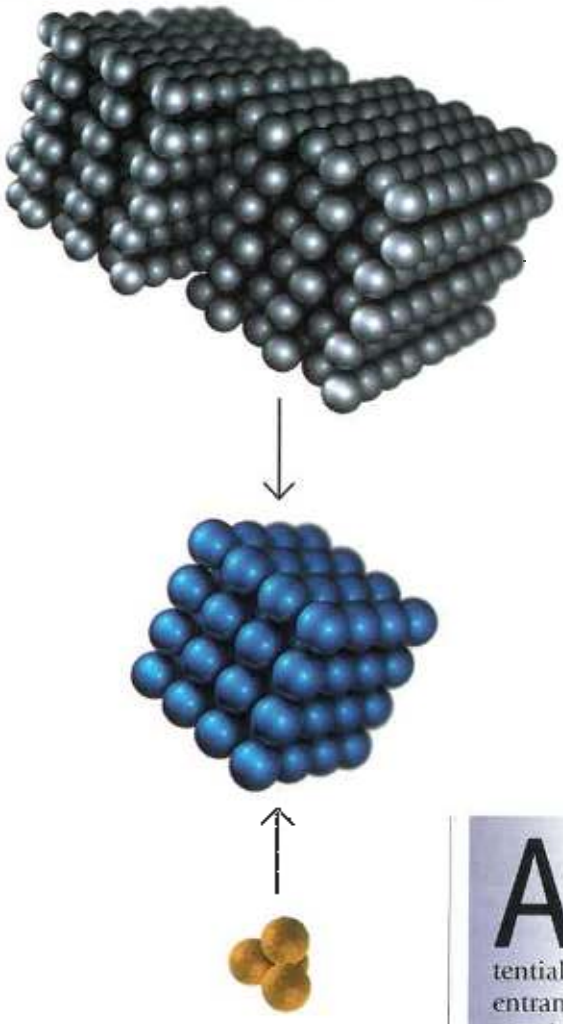

Nanotech for Coatings:

Moving from Discovery to Commercial Reality

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As buzzwords go, nanotechnology has been a pretty good one. The potential for nano-sized materials to impart unique properties to coatings has entranced many in the industry and led to significant investments in research and development efforts to convert that potential into practical applications. In fact, the use of nanotechnology has been a natural progression for some coatings, where micron-sized materials (10–6 meters) have been replaced with nanoparticles (10–9 meters) and nanostructured materials. The ability to control and manipulate nanostructures enables the control and manipulation of chemical and physical properties of specific materials.

In coatings, nanotechnology has been introduced via nanoparticle additives and creation of nano-sized resins and particles through the sol-gel process, where the coating structure is designed beginning at the nanoscale, according to Dr. Li-Piin Sung, a research physicist in the Polymeric Materials Group of the Building and Fire Research Laboratory at the National Institute of Standards and Technology. She adds that the list of demonstrated performance enhancements derived from incorporation of nanotechnology into coatings has grown quite lengthy.

With so many real benefits to be gained, it is not surprising that numerous companies—both large, well established corporations and small, entrepreneurial firms—have focused on developing products for the coatings marketplace that aim to differentiate themselves with nanotechnology. Several novel additives, nano-sized resins, and coating formulations incorporating one or both of these technologies are now commercially available.

The manufacturers of these products still face some serious challenges, though. "Some nano-coatings have been shown to offer better short-term performance, but the cost of these novel materials is often high, and we also don't have any data on the long-term performance," notes Sung. "Therefore, there isn't yet a way to evaluate life-cycle costs." Some developers of nano-

Above photo courtesy of Altana.

coatings disagree, and point to several products on the market that are cost competitive.

Environmental, health, and safety (EH&S) issues must be addressed as well. Current rules and regulations are inadequate for addressing issues associated with nanomaterials. The small size of nanomaterials combined with their chemical and physical behaviors make it difficult to establish hazard ratings. Novel chemistries and complex nanoparticles pose additional problems. Both the European Commission and the U.S. Environmental Protection Agency (EPA) have initiated programs to collect data on nanomaterials.

The EPA's Nanoscale Materials Stewardship Program, launched in January 2008, is designed to "help provide a firmer scientific foundation for regulatory decisions by encouraging submission and development of information including risk management practices for nanoscale materials," according to the agency. Companies are requested to voluntarily report available information on the engineered nanoscale materials they manufacture, import, process, or use. In the longer term, EPA hopes that participants will voluntarily conduct tests and develop additional data.

PPG Industries is one company that is actively participating in the EPA program. "We hope that by providing information on our CeramiClear products, which meet all current requirements, we will gain some guidance on risk management for these and other products that we will introduce in the future," says Dr. Daniel Bardon, manager of Advanced Technologies in PPG's Office of Science & Technology. Sung, too, believes that the government and industrial sectors must work together to identify risks and develop appropriate policies for managing them.

Taking a proactive approach to managing such EH&S issues and other challenges reflects the entrepreneurial nature of many of the companies developing new coating technologies based on nanomaterials. Below is a survey of some of these companies and the products they have developed for coatings applications.

Advanced Nano Coatings

Advanced Nano Coatings manufactures and markets high performance, environmentally friendly epoxy coatings based on incorporation of nanomaterials into polymers prepared using unique chemistry. The company's ANC coatings are VOC-free and exhibit excellent surface tolerance and superior flow properties, allowing for application over marginally prepared steel surfaces and inorganic zinc primers. They have application as protective coatings for wood, steel and concrete protection, thermal insulation of building materials, and provide fire protection and retardancy. ANC Fire Retardant Coating is a high performance, two-component thin film intumescent flame-retardant epoxy that suppresses smoke and retards flame spread across a wide variety of materials including wood, metals, concrete, plastics, and insulating foams. It has been tested to the ASTM E84 standard by an independent laboratory, achieving both a Class 1 flame spread and a Class 1 smoke rating. Incorporation of nanoparticles into the coatings results in improved moisture resistance, flow properties, adhesion, and tensile strength.

Table 1—Nano-Derived Performance Enhancements

Anti-microbial
Anti-static
Barrier Properties
Corrosion Resistance
Fire Retardancy
IR-Absorption
Magnetic Properties
Mechanical Properties *(toughness)*
Optical Properties
Scratch Resistance
Self-cleaning *(photocatalysis)*
Surface Energy Modification
UV Stability

Source: Dr. Li-Piin Sung, NIST

AkzoNobel

Many products of AkzoNobel's Sikkens Cetol wood care products line contain nano pigments to reflect and selectively filter UV radiation. The nanoparticles help maintain the natural color appearance of the underlying wood surface while at the same time substantially increasing the UV and weathering stability of the coatings layer.

AkzoNobel also introduced a new façade coating in January 2008, resulting from a development collaboration with BASF and employing their new nanobinder (see below). Herbol-Symbiotec™, which incorporates the advantages of both organic and inorganic coatings in a single product, exhibits much higher dirt pick-up resistance and color retention than traditional materials due to the nanotech-based formulation. The paint generates a hydrophilic (water-attracting) surface. Rain drops falling onto walls coated with Herbol-Symbiotec wet the substrate evenly and do not leave non-wetted spots on which dirt can settle. This technology is a completely different concept compared to other dirt repellent façade coatings, which create hydrophobic (water-repellent) surfaces—the famous "lotus effect."

BASF

BASF's COL.9 binders homogeneously incorporate inorganic silica nanoparticles into organic polymer

particles in a water-based dispersion. When applied, they form a three-dimensional network in the façade coating which results in a very hard and hydrophilic surface that provides an excellent moisture barrier but remains permeable to water vapor. Dirt does not stick to the hard surface, so when water droplets wet the substrate evenly and dry faster, dirt is removed. The superior color retention is a result of the homogeneous incorporation of the inorganic nanoparticle into the binder. The water-based coating is easy to work with, comes in a wide range of colors, and is ideally suited for concrete and other mineral and organic bonded substrates. The binder is sold to AkzoNobel in Europe and exclusively to a coatings manufacturer in the U.S. In addition to façade coatings, COL.9 has potential applications in water-based wood stains and floor coatings.

Bayer MaterialScience

Carbon nanotubes (known as Baytubes) are now available in large quantities and at reasonable cost from Bayer MaterialScience (BMS). The company has the capacity to produce ~60 tonnes/year of Baytubes and is adding a further 200 tonnes/year of capacity that will be online by the end of 2009. BMS ships the amorphous nanotubes produced via its proprietary catalytic chemical vapor deposition (CVD) process to system suppliers such as Amroy in Finland, a company that has developed the technology to uniformly disperse the Baytubes into a variety of materials including epoxies. These dispersions are then incorporated into coatings by the formulator. Properties of carbon nanotubes of interest for coatings applications include their electrical conductivity, thermal conductivity, and mechanical properties. There is at least one commercial marine coating on the market that incorporates Baytubes to provide enhanced abrasion resistance. Formulations with nanotubes are also being investigated as anti-fouling coatings for marine applications and as additives for anti-static coatings where static discharge may otherwise be considered dangerous.

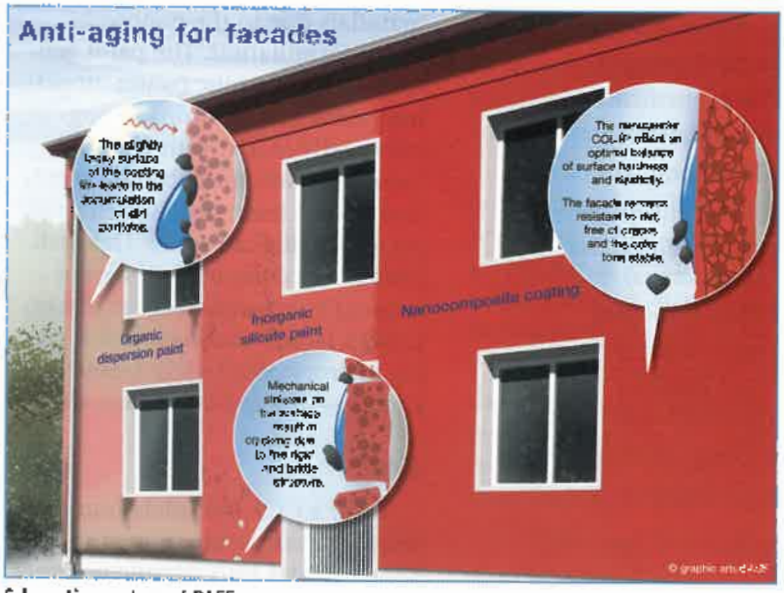
Separately, in February of 2008 BMS introduced Bayresit® VPLS 2331, a new, highly-functional ethoxycarbosiloxane crosslinker tailor-made for the formulation of films and coatings using the sol-gel process that is compatible with the use of nanoparticles. Coatings produced with this crosslinker have high flexibility, hardness and scratch resistance, pronounced chemical and corrosion resistance, and exhibit very little shrinkage during thermal curing, making thicker coatings possible.

Behr Paints

NanoGuard® technology from Behr Paints is based on nanoparticles that create an interlocking molecular structure that fills the voids created by larger particles, resulting in coatings products that provide better adhesion, more durability, and dirt, moisture, and UV resistance. Four products incorporate the NanoGuard technology: BEHR Basement & Masonry Waterproofing Paint, BEHR Premium Plus Ultra™, BEHR® Premium Solid Color and Semi-Transparent Weatherproofing Stains, and BEHR® Premium Plus Interior Sateen Kitchen and Bath Enamel. All of these products are formulated to provide maximum durability and stain and water resistance, plus each provides additional performance features designed for its specific application.

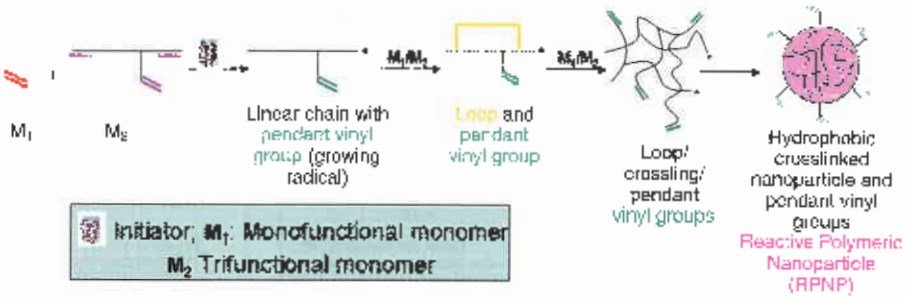
Bioni CS GmbH

Working with research scientists at the Fraunhofer Institute for Chemical Technology, Bioni CS GmbH developed an antibacterial coating, Bioni Hygienic®, that contains silver nanoparticles that destroy mold and mildew, fungi spores, and bacteria on contact. The nanoparticles are stabilized with additives and integrated homogeneously into the polymer matrix. Antimicrobial activity does not decrease with time because the solid nanoparticles are not volatile, like many commonly used biocide additives. Good antimicrobial, antiviral, and antiallergic performance has been demonstrated through independent testing. The waterborne, volatile organic compound (VOC)-free, and nearly odorless coating is resistant to disinfectants, acid, and solvents; permeable to water vapor; nonflammable; exhibits good washability; and comes in a wide range of colors. The coating has application in medical facilities and sensitive building appli-



Schematic courtesy of BASF.

cations such as schools, bathrooms, food industry facilities, and retirement homes. Additional applications being explored include dental implants, synthetic bones, catheters, artificial heart valves, food packages, and toys.



Scheme 1—Formation of reactive polymeric nanoparticles (RPNPs) in emulsion.

BYK USA

For a number of years, BYK USA has offered dispersions of nano-sized alumina particles, initially developed jointly with Nanophase Technology Corporation, to improve scratch and wear resistance. Today, BYK offers nanoparticle dispersions of aluminum oxide, silica, zinc oxide, and ceria under the NANOBYK tradename. The particles are dispersed in a variety of solvents, providing easy handling and simple incorporation via post-addition into a wide range of coatings formulations. Silica- and alumina-based nanoparticles provide improved scratch and abrasion resistance, while ceria- and zinc oxide-based nanoparticle dispersions provide stabilization against UV radiation (UVA by zinc oxides and UVB by ceria). Because of the size of the nanoparticles, they do not scatter light and can be added to a coating formulation without affecting its optical properties such as gloss and transparency. Incorporation of nanoparticles also provides a mechanism for efficient dissipation of stress throughout the polymer matrix, preventing catastrophic failure.

Ecology Coatings

Ecology Coatings develops nano-enabled, UV-curable "cleantechnology" coatings that are designed to drive efficiencies and clean processes in manufacturing. The company's coatings incorporate dispersions of metal oxides through mechanical mixing into the coating formulation. Properties enhanced by nanotechnology include hardness, abrasion resistance, and optical clarity, plus improvement in flow, better coverage with less pigment, improved corrosion resistance due to reduced flaws, and tenability of barriers to water, air, and solvents have also been achieved. In April of 2008, Ecology Coatings launched its EcoQuik™ line of products—EcoQuik Clear Coatings, EcoQuik Pigmented Coatings, and EcoQuik Barrier Coatings—for the automotive, electronics, industrial, medical device, paper, and other markets.

ElizaNor Polymer and BBS Biochemistry Ltd.

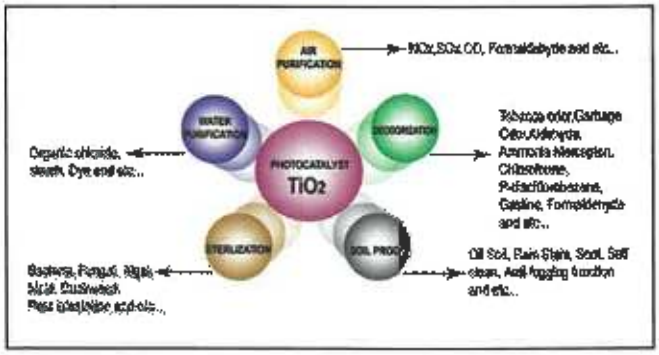
ElizaNor Polymer and BBS Biochemistry Ltd. have developed nanostructured polymeric particles for high solids systems and reactive polymeric nanoparticles (RPNPs) with the potential for use in low-VOC, environmentally friendly coating formulations. Both systems have been prepared by non-linear free radical copolymerization of acrylic monomers (*Scheme* 1). The Core-Shell Nano-Particle Technology allows for manipulation of the composition to suit different applications along with retention or improvement of mechanical properties such as adhesiveness, viscosity, flexibility, gloss, and hardness. The nanoparticles can be solubilized at high solid content while retaining a low viscosity of the solution. The inside of the nanoparticle is made of high molecular weight polymers and is hard, while the outer shell is soft. The nanoparticles react when sprayed onto a substrate, releasing the high molecular weight resin. A very low viscosity coating formulation comprised of RPNPs and butyl acetate was found to exhibit good adhesion and flexibility when cast on an aluminum surface. The technology has been patented and the companies expect to commercialize it in the near future.

Green Earth Nano Science Inc.

Green Earth Nano Science Inc. (GENS) offers X500, a light-activated, water based, VOC-free hygienic coating containing nano-sized titanium dioxide particles that the company claims destroy viruses, bacteria, odors, harmful gases (VOCs), allergens, air/water pollutants, and protects treated surfaces against growth of algae, fungus, and mold. GENS subsidiary MCH Nano Solutions offers a range of products for interior and exterior applications.

Green Millennium, Inc./Jita Enterprise

Clear photocatalytic coatings from Green Millennium, Inc./Jita Enterprise are also based on titanium dioxide nanoparticles. At the nanoscale, both the surface area and the redox potential of the TiO2 particles increase dramatically. As a result, any ambient light source can be used effectively as the energy source for the photocatalytic reaction. The company offers several different formulations, which are typically spray applied. For certain products, the titanium is in an amorphous state and the coating must be heated to greater than 250°C to cause conversion to the active anatase crystalline state. Other products contain the crystalline form, but heating is recommended to improve the



Scheme courtesy of Jita Enterprise.

hardness of the coating. Still others are a mix of these two product types. Depending on the formulation, these photocatalytic coatings can be applied to organic substrates, metals, plastics, and over painted surfaces. For interior applications, the coating is designed to oxidize unwanted contaminants such as VOCs, fungi, bacteria, viruses, and other harmful substances found in air or water. When used on the exterior of a building, the coating reduces contamination by mold and other organisms, soot, hydrocarbons, and oil grime, helping to maintain the aesthetics of the facade.

Henkel

Bonderite NT-1 from Henkel is an ultra thin (nanometer scale), uniform, nanotechnology-based conversion coating for metals—free of phosphate and heavy metals. It is designed to replace conventional iron phosphate systems for industrial pretreatment applications. The nano-ceramic coating is suitable for surface pretreatment prior to conventional powder and wet paint coatings. The process streamlines paint pretreatment operations, reduces energy consumption, and minimizes the environmental impact of the process. Bonderite Tecfalis is based on a different nano-ceramic material and is targeted to replace conventional zinc phosphates in automotive OEM processes. Both Bonderite systems meet desired performance specifications, and the company is working to further improve the processes so that they are better than traditional methods.

Industrial Nanotech

Nansulate translucent waterborne coatings from Industrial Nanotech contain a nanocomposite material (Hydro-NM-Oxide) that possesses a nano-scale internal architecture and surface chemistry. This nanomaterial is suspended in a water-based acrylic resin system that adheres well to a variety of surfaces. Because the nanocomposite has a very low thermal conductivity, the coating acts as a barrier to heat transfer and is used for thermal insulation in a number of industrial and commercial applications. Nansulate has also been shown to provide good corrosion, mold and moisture resistance, and has the ability to encapsulate lead. Recently, the company received certification of its Nansulate products under European Union building codes. It also expects to launch a new 2-part epoxy system based on its nanotechnology that will incorporate both fire and chemical resistance.

Intumescent Associates Group

Intumescent Associates Group (IAG) produces high performance, VOC-free epoxy intumescent coatings to protect steel, wood, and other substrates from high intensity hydrocarbon pool and jet fires; and, depending on the substrate, Nanochar™ also provides corrosion protection to the substrate. Nanochar is its latest product designed for fire protection and, according to the company, is the first epoxy intumescent fire proofing material formulated to incorporate nanotechnology. By incorporating nanoparticles into the formulation, the key benefits are enhanced fire performance, improved material application characteristics, cohesive and adhesive properties, impact resistance, and overall durability. Among others applications, Nanochar is currently under evaluation by the U.S. military for a wide range of fire protection requirements, from live munitions to munition storage containers.

LaamScience, Inc.

LaamScience, Inc. (Light Activated Anti-Microbials) has licensed a novel coating technology from North Carolina State University. Developed by Dr. Stephen Michielsen, associate professor in the school's College of Textiles, the nano-coating inactivates most viruses (influenza, RSV, astrovirus, vaccinia) and kills bacteria (including Staph, MRSA) when exposed to visible light. A photoactive dye, used previously in medical applications, is covalently bonded to the outside of fabrics and when exposed to visible light, converts oxygen to a short-lived reactive species that inactivates 99.99% or more of viruses and bacteria on the surface. Current product development efforts are focused on textile applications, but the company expects the technology will be adaptable for numerous other substrates.
LaamScience will soon produce the coating in kilogram quantities and is currently manufacturing thousands of yards of coated fabrics in collaboration with a German company. A New England mask manufacturer is also working with the company to produce an antiviral/antibacterial mask for use by medical professionals and the public during pandemics. The coating has been subject to many testing procedures and LaamScience hopes to submit applications for approval to market to the FDA and NIOSH (National Institute of Occupational Safety and Health) in late summer 2008.

Nanophase Technologies

Nanophase Technologies manufactures nanopowder metal oxides such as aluminum oxide, zinc oxide, cerium oxide, and others. Its Discrete Particle Encapsulation process coats the surface of the nanoparticles with a thin polymeric shell that enables compatibility of the particles with a wide variety of fluids, resins, and polymers. The company also has developed a process for dispersing its nanoparticles in a wide variety of liquids, including water, polar, and nonpolar organic solvents. This integrated set of technologies makes it possible for Nanophase to nanoengineer materials to fit specific customer needs, which often include improving the performance of anti-fouling, antimicrobial, UV-attenuation, scratch-resistant, and charge dissipating coatings. Performance properties are achieved without influencing the final formulation in terms of clarity, rheology, surface texture, gloss, or physical/mechanical properties due to the small particle size of the NanoDur™ and NanoTek® materials. Functional coatings containing Nanophase products can be applied to metal, plastic, and glass.

Nanovations Pty Ltd.

Nanovations' Lignol® wood coatings are water-based, VOC-free, clear impregnating wood coatings containing nanoscale UV absorbers. Lignol Teak Guard Marine has been specifically developed for wood protection in the marine environment. The penetrating coating provides excellent water and stain repellency in addition to UV protection. Nanovations 3001, designed for use on masonry and concrete surfaces, provides superior water repellency, reduces efflorescence, and provides significantly improved abrasion resistance. In addition, the coating is applied at the manufacturing stage without any modification to existing production machinery. The company also offers hydrophobic scratch-resistant, easy to clean coatings for many substrates including glass, ceramic, metal, and plastic.

Nanovere Technologies

The Zyvere coating platform from Nanovere Technologies includes a two-part ambient cure clear coating system and a single-component bake clear coating system that serve as topcoats for automotive, aviation, marine, and industrial applications. Rather than choosing to simply add nanoparticles to its formulations, Nanovere has focused on developing novel nano-structured polymers as the backbone of its coatings. These nanostructured materials form three-dimensional molecular networks resulting in a high crosslink density. They can be applied by conventional high volume low pressure (HVLP) spray guns or rotary atomizers. Special characteristics of Zyvere coatings include dramatically enhanced scratch (6H pencil) and impact resistance, gloss retention, flexibility, and chemical, UV, and corrosion resistance. The products also exhibit self-cleaning characteristics including water repellency plus oil, dirt, and ice release properties.

NaturalNano, Inc.

The key component of nanocoatings from NaturalNano, Inc., is halloysite clay, a naturally occurring alumina silicate tubular clay material. Halloysite natural tubes (HNTTM) exhibit a hollow tubular structure that is about one micron in length (1/1000 of a mm) with an average outer diameter of approximately 100 nm and an average inner diameter of 20 nm. They impart increased strength, abrasion resistance, and durability to polymer composites and coatings while maintaining transparency. In addition, the tubes themselves can be filled with active agents such as antimicrobials, lubricants, or flame retardants, enabling the creation of new products with time-release and other advanced properties. HNT can be dispersed in both aqueous and solvent-based coating formulations and forms stable solutions at concentrations as high as 30%. NaturalNano has successfully dispersed HNT into acrylic, fluoropolymer, urethane aqueous dispersions, and solvent-based polymer solutions.

nCoat, Inc.

nCoat, Inc. manufacturers high performance nanoformulated and micronized coatings with improved bond strength, heat management, corrosion resistance, abrasion protection, friction reduction, and appearance

Photo courtesy of Behr Paints.

enhancement for the automotive, aerospace, defense, diesel engine, recreational vehicles, and energy services industries. R&D efforts focus on creating new nanoparticles, triggering nano-level chemical reactions to manipulate and change molecular structures, and utilizing proprietary chemistries to produce universal dispersion and eliminate clumping of nanoscale particulates. Products include thermal barrier coatings designed to enable the fuselage of spacecraft to endure exposure to 4,200°F for a period during orbital re-entry; anti-corrosion coatings used to reduce aluminum degradation in exhaust gas recirculation for diesel engines; formulated high density, low porosity composite materials providing abrasion resistance for aircraft wings subjected to rain and particulate matter at top airspeeds; thermal management surface treatments minimizing under-hood heat from headers and exhaust systems of NASCAR engines, and at the same time maximizing air density and increasing horsepower; and lubritic surface protection for internal engine parts to reduce friction, control heat, and increase engine efficiency. Subsidiary nTech, Inc. supports the activities of nCoat through management of intellectual property; engineering, prototyping, and testing operations; and technology licensing activities.

PPG Industries

CeramiClear® clearcoat from PPG Industries has been attracting growing interest since its introduction in 2002. This automotive coating contains nanoceramic particles that are designed to self-align during cure toward the top surface of an organic bulk film and form an almost glass-like layer that provides improved scratch and mar resistance during every day use. The company is continuing to improve the technology and make it more amenable for a wider array of applications. Research efforts at the company are focused on nano-based products for the aerospace and other industries. Nanostructured materials are used to provide corrosion protection equal to or greater than that attained with older chrome systems that have been eliminated for safety and environmental reasons. PPG's proprietary process for manufacturing its nanomaterials allows access to newer types of mixed metal oxides and other compounds that exhibit novel chemistries, making it possible to achieve protection without impacting visual appearance. Initial testing has been performed and the company is in the process of scaling up production to conduct large scale evaluations.

QuantumSphere, Inc.

Using its patented process to manufacture metal nanoparticles, QuantumSphere, Inc. (QSI) is developing unique dispersion and coating methods to integrate metal nanoparticles into electrodes, composites, and films for clean hydrogen generation from water, batteries, fuel cells, magnetic sensors, and antimicrobial coatings. Specifically, QSI has developed a nanoparticle-coated electrode, QSI-Nano® NiFe, for hydrogen generation by water electrolysis that provides a two to three fold improvement in gas output without an increase in energy consumption. The large surface area of the nanoparticles is responsible for the increased efficiency of the reaction. The nano-coating can provide a cost-competitive solution, enabling the use of hydrogen as a fuel in existing commercial, industrial, and transportation applications. In addition, water electrolysis is a zero emissions process.

Both the activity of the nanoparticle catalyst and the method by which the nanoparticles are dispersed are critical to coating performance. In QSI's nano-coating process, nickel and iron nanoparticles (less than 20 nm in diameter) are functionalized and then dispersed into solvents to form an ink. The ink is then applied to a standard commercial electrode surface, usually nickel or stainless steel metal, by spraying or screen printing. The nano-coated electrode is then heat treated to adhere the nanoparticles to the substrate. Electrodes can be cut to any shape or size, depending on a customer's requirements. Because the coating does not require any fundamental change to the system, it is a "drop-in" solution for existing commercial electrolyzers. Commercial products incorporating QuantumSphere's technology include a non-rechargeable battery with increased capacity that will be launched in the second half of 2008.

Silco International

Silco International manufactures and markets ultra pure silica nanoparticle dispersions produced in its modern state-of-the-art manufacturing facility in Portland, OR. These dispersions are incorporated into coatings to improve scratch resistance and durability without negatively affecting color, clarity, or gloss. Sizes (diameter) from 5 nm to 135 nm are available. Because the particles have never been agglomerated during processing, precise control of particle size distributions is possible. Also, the dispersions are free of large agglomerates, which range in size from 200 nm to microns, which can cause catastrophic coating failure. The particles are dispersed in water or selected organics, and are easily incorporated directly into the coating formulation. Because Silco International directly controls the entire manufacturing process, custom particle sizes and distributions can be tailored for unique coating formulations. CT