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Enhancing Functionalities of Paints with Nanoparticles: A Review

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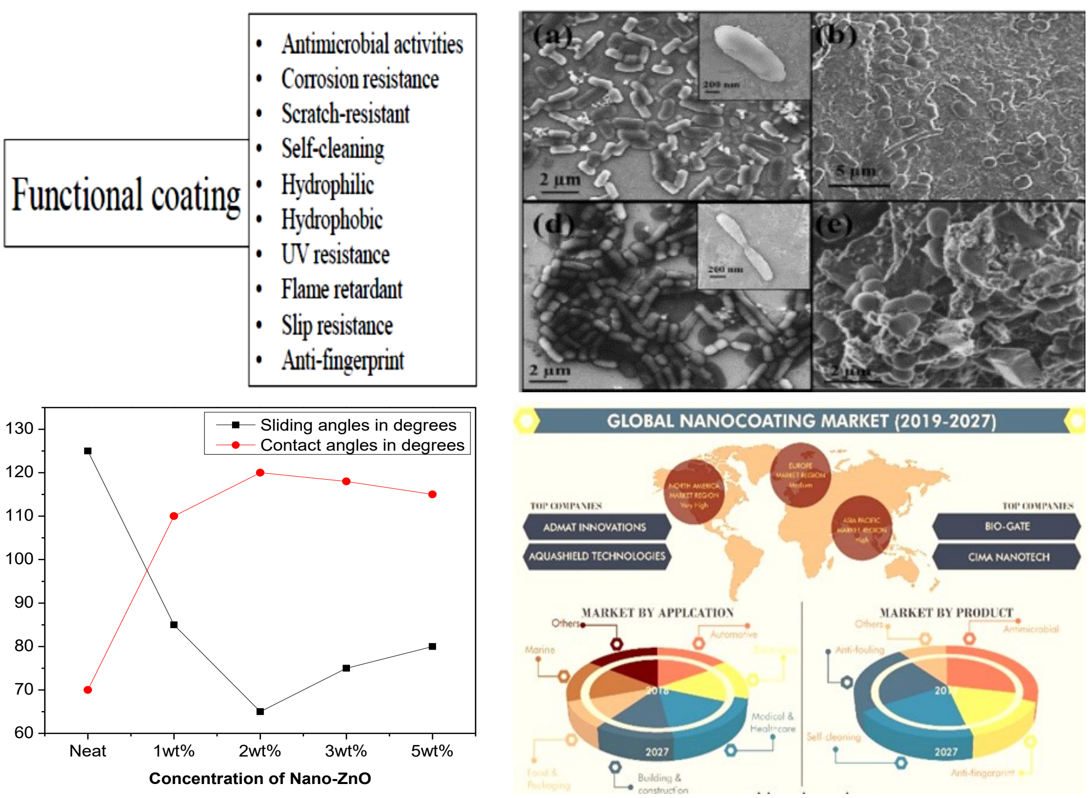
Highlights

- This paper reviews synthesis, characterization, and applications of nanoparticles for enhanced functionalities of paints.
- Limitations of nanocoating were identified.
- Future trends were predicted.

Graphical Abstract



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Abstract

Nanoparticles-modified paints have shown huge potentials in a broad range of functionalities like surface protection, antifouling, corrosion resistance, self-cleaning, slip resistance, abrasion resistance among others. Consequently, they have been deployed for several industrial applications including pipelines, buildings, automobiles, electronics, among others. To further enhance their functionalities, paint industries have expended huge resources on research and development of advanced paints that are compatible and appropriate for today's hostile environments. Studies have been conducted on the utilization of degradable biocides such as zinc oxide nanoparticles (ZnONPs), silver nanoparticles (AgNPs), copper nanoparticles (CuNPs), photocatalytic-active nano-titanium dioxide nanoparticles (TiO_2NPs), and silica dioxide nanoparticles (SiO_2NPs) as major additives in paints. These additives are designed to offer improved surface protection against microbial, physical, and chemical deteriorations as well as enhanced scratch resistance. However, the addition of nanoparticles to paints is not without its demerits. Nanoparticles can agglomerate within the paint matrix leading to poor surface protection. In addition, the health and safety concerns from human exposure to emissions of nanoparticles must be adequately addressed. A few reported studies on the toxicology of nanoparticles are either short-termed or having variant or inconclusive results. This paper reports a critical assessment of nanoparticles as additives in paints. Extensive characterization of nanoparticle-modified paints is reported while the implications on the environment are also explored. New directions, targeting enhanced functionalities and lower toxicity, are proposed.

1. Introduction

Nanotechnology is an emerging multidisciplinary field that focuses on the utilization of materials at a nanometer scale. This field is gaining momentum because of its huge potential applications in numerous areas of human endeavor such as medicine, energy, automobiles, aircraft, biotechnology, manufacturing, coating, computer, food processing among others. Nanotechnology also involves the process of creating devices that are not only smaller but with improved performance than the current technologies making them a potential replacement. These devices are created by controlling individual atoms and molecules at the nanoscale [1, 2].

Nanotechnology also involves the synthesis, characterization, and applications of nanomaterials of different characteristics, sizes, shapes, and chemical compositions for the benefit of man [3]. Nanomaterials have at least one dimension in the order of 100 nm given them a large surface area to volume ratio. In contrast to bulk materials, nanomaterials provide the desired impact when available in a minute concentration. It has been established that materials with high surface areas have improved mechanical, chemical, physical, optical, or magnetic properties [3, 4]. Despite their extremely small size, high surface activity, and large surface area, nanomaterials especially nanoparticles are easily clustered [4].

1.1 Nanotechnology in the paint industry

There are increasing demands for the development of nanomaterials for applications in solid surface coating. This is necessary to overcome the challenges being encountered in the coating industry such as corrosion, fouling, poor adhesion, blistering, and weathering of the coating surface [5]. The coating industry, being among the first to utilize the potentials of nanotechnology, invests a huge amount of money in research and development (R&D) which has resulted in the formulation of paints, which are compatible and suitable for today's aggressive environment [1]. The R&D sector in most oil companies expended huge re-

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sources to protect structures such as oil rigs, and pipelines that are located on the sea from corrosion and deterioration of the ecosystem. The coating does not only serve the purpose of ornamentation but also a means of protecting valuable metals used for the construction of oil rigs, pipelines, and buildings from corrosion [1, 6].

2. Nanocoating

Coating is applied on different substrates with the main aim of protecting and beautifying them. Most coatings contain resins, pigments, fillers, additives, and solvents. The fillers impact the specific properties on the substrate whereas the pigment provides coloration and protection to the coating system [7]. Nanocoatings such as nano-alumina, nano-silica, nano-ZnO, e.t.c contain nanomaterials [8], which significantly enhanced their functionalities owing to the high surface area to volume ratio. The nanosized additives have been reported to minimize antimicrobial activities, and enhance corrosion resistance, anti-graffiti, scratch-resistant, and self-cleaning [1, 2, 5, 8 –10]. Other advantages include improved surface appearance, superior chemical resistance, optical intelligibility, adhesive power on different types of substrates, better retention of gloss, anti-reflectiveness, improved electrical and thermal conductivity, UV blocking effect, anti-fogging, anti-fouling, and anti-skid properties among others [1, 3, 5, 11, 12]. Despite these enhanced functionalities, the production cost is still comparable to those of conventional paints. The physicochemical properties of the functional coating are enumerated in Fig 1.

Nano-coating can be applied in various ways including sol-gel methods, physical vapor deposition, mechanical application, laser beam surface treatment, chemical vapor deposition, electrochemical deposition, and electro-spark deposition among others. These techniques have been utilized to accomplish surface coating of different functions [13].

2.1 Anti-fouling

Different nanoparticles such as magnetic graphene oxide [5], nano-silica and nano-ZnO [8], clay and TiO_2 NPs [14], ZnO NPs [15], ZnO and TiO_2 NPs [16], and ZnO-AgNPs [17] have been used to solve the problem of fouling and reduce the interaction of microbes with the surface of the immersed substrate. Nanocoatings have been deployed to prevent adhesion and accumulation of harmful microorganisms and marine fouling organisms on immersed structures like ship hulls. The creation of nano-structure leads to a considerable reduction in the interaction between surfaces and germs. Nanocoating facilitates the reduction of viruses, algae, and germs by the oligodynamic effect of metal components [1, 15]. The need to incorporate antimicrobial properties in paints is increasing due to the high demand from consumers for nano-modified paints with durability and protection. Higher demand for antimicrobial paints is dominantly in the construction sector, but the hospital, school, automotive, textiles, and food industries, along with others, are also growing their demand for these paints [9, 17]. The inclusion of silver and cobalt ferrite nanoparticles in coating systems also improves the antibacterial property of the paints [5, 7, 18–20]

Paints embedded with silver nanoparticles (AgNPs) possess pronounced bactericidal activity toward several pathogenic bacteria when compared with control paints without NPs [18]. These paints are considerably less toxic to humans and more environmentally friendly. Hence, AgNPs embedded paints and coatings hold great promise for use in health care, childcare, sports, penitentiary, public catering institutions, and other places with higher-level of contamination [2, 20]. Hemicelluloses-based hydrogel coated with AgNPs possesses an excellent antimicrobial activity

Nano Plus: Sci. Tech. Nanomat. 2 (2021) 97 – 119
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against the microbes such as *Escherichia coli* and *Staphylococcus aureus* [21].

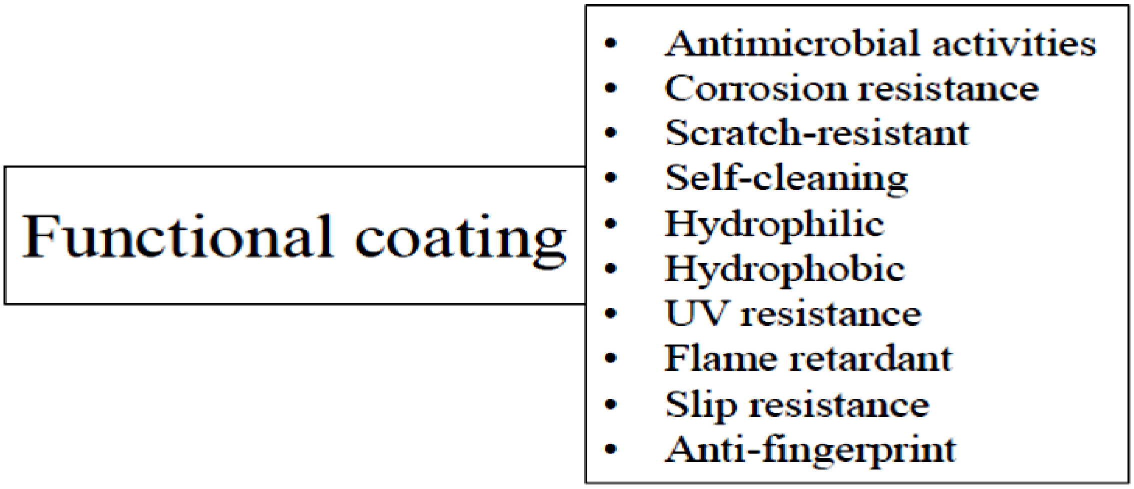

Fig. 1: Physicochemical properties of functional coating

In a study [17], flame spray pyrolysis was adopted in preparing ZnO partially coated with AgNPs as an additive incorporated into waterborne paints. The antifouling test on the prepared AgNPs modified paint indicated that AgNPs inhibited fungal and bacterial growth. In a similar study [20], copper nanoparticles modified paints showed positive results when applied to protect machinery working underwater such as ship hulls and structures installed in a marine environment (such as water supply pipes and oil platforms) from biofouling. This implies that the modified paint prevents various organisms such as mussels, small crustaceans, calcareous tube worms, and marine algae from being attached to the substrates. Epoxy and polyurethane paint modified with copper nanoparticles (CuNPs) have been reported to provide more efficient biofouling protection for vessel hulls. However, CuNPs and copper oxide nanoparticles (CuONPs) have adverse effects on aquatic animals [20, 22].

Solano *et al*. [16] synthesized ZnO and TiO_2 NPs from lemongrass extracts using a green chemistry approach. These NPs were then incorporated in enamel paint and applied on an aluminum disk substrate. The results of the antifouling property revealed that ZnONPs provided inhibition against bacteria, while TiO_2 NPs did not. In addition, Kim *et al*. [14] investigated the effects of NPs in enhancing the antifouling property of the Polyurethane (PU) coatings system. Two different types of inorganic nanoparticles namely, montmorillonite and TiO_2 were mixed with PU binder solution and applied onto the substrate which subsequently did not provide a regular nanopatterning. The antifouling property films were compared with bare PU. The NPs made random nanopattern on substrate film and the surface of bare PU film did not show considerable protrusion using atomic force microscopy. The biofouling resistant property of film was analyzed by comparing the amount of mucins adhesion on the films and it was discovered that inorganic coated films exhibited more than 80% of biofouling resistant effect when compared to bare PU film [14].

Zinc oxide NPs are applied as inorganic antimicrobial agents due to their oligodynamic effect. Zinc oxide was added to acrylic paints at different proportions and a microbiological test was conducted. The acrylic paints with the additive of ZnO NPs showed excellent antimicrobial activity when compared to the acrylic paint without nanoparti-

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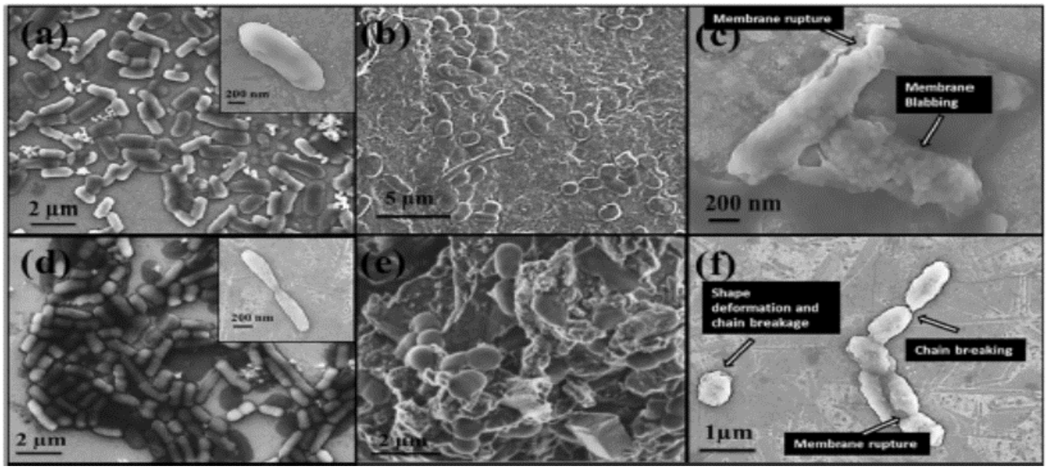

Fig. 2: SEM micrograph of bacterial strains with HMGO film (a) untreated *S. Typhimurium* (b) *S. Typhimurium* with MGO film (c) morphological changes in *S. Typhimurium* after treatment (d) untreated *E. coli* (e) *E. coli* with magnetic paint and (f) morphology changes of *S. Typhimurium* after treatment (inset in a, d shows single bacterium) [5].

cles. The antimicrobial activity is effective for the bacteria *Staphylococcus aureus* when associated with *Escherichia coli* [15].

The incorporation of nano-silica into the coating system enhances the anti-fouling effect. Nano-silica particles are excellent leveling agents which enable the surface to be smoothed and this consequently made it difficult for microbes, barnacles, and sea-weeds to adhere to the immersed structure. This was shown after immersing and exposing coated panels in seawater for 60 days [8]. Hybrid magnetic graphene oxide (HMGO) paint was synthesized using high-energy ball milling with the integration of cobalt ferrite magnetic NPs, graphene oxide, and other paint additives [5]. The antibacterial activities against *E. coli* and *S. Typhimurium* were investigated for the synthesized HMGO film. The antibacterial effectiveness of HMGO film was excellent with a process of generating reactive oxygen species and destroying bacterial membranes. The SEM micrograph of bacteria strains with HMGO film is shown in Figure 2. The growths of the bacteria strain in untreated films are shown in Figure 2 (a and d). Figure 2 (b and e) depicts the influence of films treated with HMGO on the bacterial cells. The bacterial cells completely adhered to the substrate owing to the charge interaction between the bacteria cell membranes and HMGO coat. The bacteria cells were morphologically deformed as shown in Figure 2 (e and f) due to the neutralization of the negatively charged bacterial covering with positively charged HMGO film. Thus the addition of HMGO in paint inhibited and damaged the growth of the bacteria membranes.

Lateef *et al*. [23] carried out biogenic synthesis of AgNPs from pod extract of *Cola nitida*. In the study, the synthesized AgNPs were characterized and the antibacterial activities along with antioxidant activities were evaluated. The synthesized AgNPs with the concentration of 5 µg/ml were incorporated as additives into the emulsion paint and antimicrobial property was also evaluated. These samples were compared with the control sample without AgNPs. The results revealed that AgNPs eradicated and inhibited the growth of bacteria (*E. coli* and *P. aeruginosa*) and fungal strains (*Aspergillus niger*, *A. fumigatus*, and *A. flavus*) whereas there was abundant growth of the microbes in the control samples. AgNPs as an additive in paint enhance the functionalities of the paint against biodegradation, fouling attack, and chemical deterioration of the substrates [23].

In a similar study [24], amorphous silica nanoparticles were synthesized and dispersed in various dispersing agents for painting purposes. This was done by using the beads mill-

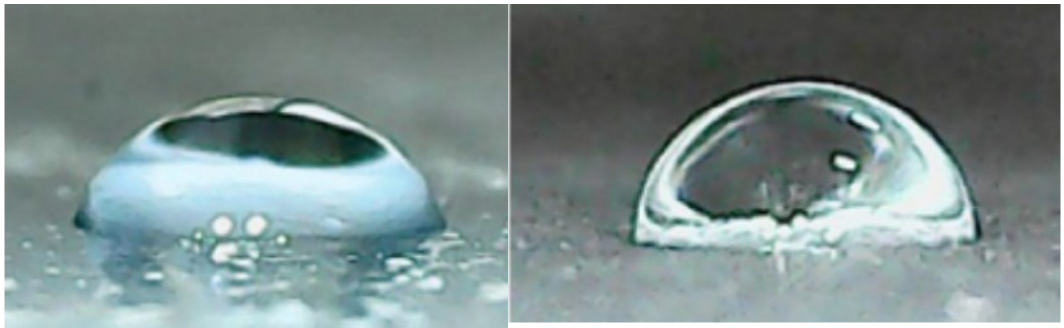

Fig. 3: Images of water droplets on the surface of the concrete with CR coating [4].

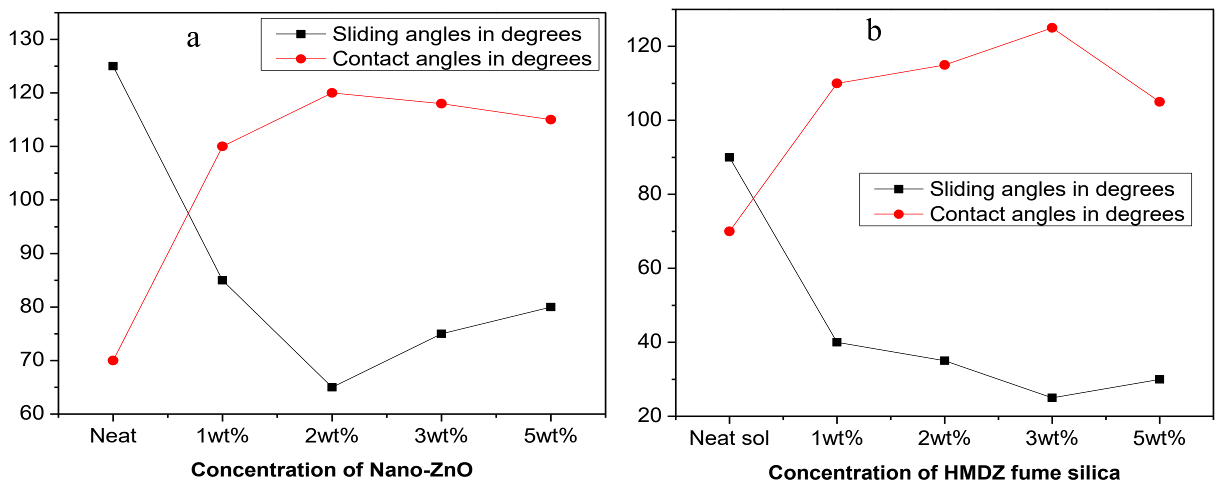

Fig. 4: (a) Variation of sliding angle and contact angle with a concentration of ZnO-NPs; (b) variation of contact angle and sliding angle with the concentration of HMDZ-SiO_2 NPs [8].

ing process to prevent agglomeration. It was noted that amorphous silica nanoparticles uniformly dispersed in 10 wt% SND 504 (Sodium salt of a polymeric carboxylic acid with water) dispersing agent showed better dispersion than other dispersing agents used in the research such as polymeric surfactant, polysorbate, and ammonium salt of polymeric carboxylic acid, ammonium sulfate, and water. In addition, the dispersed amorphous silica nanoparticles displayed excellent antimicrobial activity when embedded in the paint compared to the untreated silica. Furthermore, Zhang *et al.* [25] developed a silver nanoparticle/polytetrafluorethylene (AgNPs/PTFE) coating for metallic implants using facile mussel-inspired techniques. The reduction of bacterial growth in *Escherichia coli* was evaluated. The silver ion in the coating matrix inhibited the growth of the bacterial and the PTFE prevented the bacteria from adhering to the substrate. The collaborative effect of AgNPs/PTFE coating showed outstanding antibiofilm action against *Escherichia coli*.

2.2 Self-Cleaning Application

Lotus effect (self-cleaning surface) is common and essential in nanocoating. It prevents the accumulation of droplets or fine dirt on the surface. The dust particle from the glass surface is loosened when nano-modified paint is applied to the glass substrate, unlike water that tends to distribute the dirt across the glass surface [4].

The surface area and pore volume in-

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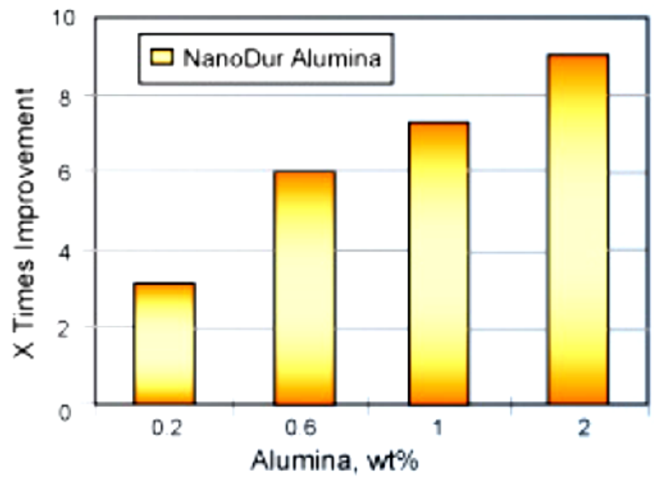

Fig. 5: Scratch-resistance performance of alumina NPs in a UV-curable transparent coating [1].

crease when NPs are added to the coating system, which in turn boosts its surface irregularity. A rise in surface roughness consequently increases the water contact angle appreciably (including other solvents) and therefore reduces the surface tension [1, 24]. This application is commonly used for self-cleaning glass windows, solar panels, corrosion prevention, and stain-resistant textiles. Self-cleaning application is achieved by creating a hydrophobic surface as the first step. A hydrophobic surface should possess low surface energy and very high roughness at a nanoscale [3, 4, 11]. The surface can be attained by combining a low sliding angle and high contact angle. The high contact angle can be achieved by reducing the surface energy using polydimethylsiloxane-based polymers, alkyl or fluorinated organic silanes, long alkyl chain thiols, per-fluorinated alkyl agents, long alkyl chain fatty acids, or their combinations. The low sliding angle can be attained by producing a surface where the contact of the bubble with the surface can be reduced. This can be achieved by including nanoparticles to modify the surface to reduce the contact area between the water droplet and the surface. The surface would not be wetted by the water droplets and the dirt would be removed easily [26].

The surface roughness can also be improved by introducing NPs like nano-ZnO [27], nano-ZrO_2, nano-TiO_2 [4], and nano-SiO_2 [4, 11]. Titanium oxide nanoparticles (TiO_2NPs) and SiO_2NPs used silane coupling agents to effectively change from hydrophilicity into hydrophobicity thereby assuring homogenous dispersion of NPs within organic film coatings and enhances the contact angles and surface roughness of the coated concrete surface [4]. The spherical shape of water droplets on the concrete with chlorinated rubber (CR) coating after the addition of SiO_2NPs was more pronounced compared with the coating without SiO_2NPs (Figure 3). This implies that hydrophobic property and the contact angle of CR coating surface increased with SiO_2NPs.

Solano *et al*. [16] evaluated the self-cleaning property of the ZnO and TiO_2 NPs incorporated into the enamel paint. It was observed that the photocatalytic activity of TiO_2 NP was slightly higher than that of ZnO NPs. This is attributed to the small particle size of ZnO NPs and surface area. Carreño *et al*. [11] synthesized super-hydrophobic surfaces (SHS) by spraying SiO_2 NPs on a partially cured polyurethane-based paint. The SiO_2 NPs at different concentrations were dispersed in Tetrahydrofuran (used as solvent).

The dispersion of NPs was sprayed on the partially cured paint samples and characterized after the final curing of three hours at 70°C. Following this approach, samples blended with 0.5 wt% of polydimethylsiloxane-functionalized nanoparticles showed that the water droplets have negligible adhesion to the glass substrate, and this consequently roll off the substrates easily. The contact angles of the water droplets are higher than 150° [11].

Wankhede *et al*. [27] hydrophobically modified a neat sol-gel with a varied contact angle of 70-75° and surface roughness of 3 nm with a six-carbon atom water-based fluoropolymer emulsion (FE) utilized as the hydrophobic precursor to accomplish improved water repellent and hydrophobic properties. The surface roughness of the FE modified sol -gel system was increased to 105 nm when 2 wt% of ZnO-NPs were added [27]. However, this caused a slight increase in hydrophobicity owing to the hydrophilic behavior of ZnO-NPs. The contact angle achieved was 120° with a sliding angle of 65° as shown in Figure 4a. Further adjustment was done on the roughness, contact, and sliding angles by using functionally changed SiO_2 NPs out of which hexamethyldisilazane (HMDZ)-SiO_2 NPs (3wt% concentration) led to the highest surface roughness of 95 nm with a sliding angle of 25° and contact angle of 125° as revealed in Figure 4b.

The multi-scaled roughness is produced by the accumulations of NPs causing bulging nubs. The surface contact area accessible to water droplets was extremely small and the hydrophobic NPs thwarted the infiltration of water into the coating matrix developing an excellent sliding action of the water droplets with a sliding angle of 25° and contact angle of 125° [27]. Other researchers [24] have shown that the contact angle of uniformly dispersed silica showed exceptional hydrophobic nature of SiO_2, in particular with a 10 wt% SND 504 dispersing agent. The surface tension of SiO_2 with 10 wt% SND 504 dispersing agent showed lesser value compared to other proportions of dispersant.

2.3 Hydrophilic Surface

Nanoparticles may boost surface-free energy and hence enhance the wetting nature of water and other solvents. This caused an anti-fog effect owing to the excessive spreading of water droplets. They also influence capillary movement in microstructure [1, 5]. Hydrophilic nanoparticles have been applied to produce a coating surface with thin water film, which can remove the hydrophobic organic foulants [28]. Amongst these, titanium dioxide (TiO_2) coatings have drawn attention to enhancing the antifouling characteristics and performance of self-cleaning coatings because of their intrinsic hydrophilicity and photocatalytic decomposition capability [29]. The modification of the anion exchange membrane surfaces with titanium dioxide (TiO_2) improves the super hydrophilic and antifouling properties of the coating system [30].

In a previous study [31], hydrophilic AgNPs led to the development of nanochannels in thin-film nanocomposite membranes which considerably improved membrane water permeability. The contact angle of a solid substrate can be changed through the modification of the outermost layer of the substrate. For hydrophilic surfaces, the value of the contact angle is less than 90° while the value of the contact angle for hydrophobic nature is greater than 90° [32, 33]. The effect of the oleic acid coating during the hydrophobic-to-hydrophilic surface transformation of nanoscale $MgFe_2O_4$ has been studied [34]. The result indicated a drastic reduction in the values of the contact angle and this implies a transition from hydrophobic to hydrophilic surface.

Mahdavi and Ashraf [35] developed Al-doped ZnO nanoparticles via sonochemical process and examined the hydrophilic activities of the varied proportion of the nanoparticles that were incorporated into the waterborne acrylic resin-based coating. The hydrophilic property of the coating was analyzed by determining the water droplet contact angle with the surface exposed to UV irradiation. The result of the analysis revealed that the contact angle of waterborne acrylic resin-based coating incorporated with doped NPs is lower compared with pure ZnO NPs. Samree *et al*. [36] investigated the hydrophilic properties of the polyvinylidene fluoride (PVDF) membrane coated with TiO_2NPs and AgNPs at different concentrations and coating periods. The water droplet contact angle of the membranes was determined and it was observed that the angle reduced with the rising coating period and TiO_2NP/AgNPs ratio. The permeate fluxes and surface coarseness of the coated membranes were enhanced due to improved hydrophilicity.

Ahmed *et al*. [37] deposited AuNPs on different substrates of glass and polydimethylsiloxane (PDMS) which were treated under different conditions. The contact angle of the treated PDMS after deposition of AuNPs considerably decreased from 113.3 ± 4.5° to 45.3 ± 2.4° in the wake of the oxygen plasma treatment. The untreated glass was relatively hydrophobic with the contact angle of is 60.7 ± 0.7° while the glass treated with piranha washing is extremely hydrophilic with a contact angle of 13.1 ± 0.5°.

2.4 Abrasion Resistance

There is huge interest in producing protective organic coatings because many coating surfaces possess low scratch resistance. As a result of this inadequacy, there is a need to modify the coating system by using a scratch-resistant additive to maintain a prolonged attractive appearance. For instance, SiO_2NPs, ZrO_2NPs, and alumina are implanted in UV-curable glosses to enhance scratch resistance.

Asafa *et al*. [7] carried out the green synthesis of AgNPs at different concentrations via the reduction of silver nitrate using extract of cobwebs. The combined proportion of 0.35 wt% of both synthesized silver nanoparticles and biocide acticide at different proportions were incorporated as additives into the emulsion paint samples. The influence of the AgNPs on some of the mechanical and physical properties of the emulsion paint was reported. The results showed that the abrasion strength and hiding power increased by 236% and 30%, respectively for the paint sample with the optimal mix of the equaled fraction of 0.175 wt% of silver nanoparticles and biocide acticide.

The abrasion property of nanoparticles of precipitated calcium carbonate (NPCC) as an additive in water-based paints was studied by Wu *et al*. [38]. In the study, the abrasion property of paint with NP was compared with paint without NPCC. The result revealed that paint with NPs remained more stable than the conventional paint and the abrasion resistance for paint with NPCC improved by 38%. The emulsion paint prepared with NPCC showed greater scratch resistance [38]. The effect of alumina NPs as abrasion-resistant fillers in a transparent coating was also evaluated by preparing nanocomposites via the process of homogenizing nano-alumina in a UV-curable coating formulation at 30 wt%, with varied alumina NPs between 0.2 and 2 wt%. The resulting nanocomposites were subjected to a scratch test, and the results showed a significant increase in scratch resistance when compared with the coating without nanoparticles (Figure 5). It is obvious that the alumina NPs significantly enhanced the effectiveness of the UV-curable coating, up to a nine-fold increase, even with a small concentration of alumina integrated into the composite [1].

2.5 Ultraviolet Resistance

One of the major challenges encountered

in the paint and coating industries is photochemical degradation of the coating system, which is caused by ultraviolet (UV) rays. It causes the oxidation and breakdown of polymer films along with pigments (inorganic or organic). The UV resistance property can be improved by incorporating NPs like zinc oxide or titania into the coating system. The main function of the UV stabilizer is to reflect the harmful rays and therefore boost the life span and weathering resistance of paints incorporated with TiO_2 NPs from outdoor stains and lacquer [1, 39].

The weathering characteristics of water-based acrylic paint with clay and TiO_2 NPs additives applied on wood substrates were investigated using accelerated aging test and Fourier transform infrared (FTIR) spectroscopy [39]. It was observed from the FTIR analysis that there is superior weathering performance for specimens coated with water-based acrylic paint improved with TiO_2 and a mixture of clay and TiO_2 NPs when in comparison with specimens coated with water-based acrylic paint with nano clay alone and without any nano additive. This displays the capability of TiO_2 NPs alone or in a mixture with nano-clay towards impeding the photodegradation reaction at the wood surface [39]. The responsiveness of carbon black as an additive to coatings towards UV radiation has been examined and its integration into binder enhanced the UV resistance. These enhancements have been credited to the capability of carbon black to absorb UV radiation and protect the polymer matrix [40].

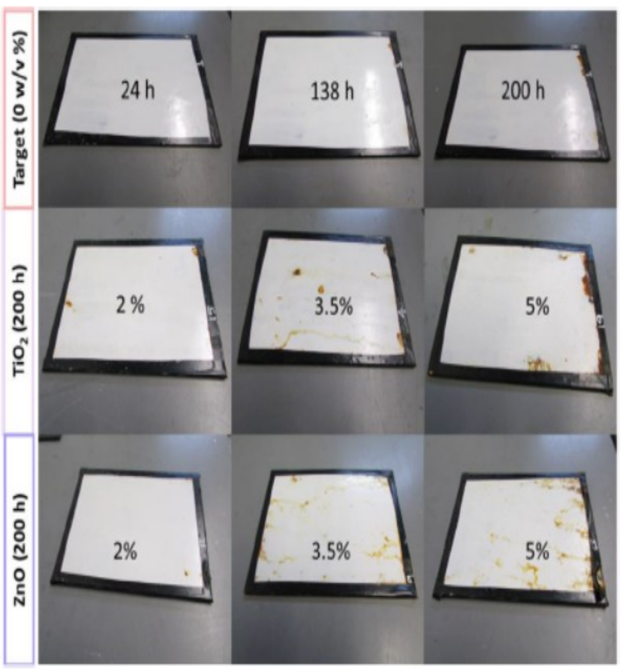

Fig. 6: Photographic record of the test saline fog camera after 200 h of exposure, using coated surfaces with unmodified paint (target) and paints modified with 2%, 3.5%, and 5% of TiO_2 and ZnO nanoparticles [16].

Dhineshbabu and Bose [41] synthesized a MnO_2-$FeTiO_3$ (MFT) nanocomposite by adding manganese acetate to $FeTiO_3$ (FT) nanoparticles which were formulated by extracting acid from ilmenite sand. The cotton fabric was subsequently designed and coated with polyurethane-based MFT. The UV resistance property was investigated by measuring the optical transmission of the coated cotton fabric. The results revealed that the UV resistance property of MFT coated cotton fabric was greater than 99.9% in contrast with the bare or uncoated cotton fabric that exhibited 78%. The MFT-coated cotton fabrics displayed a robust UV blocking capacity [41].

2.6 Fire Resistant Property

Fire-resistant coatings wrap around the surface of substrates behave as a protective barrier to impede the spread of heat when the substrates are subjected to fire. The fire-retardant coatings primarily consist of different nanoparticles and polyelectrolytes, which are categorized as organic, inorganic, and hybrid organic-inorganic coatings [42]. Firefighters used fire-retardant protection materials to eschew burn injuries through the process of resisting heat flux from transferring through the fabrics. However, hydrogel-fabric laminates inhibit fires by absorbing energy and expend it through the evaporation of water. Thus, the hydrogel–fabric laminates can be potentially used in firefighter-protective apparel to halt flames or decrease the temperature to a satisfactory level for the human body when exposed to fire [43]. The enhancement of composites' fire resistance properties leads to a decrease in mechanical strength in most cases and a consequent reduction in the life expectancy of the substrate [44].

Fire retardant coatings (FRC) especially ammonium polyphosphate and melamine are not effective as fire-resistant since they effortlessly separate from the substrate due to reduced char creation in the fire and lower mechanical properties of the coating system. The chemical and mechanical properties of FRC can be enhanced with the addition of nano-concentrates such as magnesium-aluminum–layered double hydroxides (LDH) nanoparticles incorporated into the different FRC systems. Nano –LDH absorbs heat and discharges water and carbon (IV) oxide when burnt. Therefore, the temperature of the substrate is lowered with an increase in char formation. Nano-LDH with a considerable quantity improves the flame-resistant property [1]. Silica coating significantly enhanced the thermomechanical permanence and granted the polyimide nano fabric with exceptional fire resistance [45]. Also, sol-gel-based silica coatings efficiently and consistently mitigate combustion of the substrate [46].

Ahmad *et al*. [47] investigated the fire-resistant property of nano-alumina at different concentrations added to boron nitride reinforced epoxy-based intumescent fire-retardant coating. The nano-hybrid coating system was applied on steel substrate and further subjected to heating inside a Bunsen furnace for 1 hour. The char mass and morphology improved due to the addition of nano-alumina to the coating system. Also, the hardness and microstructure of the steel substrate did not change after the fire test. The incorporation of the nano-alumina into the coating system improved the fire resistance of the substrate when compared with the conventional type [47].

Dhineshbabu and Bose [41] synthesized a MnO_2-$FeTiO_3$ (MFT) nanocomposite by adding manganese acetate to $FeTiO_3$ (FT) nanoparticles which were formulated by extracting acid from ilmenite sand. The cotton fabric was subsequently designed and coated with polyurethane-based MFT. The fire resistance property was determined by using a thermal analyzer. The limited oxygen index of all the samples of the cotton fabrics was also tested. The fiber in the uncoated fabric burned spontaneously, rapidly, and completely into ashes. Although, the MFT coated cotton fabric did not burn easily and there was a formation of char at the edge of the fabric. This observation was attributed to the development of a protective nanofiller coat on the surface of the cotton fabrics. MnO_2-$FeTiO_3$ (MFT) nanocomposite possesses fire-resistant and UV blocking properties [41].

Rao *et al*. [48] examined flame retardant properties of a coating matrix consisting of an epoxy resin, boric acid, melamine, chitosan, and ammonium polyphosphate reinforced with different proportions of zirconia nanoparticles (ZrO_2NPs). The synthesized coatings were characterized by combustion tests, flammability tests, and thermogravimetric analysis. The results of the analyses revealed an increase in the weight percentage of ZrO_2 NPs when the limit of oxygen index (LOI) value increased. Thus, the addition of ZrO_2 NPs at an optimal level in the formulated coatings improved the char and flame retardancy of the coatings [48].

Ortelli *et al*. [49] synthesized two different nano-TiO_2/protein suspensions namely TiO_2/whey proteins and TiO_2-citrate/caseins. The cotton fabrics were dipped and soaked into the two different nano-TiO_2/protein suspensions. The fire-retardant properties of the treated fabrics were examined using the flammability and cone calorimetry tests. The results of the tests showed that TiO_2-CIT/

caseins coatings were robust and efficient fire -resistant finishing options to standard fire-resistant treatments for cotton owing to their superior char-forming nature. On the other hand, TiO_2/whey proteins seem not to be efficient in shielding the treated fabric from the heat flux.

2.7 Anti-Corrosive Property

Metal corrosion poses severe challenges in industries because most industrialized nations spend about $1.8 trillion or 3-4% of GDP on corrosion-related activities [50]. One of the main purposes of developing paints is to protect structures from corrosion due to exposure to marine or other hostile environments by creating obstacles against transportation pathways [51]. The use of coatings is therefore to protect metals by providing a barrier between the metal substrate and its environment. Nanocomposite coating can defer the oxygen or moisture transfer phenomena at corrosion sites thereby delay or impede the electrochemical reactions. This enhances resistance against corrosion [52].

Fillers or additives significantly improve the properties such as mechanical, thermal, corrosion protection, and electrical conductivity, of organic coatings [53]. Epoxy resin is extensively applied in organic corrosion-resistant coatings owing to its relatively low cost, good corrosion protection, and strong adhesion to the metal substrate. To enhance resin performance, NPs are embedded as fillers to barricade the micropores, and subsequently improve the anti-corrosion and mechanical properties of the resins [54]. Steinerová *et al*. [55] studied the effects of magnesium oxide (MgO) nanoparticles on the anticorrosive property of synthesized water-based polymeric acrylate dispersions. The anti-corrosive property of the nano-paint was compared to the reference paint. The results obtained from the mechanical and chemical properties as well as the corrosion resistance of the coating systems indicate improved protective properties of the MgO nanoparticles modified paint compared to the standard system without NPs [55].

Zhang *et al*. [25] developed silver nanoparticle/ polytetrafluorethylene coating for metallic implants using facile mussel-inspired techniques. The potentiodynamic polarization test was carried out to determine the performance of the corrosion resistance of the coating matrix. The result revealed that the coatings have lower corrosion current densities and high positive corrosion potentials than the uncoated substrate, thus the corrosion resistance was enhanced using the coating matrix [25]. Aboorvakani *et al*. [53] synthesized ZnO nanoparticles via chemical precipitation methods and investigated the anticorrosion property of epoxy/ZnO coating on mild steel substrate by applying the electrochemical impedance spectroscopy (EIS) method in both neutral and acidic media. The EIS analysis revealed that epoxy/ZnO coating on mild steel substrate is highly anticorrosive/ protective in both acidic and neutral media.

Jeen-Robert *et al*. [56] developed a super-hydrophobic polymer nanocomposite (PNC) coating by mixing polyvinyl chloride, copper stearate, and ZnO NPs. The PNC coating was applied on Al-6061 alloy and the corrosive resistant behavior of the coating was examined. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PP) analysis were done on uncoated and PNC coated Al-6061 using 3.5% NaCl as the electrolyte. The corrosion rate of coated substrate decreased from 23.75 mils per year (mpy) to 0.2253 mpy when compared with bare Al-6061. It was concluded that the developed super-hydrophobic polymer nanocomposite coating exhibited good anticorrosive property on Al-6061 alloy due to the super-hydrophobic activity of the nanocomposite [56]. Solano *et al*. [16] also characterized and analyzed the ZnO and TiO_2 NPs

Nano Plus: Sci. Tech. Nanomat. 2 (2021) 97 – 119
https://doi.org/10.48187/stnanomat.2021.2.007

when incorporated at different proportions into enamel paint. The nano-paints were applied on carbon steel sheets and the anticorrosive property was evaluated. The anticorrosion results showed that nano-paints provide a barricade using fewer concentrations of nanoparticles because there is low porosity on the surface to prevent accelerated oxidation. The photographic record of the substrate coated with different concentrations of NPs and tested in saline fog is shown in Figure 6. The modification of enamel paint with optimum concentration (2wt%) of NPs significantly displayed a low degree of corrosion in contrast to the samples with higher concentrations. Thus, rapid oxidation of the substrates occurred as the concentration of the added NPs in the paint increased [16].

Yuan *et al*. [54] synthesized three different composite coatings by incorporating graphene oxide (GO), titanium (Ti) nanoparticles, and GO-Ti composites with different proportions as an additive into epoxy resins. These composite coatings were stirred mechanically to ensure homogenous dispersion of the NPs in the resin and applied on the Q235 steel substrate. In contrast with GO and Nano-Ti particles, the GO-Ti composite showed considerable advantages in enhancing the anti-corrosion property of epoxy coatings, which was credited to the even distribution of the Nano-Ti particles on the GO sheet and intrinsic corrosion resistance.

Narenkumar *et al*. [57] synthesized plant extract AgNPs using the leaf extract of *Azadirachta indica*. In their study, the synthesized AgNPs were characterized and the corrosion resistance properties were evaluated. The EIS analysis was evaluated on the AgNPs coated mild steel (MS1010). The existence of AgNPs in the coating matrix exhibited a significant increase in the corrosion resistance of mild steel and could be ascribed to the anti-bacterial property of AgNPs and the collaborative impact of barrier property caused by the NPs. This study unveiled bioengineered AgNPs formulations as an effective corrosion resistance inhibitor [57].

Similarly, studies were conducted to quantify the influence of AgNPs on inhibition of corrosion of mild steel, stainless steel, and aluminum in 1.0 M HCl using potentiodynamic polarization and gasometric (hydrogen gas evolution) approaches. The study showed that inhibition efficiency was enhanced by 52% for mild steel, 70% for stainless steel, and 62% for aluminum while the gasometric study revealed that increased concentration of AgNPs solution lowered the volume of hydrogen gas evolved. Through potentiodynam-

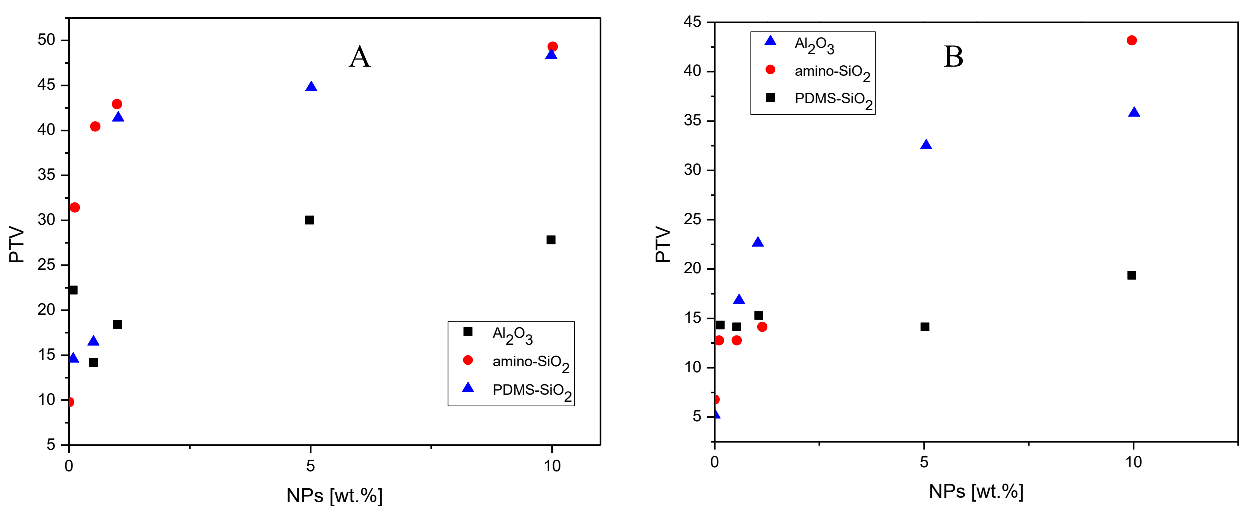

Fig. 7: Pendulum test value evolution with nanoparticle content for the: (a) water-borne and (b) solvent-borne epoxy coatings under wet conditions.

ic polarization results, it was discovered that the presence of AgNPs modified the mechanism of anodic dissolution and cathodic hydrogen gas evolution [50]. Odusote *et al*. [58] also presented equivalent inhibition efficiency of 88%, 98%, and 96% for aluminium, mild steel, and stainless steel, respectively for gold nanoparticles (AuNPs) modified 1M HCl solution. It was concluded that AuNPs can be incorporated into existing inhibitors towards minimizing corrosion rate [58].

2.8 Slip resistance property

Many anti-slip remedies are based on increasing the surface roughness of the floor to prevent slips and falls on wet surfaces. Slippery can also be reduced by increasing the coefficient of friction of the smooth or wet surfaces [59, 60]. This can be achieved by incorporating additives such as silica sand, polypropylene microspheres, aluminum oxide in the paints. A considerable improvement in the surface roughness makes it hard to clean the floor because it aids the confining of dust between the surface coarseness of the floor and thus requires high maintenance expenses [59].

The application of NPs in coating industries increases the coarseness of a surface without creating macro roughness, hence eschewing the dirtiness and high maintenance cost of the surface.

Blanco *et al*. [59] developed an anti-slip coating system by adding three different types of ceramic oxide NPs namely; Al_2O_3, amino-functionalized SiO_2 (amino-SiO_2), and polydimethylsiloxane functionalized SiO_2 (PDMS-SiO_2) to solvent-borne and water-borne epoxy paint formulations. On one hand, the conventional coating systems employed by coating industries for slip resistance property were developed by adding polypropylene thermoplastic microspheres and silica sand to water- and solvent-borne epoxy formulations. The slip resistance property was investigated in all these coating systems with unmodified paint formulation after the coats were applied on stainless steel sheets. The Pendulum test value (PTV) (shown in Figure 7) of the differently coated surfaces showed that the inclusion of NPs to both water and solvent-borne coatings significantly improves the slip resistance of the substrates. The surface coarseness of the nano-coated surface is between 5–10 times lower than other solutions typically used in the paint industry to accomplish anti-slip properties. The surface gloss of the NPs modified paints indicated that the brightness is higher when compared with conventional slip resistance paints. The cleaning easiness was assessed and it was observed that untreated and nanoparticle-modified coatings were effortlessly cleaned, although the coatings of paints improved with microspheres and silica sand were more complicated to be cleansed [59].

Lv *et al*. [61] studied the wall slipping behavior and flow resistance of foam with nanoparticle-armored bubbles in a capillary tube. The results revealed that the slipping friction force increased appreciably by the addition of hydrophobically modified SiO_2 NPs. The slip force improved when the feature of the foam increased from 85% to 98%. Alberto *et al*. [62] reinforced and incorporated liquid polyurethane resins films with few-layer graphene NPs via the process of high shear mixing to achieve homogenous dispersion of few-layer graphene NPs in the matrix. The dispersed few-layer graphene NPs considerably enhanced the grip and robustness resulting in excellent slip resistance coating performance.

2.9 Anti-fingerprint Coating

The deposition of fingerprints on a translucent surface such as the touchscreen of iPad, phones, and laptops hamper the visibility and reduce the optical transmittance [63]. Anti-fingerprint coatings are extensively applied for touch screens in electronic devices. Smart coatings offer a fingerprint disappearing effect with the release of surfactants in reaction to the substrates by fading the deposited fingerprints [64]. This involves the development of an extremely flat surface using NPs after producing a surface with low free energy. Such a surface considerably reduces fingerprints and other foul substances. The time required to clean the surface reduced considerably because of the lack of oxidation and reduced adhesion of the fingerprint [1].

Anti-fingerprint properties can also be achieved by creating hydrophobic and oleophobic surfaces because fingerprints are largely made of water and sebum. The characterization technique for evaluating the properties of fingerprint resistance is achieved by determining the static contact angle against organic liquids and water for oleophobic and hydrophobic surfaces, respectively. The reduction of adhesion of fingermark on the coating surface is achieved by minimizing the surface wettability against water and oil [65]. Low surface energy is known to reduce the intermolecular attraction and this consequently reduces the adhesion of fingermark on the substrate [66]. Superoleophilic/superhydrophobic surfaces can be produced by suitable surface chemistry and multiscale surface coarseness [67]. Heo *et al*. [68] developed a protective layer/AgNPs/SiO_2/glass by depositing SiO_2 film (protective layer) onto AgNPs on a glass substrate. The fingerprint resistance of the protective layer/AgNPs/SiO_2/glass was investigated after repetitive touches and swipe. The protective layer showed effective fingerprint resistance properties based on a wetting angle of 116° and excellent mechanical durability of the AgNPs/SiO_2/glass [68].

Similarly, Matsubayashi *et al*. [69] conducted a fingerprint adhesion test (using a colour difference meter) by applying hollow cyanoacrylate nanoparticles (HCNPs) on bare glass. The nanoparticles were synthesized using supersaturated gas cored instant polymerization (SGCIP) technique which blends Ethyl cyanoacrylate (ECA) and nanobubbles produced by polymerization and a change in gas solubility, respectively. The result showed that the colour difference after and before the fingermark adhered to the substrate decreased by 14.4% in the coated glass compared to the bare glass. The surface tension decreased due to silanization of the substrate's surface using fluoroalkyl silane (FAS) and the topography of the surface based on the presence of HCNP self-assembly [69]. The low surface tension of a solid surface implies that dust, water, oil, and other materials available on fingers are more prone to stay attached to the fingers and not impressed to the glass substrate with low surface energy [64, 69].

Heo *et al*. [70] also investigated the anti-fingerprint behaviors of AgNPs deposited on flexible polymer Polyethylene terephthalate (PET) substrates. The addition of a thin protective layer (15 nm of thickness) of fluoride/SiO_2 films into the AgNPs–PET substrates effectively improved the anti-fingerprint quality and good mechanical durability after repeated touches and swipe. Also, Choi *et al*. [71] fabricated superoleophobic titania-based porous nanoparticle coatings using layer-by-layer assembly and calcination methods with subsequent application of the nanocoating on a flexible glass substrate. Titania-based porous nanoparticle coatings that are highly transparent with scatter visible light. The result showed that the fingerprint on TiO_2 nanostructured surfaces disintegrated under a short period when exposed to UV light. The painted surfaces are photocatalytically effective against fingerprint oils in natural sunlight and are also fitting with elastic glass substrates [71].

3. Future of nanocoating in the

Nano Plus: Sci. Tech. Nanomat. 2 (2021) 97 – 119
https://doi.org/10.48187/stnanomat.2021.2.007

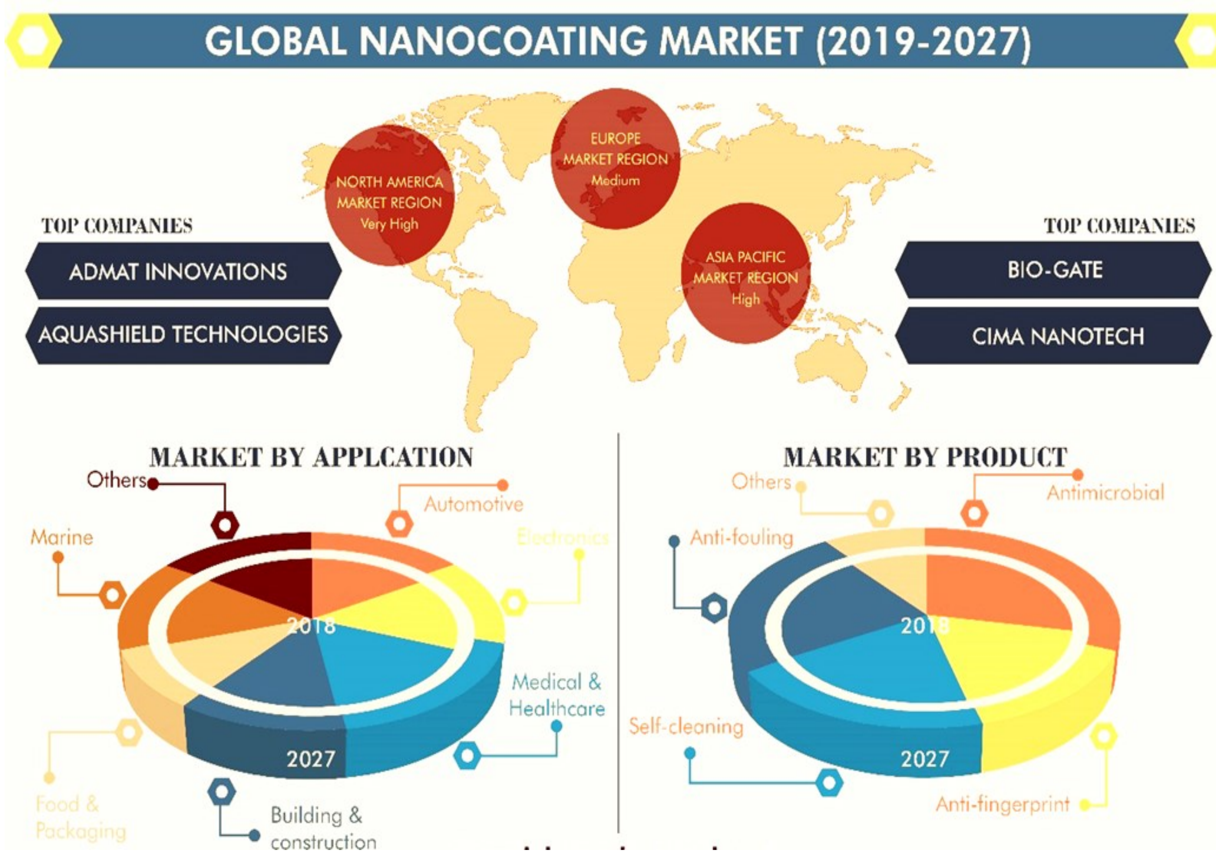

Fig. 8. The expected compound annual growth rate of 22.07% for the forecast period 2019-2027 for the global nanocoating market [72].

global market

The future of nanocoating looks promising due to the huge resources that have been invested and expended in developing multifunctional hybrid nano-modified paints. Thus far, the market growth in the application of nanotechnology in the paint industry is booming due to several factors including superior properties of nanocoatings, flourishing automotive industry, increasing demand for medical equipment coatings, growing industrialization in the Asia Pacific, technological improvements, and so forth. The global nanocoating market is anticipated to grow with an estimated compound annual growth rate of 22.07% for the forecast period, 2019-2027 (Figure 8), using 2018 as the baseline [72].

Marine and automotive industries are promising segments of nanocoatings application. In the marine sector, there is a high demand for antifouling coating systems that is non-toxic and invulnerable to harmful microbe attacks and accumulation on the ship hulls. Fouling formation has impacted negatively on the performance of the marine vehicle and there is a dire need for antifouling nanocoating that is environmentally friendly. The adverse effects of fouling on marine vehicles are speed reduction and excess fuel consumption. There is competition in the automotive sectors and the application of nanocoating is huge in these industries with coating systems that can exhibit unique properties in many ways: corrosion resistance coatings to anti-graffiti to scratch-resistant coatings to self-cleaning surface coatings.

Nanocoatings are also applied for small applications in other industries such as consumer goods, electronics, and medical products. Antimicrobial nanocoatings are majorly applicable in food packaging, food production, water treatment, healthcare, and medical sectors. They represented about 30% of the total market share in 2014 which is expected to rise in years to come. Self-cleaning nanocoatings are used in different sectors such as food manufacturing, electronic, and automobile industries which significantly increased between 2013 and 2019 [73, 74]. Anti-fingerprint coatings are used in the touch screen of electronic devices, kitchens, textiles, floor sealants, optics, restaurants, automotive, cafes, HVAC systems, and so on [64]. This is also expected to receive more attention in the next couple of years given huge development in these areas. Finally, manufacturing hybrid coating using nanoparticles may possess most of the properties necessary for an efficient coating system to withstand different environmental impacts.

4. Challenges of nanocoating

With the increasing adoption of nanocoatings, fresh challenges are emanating from these applications. Factors like harsh or lack of government regulations, unstable prices of raw materials, high investment rates, strong competition among manufacturers, new technologies, and complex methods are impeding the market growth. Getting these challenges under control will go a long way to promote further adoption of nanocoating technology.

One of the technical difficulties associated with nanocoating formulation and preparation is the agglomeration of NPs in the paint matrix. Agglomeration reduces the desired functionalities and subsequently eliminates the benefits of incorporating nanoscale materials into paints. Dispersion and stabilization of NPs within the paint matrix are the most essential aspects of the final properties of the resulting paint. Chemo-mechanical processing is one of the promising innovative methods designed to ensure adequate nano-dispersions and stability of NPs [73]. Chemo-mechanical processing comprises agitator bead mills synchronized for chemical and mechanical effects. The materials are ground in the vessel in which rupturing and modification of surface take place at the same time. Bead mill agitators have been utilized in the paint industry to disperse fillers and pigments [73]. For instance, the sodium salt of the polymeric carboxylic acid (dispersing agent) was used to disperse SiO_2 in the paint by beads milling process to prevent agglomeration of the NPs [24]. It also permits the processing and addition of powders into the liquid matrix. There is a need to stabilize the NPs in the paint after they must have been dispersed to prevent agglomeration [73].

Consumers concern with the existence of NPs in paints and the threat of exposure to the adverse effects of nanocoatings on the environment and human body. As a result, the paint industry now concealed those paints with nanoparticles during marketing. The adverse effects of NPs on the ecosystem have been reported by some researchers. Several nanoparticles have toxic effects on vital organs of human beings such as the liver, skin, eye, lung, reproductive disturbance, and blood cells. The main process of toxicity of nanoparticles is owing to an increase in its concentration in non-target tissue of therapy through genotoxicity, oxidative stress, or hemotoxic effects [75]. So NPs may interfere with the normal physiological mechanisms of the embryos, growing animals, and adults, and it is imperative to be aware of their harmful effects on living organisms. It has been proven that NPs could be toxic to bacteria, algae, invertebrates, and vertebrates [76].

Jørgensen *et al*. [77] investigated the emission of NPs in four indoor paints (one solvent-based alkyd paint and three water-based acrylic paints). The emission was examined for both reference and full-pigmented types of paints. The Fast Mobility Particle Sizer (FMPS) was applied to determine emissions released during the paint drying process. The results obtained from this analysis revealed that the exposure to NPs by the people for around 7-28 days was low and that indoor paints are possibly not very critical when classifying products that release NPs into indoor environments [77]. Göhler *et al*. [73] pointed out that there is no standardized method for treatment processes and characterization of NPs release from the surface. Creating the correct approach for conducting the analysis which generally suffers from a terrific deal of disparity in the outcomes is one of the major challenges faced during the investigation of the NP's emission on human beings and their environment [73]. Air pollution is deemed to occur if the NPs are not properly handled during the production of nanocoating. This can consequently cause severe respiratory diseases. Moreover, there is no assurance that nanomaterials in paints will accomplish the long-lasting application because of the non-availability of long-term investigation in the literature so far encountered. For instance, silver is easily washed off by rain in nanosilver incorporated paints. Photocatalytic active nano-titanium dioxide absorbs ultraviolet light and produces hydroxyl radicals, which impede microbial evolution and begin or hasten the photocatalytic dilapidation of the coating matrix. Hence, doubt was cast on the need to include nanomaterials into paints [78]. This must be studied further and appropriately documented.

5. Conclusions

The application of nanotechnology in the paint industry is an auspicious market that is anticipated to promote the economy of the industry. Nanocoating possesses improved properties like gloss retaining, anti-corrosion, ultraviolet stability, flame repellent, abrasion resistance, e.t.c, which can be used in numerous sectors. The challenges faced in nanocoating are the agglomeration of NPs in the paint matrix and the health and safety concern of exposure of human beings to the emission of nanoparticles. Agglomeration of NPs should be avoided to maintain the benefits of nanoscale materials. It is difficult to clear the gray areas in the emission of NPs to human being and their environment because there are no standardized methods for treatment processes and characterization of NPs release from the coating surfaces. More studies are required to clear these gray areas. However, the huge benefits of nanocoating significantly overshadow its shortcomings.

Conflicts of Interest

The authors proclaim no conflict of interest.

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