Nanomaterials applications in "green" functional coatings

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The global coating market is huge, worth over US$100 billion annually, with applications for physical and chemical protection, decoration and various other functions. In the last decade, the trend is definitely pointing toward the replacement of traditional VOC (volatile organic chemical)-based paints and polluting processes like electroplating with environmentally friendly materials and technologies. Nanomaterials play a significant role in the new generation of "green" functional coatings by providing specific functionalities to the base coating. For the replacement of electroplated metal coatings, a multilayer coating stack providing anticorrosion, mirror-like reflective and antiscratch functions was developed. Nanosized metal and ceramic particles are used to achieve these functions without the use of any polluting chemicals nor the release of any heavy metal contamination typical from electroplating processes. Furthermore, a multifunctional environmental paint was developed for wood surfaces. The key ingredient in this water-based paint is mesoporous silica nanoparticles, which offers high water resistance and a short drying time. This versatile material also offers high chemical tunability, which allows the incorporation of various additives to achieve multiple functions including antibacterial action and resistance to fire, household chemicals and UV (ultraviolet) exposure.

Introduction: The Global Coating Market

Coatings for metal and nonmetal processing comprise a large part of the global coatings market, which is forecasted to reach 8.7 billion gallons in volume and US$107 billion in value by 2017.[1]

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[1] http://www.prweb.com/releases/architectural_coatings/OEM_special_purpose/prweb9264512.htm. US billions (10^9) are indicated (here and throughout this paper).

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Major factors driving growth in the market include the recovery of global economies from the recent economic turmoil, rapid industrialization and increasing demand from end-use sectors, such as automotive and construction. Additionally, growth in the global market is spurred by rising competition, growth in unique formulations and the increasing stringency in regulations, which necessitate technological and product developments.

Global paints and coatings production is witnessing a major shift away from the developed regions in Europe and the USA to the developing economies such as Asia. Asia–Pacific represents the largest regional market for coatings worldwide. Major markets driving growth in the Asia–Pacific coatings market include China, India and Indonesia. Europe represents the second largest regional market for coatings worldwide, followed by the USA. Asia–Pacific also represents the fastest growing regional market worldwide. The Asia–Pacific paint and coatings market for 2010 has been estimated to be worth approximately US$48 billion with a market size (quantity of materials) of 15 million MT (metric tons) with a growth rate of 8 to 11%.[2–4] This was brought about mainly by the strong growth of China and India as well of key Association of Southeast Asian Nations (ASEAN) countries such as Indonesia and Vietnam.

For the end-use segments of paint and coatings, decorative coatings are the largest subsegment of the Asia–Pacific coatings industry. Productwise, architectural coatings or decorative coatings dominate the global coatings market, accounting for the single largest share in value terms. However, growth in the market would be spearheaded by special purpose coatings or protective coatings, which is projected to record a CAGR (compound annual growth rate; i.e., the geometric average of annual growth rates over several years) of 5.3% over the analysis period. The third segment of the coating market is OEM product coatings or functional coatings.[5]

Environmentally friendly ("green") materials and technologies will be the driver for the coatings industry in the next few years. The paint and coatings industry is heavily reliant on the end-use industries it serves. The term "green coatings" is not new within the industry, but in recent years they have been slow to proliferate because of low demand from industrial end-users. This is mainly due to the lack of awareness and incentives and the higher cost of using these types of coatings to consumers. Therefore, there are tremendous opportunities in the market for green coatings if the benefits to customers can be clearly defined and communicated, and the price is competitive. Some of the key industrial sectors targeted are construction, steel, marine, automotive and furniture. It is expected in the near term that industry players will create a competitive edge by introducing new innovative products in the market with environmentally friendly features that are cost effective. Many have already set in place strategies to recapture market share after a two-year lull. Green technologies will see high growth in this region especially in areas of energy conservation, and targeting replacement products with low VOC emissions and a significant shift from organic solvent-based to water-based paints.

Coatings usually combine protective, functional and decorative roles, which have very wide application areas, including transport, construction and infrastructure, packaging and

[2] http://www.frost.com/prod/servlet/press-release.pag?docid=219572747&gon11042=CHEMMI3
[3] http://www.pcimag.com/articles/asia-pacific-paint-and-coatings-market-expects-growth-in-2011-1
[4] http://www.coatingsworld.com/issues/2011-08/view_features/the-asia-pacific-paint-and-coatings-market/
[5] http://www.ft.lk/2012/02/17/asia-pacific-decorative-coatings-market-to-experience-dynamic-shifts/

general industrial use. Coatings can be used on automotive OEM, automotive refinish, motorcycles, trucks, buses and other vehicles, rail, aircraft and marine vessels. The application areas in construction and infrastructure are industrial wood coatings, agriculture, construction and earthmoving, and precoated metal sheet. Coatings in the field of packaging and general industry include metal packaging coatings, general industrial coatings and plastic coatings.

1. Protective Coatings

Protective coatings refer to those coatings that protect the underlying material against the environment, which includes anticorrosion, anti-gas permeation, tribological and thermal barrier coatings. Anticorrosion coatings can be divided into corrosion protection paints, self-repairing coatings (smart paint), and erosion-resistant coatings to protect turbines, pumps and other metallic machinery. Anti-gas permeation coatings use smectite clays dispersed in a polymer and can be applied to juice cartons using Aegis™ Nylon nanocomposite and to plastic bottles using Aegis™ polyamide nanocomposite. The tribological coating has functions of both corrosion and scratch resistance, which prevents wearing, abrasion, erosion and friction. As for the nanophase thermal barrier coating, it is used on gas turbine engine blades and hot section walls to confer significantly lower thermal conductivity. In protective coatings, waterborne technology has increased market share considerably to 15%, while powder coatings have a 4% market share. Organic solvent-borne accounts for 81% of the technology, of which 36% are medium solids and 45% are high solids.

2. Decorative Coatings

Decorative coatings are employed to provide colour, patterning and other visual features on substrates. All decorative coatings are also functional or protective. Decorative coatings are applied on-site to interior and exterior surfaces of residential, commercial, institutional and industrial buildings. This type of coating includes interior and exterior coatings, as well as both organic solvent-based and water-based coatings capable of providing a wide array of gloss levels, and also includes stains, varnishes, lacquers and primers that are applied on-site. Decorative coatings comprise the largest coatings segment in the world, accounting for approximately 51% of the volume and 44% of the value of all coatings in 2009. Revenues for 2009 were $38,121 million on sales of 13,892 million litres. Examples of decorative coatings include paints and inks, decorative colour-shifting coatings, consumer coatings etc. The most popular products are antiforgery coatings for currency bills or cool automotive paints. Thermal or photochromic additives can be added to fabricate even more fancy decorative coatings that can change colours, which are used for consumer products such as mobile phones, cosmetic packages and high-end watches.

3. Functional Coatings

Functional coatings are applied to a wide variety of products, providing specific functions such as imparting special optical effects, improving chemical, mechanical or electrical properties, or even radar absorbability. Examples of functional coatings include lubricants, corrosion inhibitors, wear and corrosion indicators, chemically resistant and UV-absorbing coatings.

Consumer functional coatings are used heavily in the cosmetics industry, in lipsticks, creams, hair products to dispense oils, lipids etc. in the nanoscale through nanomaterials such as liquid-carrying globules like nanovesicles and lipid nanoparticles carrying oil. Other cosmetic product functional coatings include razor blade lubricants and sunscreen products, in which nanomaterials like TiO_2, ZnO and Al_2O_3 can add UV protection. Functional coatings are also used on MEMS (micro-electrical and -mechanical systems), which requires compatible electrical and mechanical properties. One of the most prominent functional coatings is the radar-absorbing coating on advanced military jets.

Technologies and Applications in Functional Coatings

The areas in functional coatings that have the biggest opportunities for the application of environmentally friendly technologies are the electroplating processes and the VOC-based paints. Electroplating technology can produce high quality metallic coatings but is one of the most contaminating technologies for the environment, especially in the South China region. VOC-based paints have a large market and have excellent properties, except for the large emission of VOCs to the environment. Two different green technologies offering alternatives to these two applications were recently developed:

(a) Spray or Dip Coating of Mirror-Like Coating

There is considerable motivation, both environmental and economical, for industrial electroplating users to develop and switch to alternatives. The conventional surface treatment of metal is electroplating, which confers the excellent properties of corrosion resistance, hardness, durability and mirror-like gloss together. However, electroplate production releases a large quantity of toxic by-products and waste to the environment and is being heavily regulated by local governments.[6] The cost of waste water treatment and clean-up is becoming prohibitive for many electroplating factories. The whole electroplating industry is being gradually phased out of many industrial regions, including Shenzhen and other Southern China districts.

Currently there is no established and proven cost-effective technology to replace electroplating and its products, and ongoing efforts are focused on the development of lower cost alternatives with similar performance to that of electroplating. To replace an established technology like electroplating, a new technology either has to significantly outperform the established technology or it needs to cost significantly less without sacrificing performance. Since electroplated product performance is excellent but its cost is increasing due to the contamination issue, the direction taken by industries to replace electroplating is mainly pointed toward the cost angle.

Several new products are available in the market to provide a mirror-like coating without using electroplating, but either their costs or performance are not competitive with electroplated products. A Swiss research institute provides a mirror-like metallic coating that has high reflectivity (more than 95% in the infrared) and good thermal stability (up to 500 °C in air for 300 hours).[7] The coating appears to provide an excellent hermetic diffusion barrier and protection layer. However, expensive high vacuum PVD (plasma vapor deposition) equipment

[6] Emission standard of pollutants for electroplating, GB21900-2008 (2008).
[7] http://www.sirris.be/defaultPage.aspx?id=7854&LangType=2067

is needed and the product is not price-competitive. The Fantachrome coating system uses the low-cost and simple spraying process to apply a shiny chrome coating.[8] It is water-based and seems to be an environmentally safe product. However, no performance data about the coating has been provided, and it also requires special equipment manufactured and supplied by the company to apply, which may add substantially to the overall cost. Krylon provides a Glass®-mirror-like paint, which transforms clear glass into a highly reflective mirror-like surface.[9] The coating is low-cost and is sprayed on with a short drying time of just 1 hour. It is primarily a decorative layer, with no protection performance data on metal available. Finally, Specialist Paints provides a chrome/mirror effect coating product named Deception Chrome, which is priced very high at £59.99 for 250 mL.[10] The coating can achieve up to 98% of real chrome plating reflectivity, the most reflective non-electroplated coating available in the market now. However, besides its high price, it also requires a black basecoat and a topcoat of lacquer, which together need more than 36 hours drying time. This highly priced and complicated coating is likely limited to applications in niche areas.

A new mirror-like coating based on low-cost dipping and spraying methods was recently developed, which has both decorative and protective functions similar to electroplated metal coatings. This coating was first developed on steel and zinc products, but can eventually be applied on other metal and nonmetal surfaces. The formulations and manufacturing processes of the coating are environmentally friendly and low-cost. The coatings are water-based with low organic solvent content. All manufacturing steps are solution-based with no high vacuum equipment involved. Figure 1 shows examples of the mirror-like coating on steel wheelchair accessories.

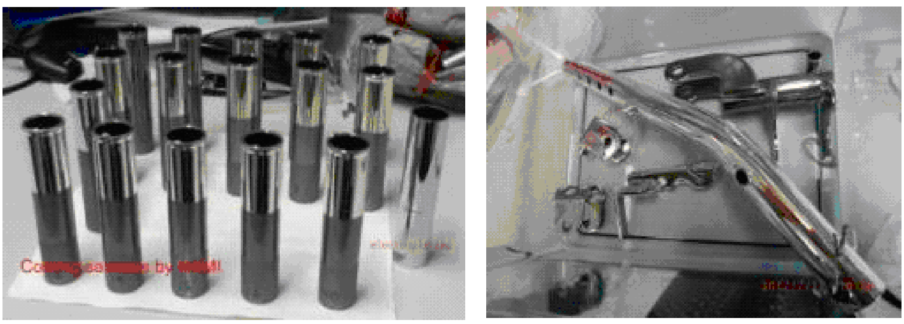

Figure 1. Mirror-like coating on steel wheelchair accessories (see text for further explanation).

Nanomaterials and nanotechnologies play a key role in the development of this mirror-like coating to enhance both its decorative and protective properties. The basic mirror-like coating stack consists of three main layers—the bottom epoxy-based anticorrosive layer, the middle silver-based reflective layer, and the top siloxane-based antiscratch layer. The formulation of the bottom anticorrosive layer is optimized to create a nano/micro pore structure to enhance adhesion between the bottom substrate and the top reflective layer. Nanosized functional materials can be added to further improve the hardness of the coating for substrate protection,

[8] http://www.newfantachrome.com/index.php?id=100
[9] http://www.krylon.com/products/looking_glass_mirror_like_paint/
[10] http://www.specialistpaints.com/products/chrome-paint

possibly at a level that exceeds the electroplated coating performance. In addition, nanosized highly conductive metals like Ag or Cu can be added to significantly increase the thermal or electrical conductivity for applications as a conductive layer. Surface modification of these nanosized metals is necessary to prevent oxidation of the highly reactive Ag or Cu. For the top antiscratch layer, nanosized hard metal oxides such as SiO_2, Al_2O_3, ZnO or TiO_2 can be added to the transparent siloxane base to tune the colour of the coating for decorative purposes and at the same time improve the hardness.

These coating formulations and methods are very versatile and can be applied beyond mirror-like coatings on steel and zinc alloys. Additives and interface structures can be optimized to achieve good adhesion to other metallic products apart from steel and zinc; plastics, glass, ceramics and even wood. Additives with photo- or thermo-chromic properties can be introduced into the coating solution to produce an antiscratch top layer with the additional functions. This kind of coating product has many potential applications in smart windows, fashionable electronics, sunglasses etc.

The development of this mirror-like coating is near completion, and in the process of scaleup to pilot manufacturing. Additional new applications with these coating materials and manufacturing technology are being explored at present.

(b) Multifunctional Environmental Paints for Wooden Furniture

Wood is one of the most important and preferred materials for the furniture and building industries because it is renewable, environmentally friendly and has a high strength-to-density ratio. However, it can be damaged by the impacts of oxygen, light and water. It is also susceptible to attack by microorganisms and insects, and can easily catch fire. Protection with an appropriate paint coat is essential. Despite the reliable performance of solvent-based (typically polyurethane (PU) and cellulose-based) paints, which have dominated the market for wooden furniture finishing, the hazardous ingredients and the environmentally unfriendly materials involved (e.g., VOCs and heavy metals like Cu, Cr, Pb and As) pose serious health and environmental problems. Motivated by the ever-stringent regulations, a high-performance water-based environmental paint is strongly and urgently required. Although having the advantage of a much lower content of volatile organic chemicals and heavy metals, the aqueous-based environmental paints available in the market typically suffer from long drying times, and limited functionality and chemical tunability.[11–15]

In order to solve these issues, a new generation of "environmental paints" based on organosilica nanosols has been developed with attractive properties incorporated through chemical modifications of the nanosol and the addition of nanomaterials and functional additives. Organosilica is a special class of chemical that possesses a hydrophilic and

[11] Kansai Paint Co., Ltd, "Water-based paint composition", US Patent Application Number US 2009/0099298 (2009).

[12] Kansai Paint Co., Ltd, "Water-based paint composition", US Patent 6,787,190 (2004).

[13] Kansai Paint Co., Ltd, "Aqueous color paint compositions and coating method using same", US Patent 5,322,865 (1994).

[14] Nippon Paint Co., Ltd, "Method of coating using pigment-containing water-based paint composition", US Patent 5,972,425 (1999).

[15] Nippon Paint Co., Ltd, "Heat-curable, water-dispersible resin composition, production thereof, water-based paint composition, method of coating and coated article", US Patent 5,747,558 (1998).

hydrolysable silane head with hydrophobic arms of high chemical tunability, as shown in Figure 2. Upon water hydrolysis, organosilica forms a nanosol, followed by the crosslinking of silane heads with one another, resulting in an extensively networked film with the physical and chemical properties of their original arms. Also, unique functions can be incorporated into the network by the use of appropriate additives.

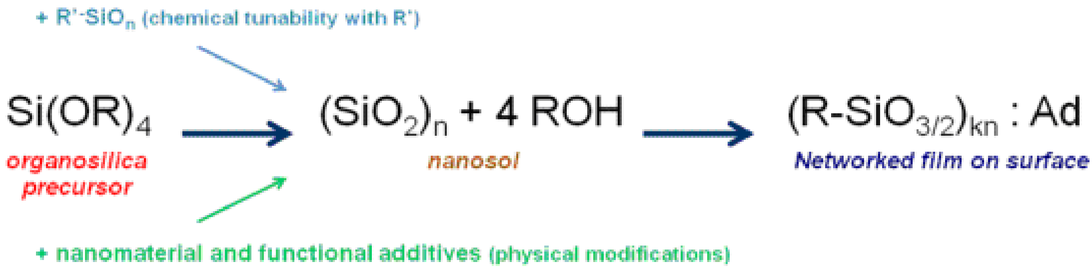

Figure 2. Schematic drawing of organosilica nanosol preparation by hydrolysis and subsequent film formation.

A nanosol is a stable transparent nanoparticulate inorganic sol to which unique functions can be added by either adjusting the chemical functionality R or by coforming the film with nanomaterial and functional additives. As the organosilica precursor is generally water-based and requires water for hydrolysis, no organic solvent is needed for the entire process, thus eliminating most of the VOCs in the final paint products. Organosilica displays the versatility of traditional organic and polymeric materials, as well as the strength and durability of typical inorganic coatings, and can functionally interact with both aqueous and organic chemicals. Therefore, in preparing high quality multifunctional environmental paint, which may involve organic as well as inorganic functional ingredients, it is much easier and more cost-effective to process organosilica compared to PU and cellulose-based paints, which require additional processes and/or additives for treatment.

While environmental paint based on a general organosilica nanosol can already achieve high performance for wood protection, addition of mesoporous silica nanoparticles (MSNs) was found to further enhance the properties of the organosilica nanosol paint. Figure 3 shows a scanning electron micrograph (SEM) of MSNs specifically prepared for the new generation of "environmental paint". The nominal diameter of the MSNs is < 100 nm, revealed by the detailed structure of the nanomaterial shown in the transmission electron micrograph (TEM) in Figure 4. Pores and cavities with diameter of 2–3 nm can be clearly found throughout the MSN structure.

The role of the nanomaterial is threefold. Firstly, the addition of MSNs can shorten the drying time of paint. Generally, organosilica nanosols require a relatively long hydrolysis process for crosslinking, which eventually leads to rigid dry paint coat. Since the MSN is already a hydrolysed silica particle, drying of a paint coat with MSNs requires only connecting up the MSNs into an extensive network, and the drying time can then be shortened. Secondly, as MSNs are porous, functional additives can be easily incorporated into them, resulting in functionalized MSNs (*f*-MSNs). Use of these *f*-MSNs can add additional unique functions to the paint coat depending on the nature of the functional additives incorporated. Furthermore, the network generated through linkage of MSNs into a paint coat allows subsequent incorporation of additives and functional chemicals for further performance enhancement.

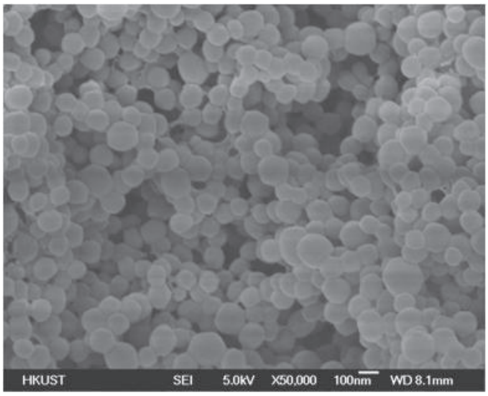

Figure 3. Scanning electron micrograph of mesoporous silica nanoparticles.

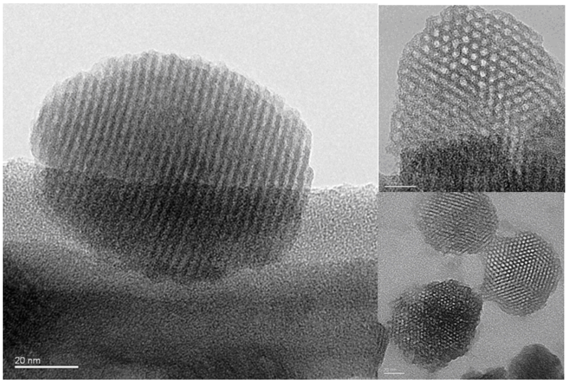

Figure 4. Transmission electron micrograph of mesoporous silica nanoparticles showing their detailed structure.

The environmental paint developed shows high hydrophobicity and also incorporates functional additives to achieve multiple functionalities including antibacterial action, flame retardance, resistance to household chemicals and resistance to UV exposure.[16] Figure 5 compares the results of a flame test on bare wood pieces with no coating, with solvent-based paint coats, with commercial environmental paint coats, and with the "environmental paint" based on organosilica nanosol with MSNs from this work. The paint developed with MSNs clearly demonstrates the highest flame retardant capability.

In summary, a novel environmental paint formulation was developed based on an organosilica nanosol and MSN. This new class of environmental paint is VOC-free and multifunctional. It is expected to outperform current products in the environmental paint industry, and offers the following technological superiorities:

- Intrinsic hydrophobicity leading to water resistance;
- High tunability through chemical engineering and incorporation of functional and nano additives;

[16] http://www.nami.org.hk/clb_tech_for_comm_e.html#EPWF

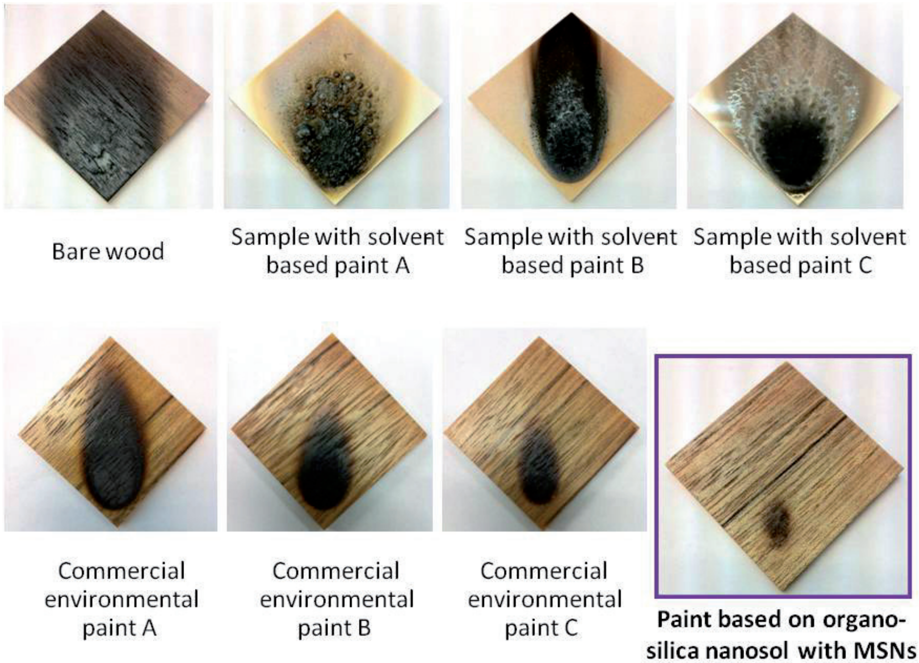

Figure 5. Flame test results on wood pieces with different paints (please refer to text for their description), showing superior fire resistance of "environmental paint" based on an organosilica nanosol with MSNs.

- High transparency—unlike many polyurethane and polyacrylate coatings, which impose a yellow colour onto their substrates, organosilica coatings are naturally transparent;
- Fire resistance and non-combustibility;
- Short drying time through nanoscale optimization of molecular structure; and
- Low cost and simple preparation—the organosilica is amphiphilic and can interact with both aqueous and organic chemicals; processing of organosilica into multifunctional environmental paint involves simple chemical procedures and requires fewer additives compared to PU or cellulose-based systems. Also, it offers high flexibility for further modification and improvement of the paint recipe.

Conclusions

Various nanomaterials can be added to different base coating solutions to form new generation multifunctional coatings that are environmentally friendly. Nanosized materials generally have high chemical activity and can be manipulated easily to be incorporated into diverse media to achieve various desirable functions. Opportunities are abundant for the use of these materials in the huge global coatings market.