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# Synthesis and Characterization of Nano-ZnO and Nano-$SiO_2$ Particles Modified Anticorrosive Paint

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*Abstract*— **In this work, proper incorporation and dispersion of nano-particles in paint medium has been described to formulate anticorrosive, self-healing and antifouling coatings. In first approach a hydrophobic surface was formed for both the cases in which a highly reactive fluoro-silane was used. The second property in each case was achieved by the incorporation of appropriate nano-particles. For the purpose of getting self-cleaning coating surface, easy sliding property of water droplet was achieved by the addition of nano-ZnO and nano-silica, while in the case of anti-fouling coating it was achieved by addition of nano-silica only, which provided a nano-roughened-surface was very much smooth and anticorrosive to keep away from any type of sticking the dirt, dust, foreign particles and water etc.**

*Index Terms*—**Anticorrosive coating, epoxy resin, nano-$SiO_2$, nano-ZnO, self cleaning coating surface.**

## I. Introduction

Nanotechnology can be defined as the science in which the effects are explained that arise from the quantum structures of fine particles (i.e. nanoparticles) are generally considered as at least in one dimension of size less than 100 nm. The interesting properties of nanoparticles are acknowledged due to the high surface area to volume ratio. The extremely small size of nanoparticles offers high surface to volume ratio and to provide the desired functionality when present in a very small concentration, compared to the bulk counterpart (Figure 1).

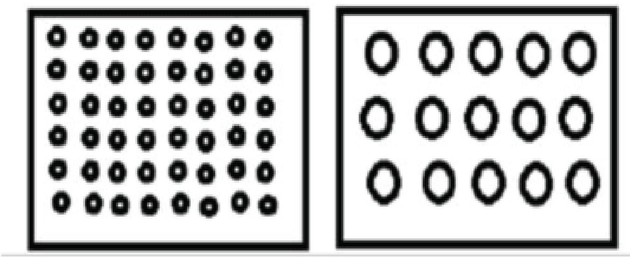


**Figure 1:** Schematic representation for comparison of the effect of small concentration of approx 0.01% nanoparticles distributed in a matrix (Fig. 1-a) against micron particles (Fig. 1-b), i.e. large number of approx ~ 10% micron sized particles distributed in the same matrix. The composite material (a) exhibits better properties than (b).

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It has been confirmed that materials with high surface areas have improved physical, chemical, mechanical, optical and magnetic properties. Because of these effects, nano-additives in paint coatings are showing superior performance.

There are several examples of addition of nanoparticles such as nano-ZnO, nano-alumina, nano-silica etc, which have helped in enhancing properties such as corrosion resistance, mechanical properties and ultraviolet radiation (UV) resistance [1,2]. Many techniques such as the sol-gel method of synthesizing coatings results in nano-structured coatings which have much superior properties than the conventional organic coatings [3-5]. Functional coatings are defined as those, which perform efficiently a specific property of the substrate, in addition to its conventional properties.

Classical examples of functional coatings are self-cleaning, anti-graffiti, antifouling, hydrophobic, self-healing etc. Silanes based sol–gel coatings are the subject of extensive research these days [5,6]. Such coatings have superior properties than conventional organic coatings and are considered in the category of "green future coatings" as they do not use any toxic solvent, heat or any toxic raw material [6,7]. The sol-gel coating technology is very versatile, can be applied on many metals, and is compatible with several paint systems. They have the advantage of being environmentally friendly with ease of application on the metal surface. They can be tailored easily with the incorporation of nanoparticles to achieve the desirable properties for their applications in different streams [6-8].

Various paint industries are considering the use of nano-materials, such as nano-silver, photo-catalytic active nano-titanium dioxide or nano-silicon dioxide to improve overall properties of paints, such as water repellency, scratch resistance and antimicrobial properties. Polyurethane coatings containing alumina and silica nanoparticles can be used to improve the scratch resistance of clear coat polyurethane coatings [7,8]. Incorporation of silver nanoparticles in paints act as a warehouse of silver ions to impart antimicrobial properties. Particles-size and surface-coatings adjust the release of the ions. These silver ions penetrate into a bacterial cell, interact with thiol groups of vital enzymes, and deactivate them, which leads to dysfunction and death of cells [8-10]. The lacquer and paint industries also use photo-catalytically active nano-titanium dioxide as biocides [11-13]. Nano-silicon dioxide is widely used in paints to improve scratch resistance, water repellency, and helps the paint in protecting against corrosion and provides the high glossy product [13, 14]. Nano-additives are also smart materials for corrosion protection because of their high surface areas that allow them to function as carriers for molecular corrosion inhibitors [15-19].

## II. Experimental

To make the self-cleaning coating surface by easy sliding of water droplet was achieved by the appropriate addition and dispersion of nano-ZnO and nano-silica in paint formulation. In order to prove the anti-fouling effect, the panels were sandblasted to SSPC SP10 (SA 2½) standard. These were immediately coated with primer supplied by Berger Paints Ltd. The panels were then coated with one coat of epoxy based anticorrosive coating. After allowing recommended coating time-intervals as per product data sheets, one coat of antifouling coating (prepared in the Lab.) was applied as a top coat. All coatings were applied on the panels using a brush. No tie coat was used between anticorrosive and top coat (Figure 9). The total DFT of the paint system was kept and measured and found to be in the range 450 ± 10 μ. These panels were then subjected to put in sea-water-immersion testing as per ASTM-D-3623 at Dockyard, Kolkata premises. A total of five panels were prepared per batch (Table 1).

The panels were taken out of the water after 30 and 60 days of immersion and visually inspected for the amount of fouling. Photographs of panels were taken immediately after taking out of the water. This is to keep a record of the amount of fouling accumulated on the panel so that a comparative analysis can be undertaken. The extent of fouling per panel is a function of the area of coverage as well as the type of fouling.

**Table 1**: Paint-coatings scheme on each panel were performed as per mentioned below:

| Panels | Name | Paint coatings scheme | |
|---|---|---|---|
| 1 | No top coat | Primer | 50 micron |
| | | Anticorrosive paint | 150 micron |
| | | Top coat | - - |
| 2 | Sample control | Primer | 50 micron |
| | | Anticorrosive paint | 150 micron |
| | | Top coat | Neat Epoxy |
| 3 | Sample A | Primer | 50 micron |
| | | Anticorrosive paint | 150 micron |
| | | Top coat | 150 micron Antifouling paint |

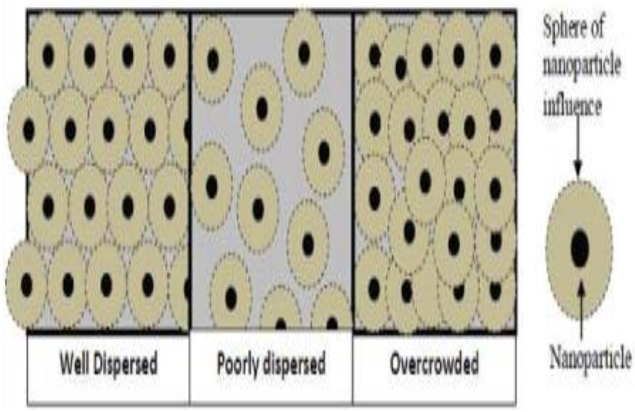
There were several examples in which two have been described where addition of nano-particles has resulted in producing functional coatings:

I. Self-cleaning paint applications.
II. Antifouling paint applications.

## III. Results and Discussion

The shape, size, structure and chemical properties of the nanoparticles (i.e., solubility parameters, additional reactive groups) produce different results. The surface density plays an important role for dispersion in organic materials. The dispersion and solubility of nanoparticles can be smartly adjusted by the preference of reactive functional groups. The presence of additional reactive groups allows the nanoparticles to be crosslinked to provide improved stability and durability to the cured coating [1-3].

The mechanism to explain the functioning of nano-additives or nano-particles based on the increase in the surface area is known as the Continuum Theory. It has been observed that nanoparticles in coatings can act effectively and provide coatings with the improved consistent property even when the particles are not attached to each other [4-6]. On the study of the several works carried out on nano-particles, it has been observed that the optimum effect of addition of suitable nano-particles has been observed at a particular concentration of nanoparticles with a uniform distribution [7,8]. As per the continuum theory of distribution of nanoparticles, effective dispersion and distribution of nanoparticles are the key factor for the performance of nano-particles in any medium or matrix. Agglomeration of nano-particles is undesirable as it makes nanoparticles lose their high surface area and thus the desired functional properties [9-11].




(a) (b) (c)

Figure 2: Schematic figures; a) a well-dispersed, b) poorly dispersed and c) overcrowded nano-particles in a paint matrix.

This is best illustrated in Figure 2; 2-a is a well-dispersed nano-particle and maintains its influence throughout the coating whereas Figure 2-b depicts less concentration and poorly dispersed nanoparticles with their 'sphere of influence' not carried over to the immediate next particle.

Figure 2-c, however, shows excess particles, which lose their influence due to overcrowding and overlapping with each other. Thus, optimum concentration and uniform distribution is one of the requirements to get the maximum positive effect of nano-particles addition in paint coatings.

For various applications such as self-cleaning of solar panels, glass windows, stain resistant textiles, corrosion prevention and anti-fouling surfaces, creating a hydrophobic surface is the first step [1,12]. In order to create a hydrophobic surface, two requirements must be convening. First, the surface should have low surface energy (hydrophobic). Second, the surface should have a roughness in nano-range. Such a surface can be achieved by a combination of low sliding angle and high contact angle; e.g., the water contact angle on a lotus leaf is as high as 160° with a rolling angle of about 2°, which is considered as a high performance superhydrophobic self-cleaning surface. The high contact angle can be attained by lowering the surface energy. The commonly used reactive molecules for low surface energy modification are mainly long alkyl chain thiol, alkyl or fluorinated organic silanes, per-fluorinated alkyl agents, long alkyl chain fatty acids, poly-dimethyl-siloxanes based polymers or other polymers, or their combinations [10-13] and low sliding angle can be achieved by creating a surface where the contact of the bubble with the surface can be minimized, which can be achieved by several methods [11,14].

The most appropriate method is by modifying the surface by incorporation of nano-particles and by creating micro or nano-structured features, which can reduce the contact area between the surface and the water droplet. The water droplets hence do not wet the surface and easily slide to remove dirt [2,3,15]. Moreover, surface roughness can be enhanced by introducing nanoparticles such as nano-$ZrO_2$, nano-ZnO, nano-$TiO_2$, and nano- $SiO_2$. The superhydrophobic surface created by sol−gel methods yields needle-like, surface roughness because of aggregation of nano-particle clusters, this minimizes contact area, enhancing non-wetting behavior. Unfortunately, the superhydrophobic nature of these kinds of surfaces is vulnerable to mechanical damage deteriorating surface roughness. Nakajima et al. [16-19,] established crater like roughness as a more robust alternative. Phase separation and subsequent thermal decomposition of an organic polymer dispersion from within silica matrix yielded thin films with voids akin to craters [18,19].

Further, post-functionalization with fluoro silanes, these surfaces yielded contact angles above 150° and pencil hardness above 4H. But this kind of approaches has been relatively under-explored in literature till now, with only a few examples utilizing crater roughness [20,21].

Incorporation of nano-ZnO (Figure 3 shows the TEM image of the nano-ZnO) in FE modified sol-gel resulted in surface roughness of 105 nm and outcome was a marginal increase in hydrophobicity due to hydrophilic nature of nano-ZnO particles. The contact angle achieved was 120° with sliding angle of 65° (Figures 4 & 5).

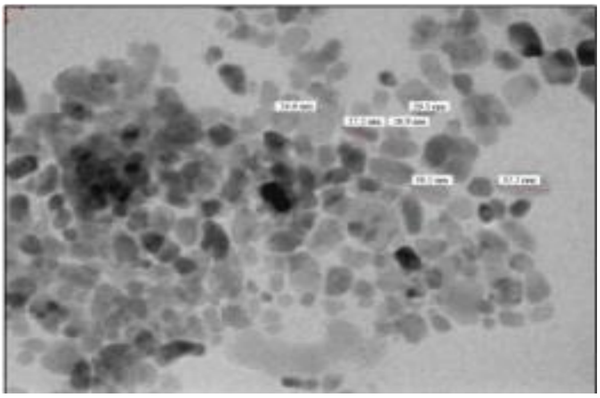


**Figure 3**: TEM image of nano-ZnO particle.

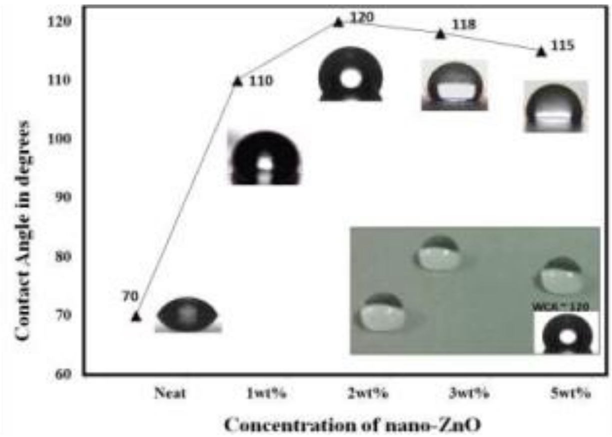



**Figure 4**: Variation of contact angle with concentration of nano-ZnO.

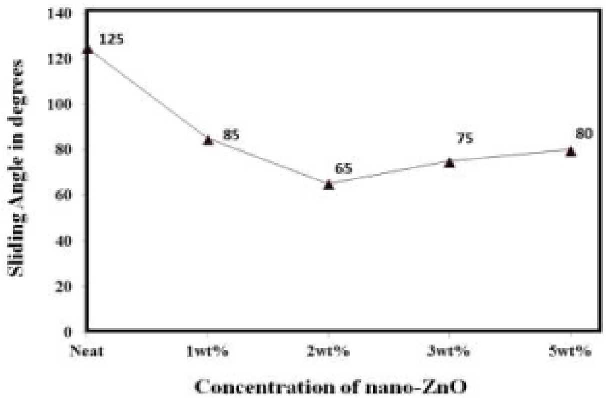



**Figure 5**: Variation of sliding angle with concentration of nano-ZnO.

Again further modification was achieved by using various functionally modified nano-silica particles out of which hexamethyl-disilazane (HMDZ) nano-silica particles (Figure 6 shows the TEM of the HMDZ modified nano silica particles) resulted in maximum surface roughness of 95 nm with a contact angle of 125° and sliding angle of 25° (Figures 7&8). HMDZ-FE sol-gel coatings when applied on non-metallic substrates viz. cotton, wood, paper, concrete and cardboard, resulted in super-hydrophobicity with contact angle >135° and sliding angle <5°[21,22].

Antifouling coating applications: subsequent to achieving required results and success in self-cleaning superhydrophobic coatings, the same was applied on conventional epoxy based coatings. Environment-friendly antifouling coatings were developed, to prevent the settling of marine organisms on artificial immersed structures such as the hull of a ship.

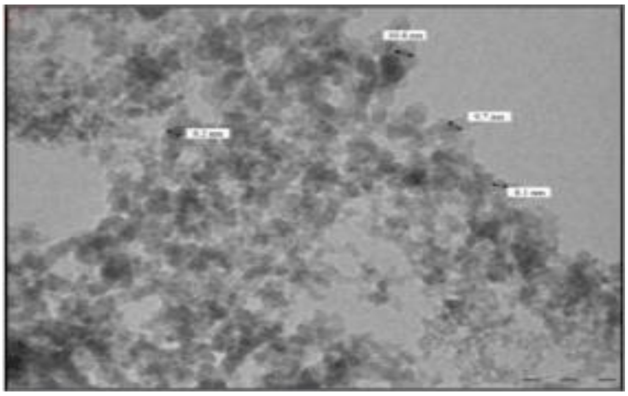


**Figure 6:** TEM image of HMDZ nano-silica particles.

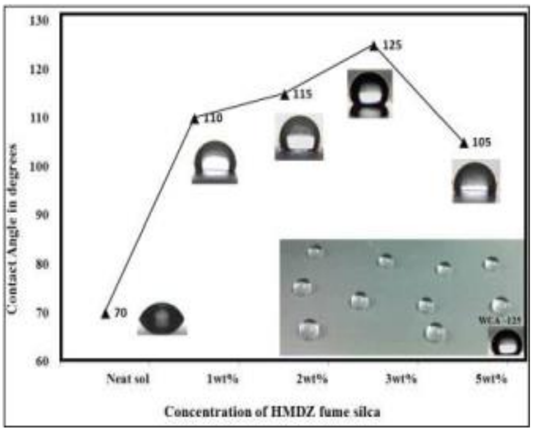



**Figure 7:** Variation of contact angle with concentration of HMDZ nano-silica particles.

The use of traditional antifouling coatings like tributyltin (TBT) has been banned since 2008 due to environmental concerns. Hence, it was desired that the coating primarily was environment-friendly while possessing properties such as hydrophobicity, ultra smoothness (roughness only in angstrom level) and mechanical strength to sustain physical damage due to day-to-day activities [18-20].

Foul release property was achieved by converting a hydrophilic epoxy surface into a hydrophobic one by modifying the resin. This was done by incorporation of two types of surface energy showed excellent hydrophobicity with contact angle ranging from 98.3° to 121° compared to 74.85° for neat epoxy. Elemental and chemical analysis revealed that the silicone and fluoro chains have migrated to the surface due to their low surface energy and synergistically contributed in releasing the fouling agents. Even though both Nano additives reduce the surface energy of the coatings, their contribution to elastic modulus was different. Silicone-based polymers reduce the elastic modulus of the coating by plasticizing it [20,21].

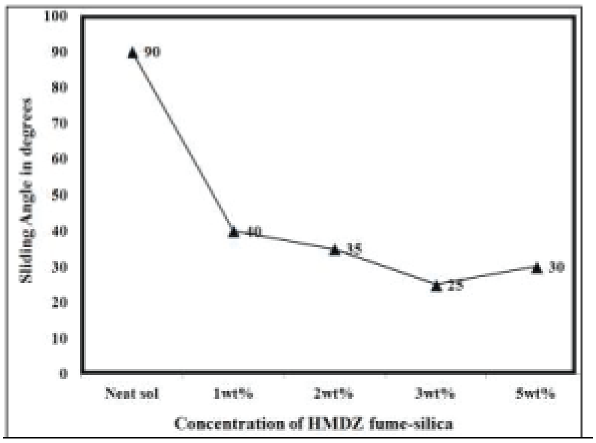



**Figure 8:** Variation of sliding angle with concentration of HMDZ nano-silica particles.

This results in a very soft coating, which was prone to physical damage, which is an undesirable feature, especially in the case of icebreakers, landing crafts, tugs, etc. where the hull is subjected to physical abuse.

On the other hand, fluoro polymers stiffen the coating due to an immobile and hard back bone. This feature is also related to bio-adhesive-coating interface failure mechanism in both cases. Therefore, a foul release coating with both types of nano additives will not only have low surface energy but also have better mechanical properties than 'silicone-only' foul release coating, due to the synergistic effect of both fluoro and silicone chains. Foul release property was further enhanced by creating an ultra smooth surface so that, it inhibits the organism to settle by denying it to anchor. This high level of ultra smoothness was achieved with the help of both the nano-additives, which are excellent leveling agents [19,21].

The natural shallow water immersion tests was also carried out and showed considerable improvement in foul release behavior of the modified coating with respect to the neat epoxy. The panels which were immersed for 30 days (Figure 10) showed organisms like bryozoans and hydroids along with small barnacle growth. After 30 days immersion, sample-(a) emerged as the least fouled coating [20,21].

Both control panels had excessive fouling as compared to other panels. The panels, which were immersed for 60 days, showed further growth of fouling. There was the presence of barnacles as well.

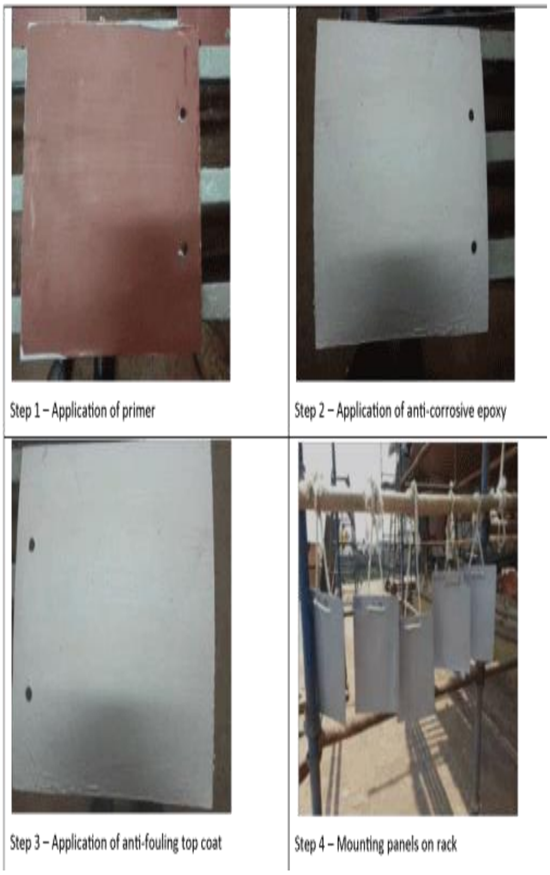



**Figure 9:** Steps in panel preparation


**Figure 10:** Image of panels after 30 days of immersion test.

After 60 days immersion, panel-(a) again emerged as the least fouled coating as shown in Figure 11. The foul release effect is achieved by two parts. One of them was by increasing hydrophobicity and other by achieving an ultra smooth surface. In other words, the absence of roughness up to nano level is required.

It was observed that roughness of sample-(a) was much lesser as compared to control sample. Thus, sample-a can be classified as the ultra-smooth surface [17-19].


**Figure 11:** Images of panels after 60 days of immersion test

An ultra-smooth surface inhibits the organism to settle. In other words, even if fouling takes place, if the adhesion strength between fouling and surface is minimized, the fouling can be easily removed with small stresses. The stress required to remove the fouling is so small that, the fouling peels off even when the ship is underway in its operational speed [18-20]. The surface morphology, in this case, is ultra-smooth and complete absence of roughness up to nano level denies the bio-adhesive to anchor on to the surface and prevents mechanical interlocking of bio-adhesive and substrate. This level of ultra smoothness is achieved with the help of silicone and fluoro-polymer additives, which were excellent leveling agents [20-22].

## IV. Conclusion

Addition of nano-materials of lower size with large surface area is one of the important factors to originate this improvement. Optimum concentration and uniform distribution of reinforcing materials are other essential factors. There was a great example of self-cleaning coating demonstrated how the presence of nano-particle helps in creating surface roughness and thereby helping to reduce the contact of a water drop with the surface to make it slide smoothly at a very small angle. The highest contact angle of approx 125° was obtained with HMDZ modification, which resulted in improving water repellent properties, corrosion resistance and other mechanical properties. Such behavior was related to both the rough morphology and the intrinsic low surface energy of the HMDZ-silica particles that stem from the chemical nature of the tri-methylated groups grafted onto the particle surface. These tri-methyl groups give rise to the asymmetric molecular forces responsible for water repellent properties. In the same way, the anti-fouling effect was achieved by the addition of nano-silica particles, which are excellent leveling agents that help in making the surface so smooth that, made barnacles and sea-weeds difficult to stick on the ship hull; this was splendidly proved by the exposure of panels in seawater environment for 60 days.

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## REFERENCES

[1] S.S. Pathak, A.S. Khanna (2008) Synthesis and performance evaluation of environmentally compliant epoxy-silane coatings for aluminum alloy. Progress in Organic Coatings 62: 409-416.

[2] S.K. Dhoke, Bhandari R, A.S. Khanna, (2009) Effect of nano-ZnO addition on the silicone-modified alkyd-based waterborne coatings on its mechanical and heat-resistance properties. Progress in Organic Coatings 64: 39-46.

[3] S.S. Pathak, Khanna A.S. (2009) Investigation of anti-corrosion behavior of waterborne organo-silane–polyester coatings for AA6011 aluminum alloy. Progress in Organic Coatings 65: 288-294.

[4] S.S. Pathak, Khanna A.S., Sinha T.J.M. (2007) HMMM cured corrosion resistance waterborne coating for aluminum alloy. Progress in Organic Coatings 60: 211-218.

[5] H.F. Raymond, (2009) Nanocomposite and Nanostructured Coatings: Recent Advancements, in Nanotechnology Applications in Coatings. American Chemical Society pp.2-21.

[6] Van Ooij W.J. et al. (2005) Corrosion Protection Properties of Organo-functional-Silanes—An Overview. Tsinghua Science & Technology 10: 639-664.

[7] W.J. Van Ooij, et al. (2005) Corrosion Protection Properties of Organo-functional-Silanes—An Overview. Tsinghua Science & Technology 10: 639-664.

[8] Matthew F.C., et al. (2009) Effects of Alumina and Silica Nanoparticles on Polyurethane Clear Coating Properties, in Nanotechnology Applications in Coatings.American Chemical Society pp. 210-231.

[9] Morones J.R., Elechiguerra J.L., Camacho A, Holt K, Kouri J.B., et al. (2005) The bactericidal effect of silver nanoparticles. Nanotechnology 16: 2346-2353.

[10] Kaiser J.P., DienerL, Wick P (2013) Nanoparticles in paints: A new strategy to protect façades and surfaces? Journal of Physics: Conference Series 429: 012036.

[11] Lai J.C.K., et al. (2008) Exposure to titanium dioxide and other metallic oxide nanoparticles induces cyto-toxicity on human neural cells and fibroblasts. International Journal of Nano-medicine 3: 533-545.

[12] Chad E.I., et al. (2009) Reactive Nanoparticles in Coatings, in Nanotechnology Applications in Coatings.American Chemical Society. pp. 188-209.

[13] Saber A.T., Jensen K.A., Jacobsen N.R., Birkedal R, Mikkelsen L, et al. (2012) Inflammatory and genotoxic effects of nanoparticles designed for inclusion in paints and lacquers. Nanotoxicology 6: 453-471.

[14] Ronald L.C., Andrew W.M. (2009) Nanoparticle Surface Modification for Advanced Corrosion Inhibiting Coatings, in Nanotechnology Applications in Coatings.American Chemical Society. pp. 64-88.

[15] Cao Z, et al. (2009) Synthesis and UV shielding properties of zinc oxide ultrafine particles modified with silica and trimethylsiloxane. Colloids and Surfaces A: Physicochemical and Engineering Aspects 340: 161-167.

[16] S. Dhoke, Sinha T.J., Khanna A.S. (2009) Effect of nano-Al2O3 particles on the corrosion behavior of alkyd based waterborne coatings. Journal of Coatings Technology and Research 6: 353-368.

[17] Dhoke S.K. Khanna A.S. (2009)Electrochemical behavior of nano-iron oxide modified alkyd based waterborne coatings. Materials Chemistry and Physics 117: 550-556.

[18] Nakajima A, et al. (2000) Preparation of hard super-hydrophobic films with visible light transmission. Thin Solid Films 376: 140-143.

[19] Dyett B.P., Wu A.H., Lamb R.N. (2014) Toward Superhydrophobic and Durable Coatings: Effect of Needle vs Crater Surface Architecture. ACS Applied Materials & Interfaces 6: 9503-9507.

[20] Wankhede R.G., et al.(2013) Development of Hydrophobic Non-Fluorine Sol-Gel Coatings on Aluminium Using Long Chain Alkyl Silane Precursor.

[21] Wankhede R.G., et al. (2013) Development of water-repellent organic–inorganic hybrid sol–gel coatings on aluminum using short chain perfluoro polymer emulsion. Applied Surface Science 283: 1051-1059.

[22] Wankhede R.G. (2014) Development of hydrophobic inorganic-organic hybrid sol-gel coatings on aluminium using nano-particles, in Metallurgical and Materials Science, I.I.T. Bombay & Monash Research Academy.

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