

Applications of Nano Pigment Particles for the Development in Corrosion and Scratch Resistance of Epoxy-Zeolite Coatings

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Abstract— For the purpose of corrosion protection and embellishment, surface coating is the most universally used practice. The applications of nanotechnology in the fields of corrosion protection and surface coatings can significantly improve the adhesion property, stiffness, chemical resistance, weathering resistance and robustness among all other important properties of surface coatings. In this work, nano particles applied surface coatings have been used to protect various types of metals and alloys from corrosion and other degradation. For this purpose, epoxy-zeolite self-cleaning super hydrophobic and antimicrobial corrosion resistant coatings have been used to protect metals and alloys from corrosion. The corrosion protection efficiency has been improved when nanoparticles have been incorporated and dispersed into paint media. Nano coatings have been introduced as smart materials; produced by shrinking the materials at the nano scale level to form a denser product to protect the surfaces with superior approach. Nano particles applied coatings demonstrated a number of advantages such as better surface appearance, chemical resistance, thermal and electrical conductivity, and improved corrosion resistance. Incorporation of nanoparticles in paint formulations improved the corrosion resistance property of antimicrobial zeolite coatings. On the basis of rigorous coating performance test as per ASTM/BIS methods, coating-film passed 3200 hours in salt spray corrosion test, 100% gloss and 100% adhesion; confirmed extraordinary improvement in the fields of corrosion protection and surface coatings.

Index Terms— Nano particles, polymeric nano coatings, epoxy-zeolite coatings, corrosion protection.

I. INTRODUCTION

In recent two decades, nano particles applied polymeric nano coatings have been introduced as the super coating materials, which are produced by shrinking the materials in resins media at the nano and molecular level to form an impassable product. The appearance and usefulness of nanoparticles brings many advantages and opportunities to chemical and paint industries. Paint industry is the one of among all to tap the prospective of nanotechnology. Addition of nanoparticles to coatings can upgrade many properties of coating system and can produce multi-purpose coatings with a little cost difference [1, 2, 3].

Hybridization in the area of paint formulations also allows getting the new and distinguished materials. Combining resins, solvents and pigments by physical-compatible blending on the molecular level (i.e. covalently bound or simple blending) can lead to new and differentiated products.

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Similar to nanotechnology, hybrids, when formulated correctly, allow continuous improvements to materials for a large number of technological applications [7, 8, 9]. Magnesium alloys have an excellent strength to specified weight-percent ratio and are attractive materials in automobiles particularly in cars, aircrafts and high end portable devices. On the other hand they are very reactive also and thus require excellent corrosion protection. Inorganic coatings offer good protection especially under mechanical and thermal strain. However, due to the low temperature stability of most magnesium alloys, dense inorganic coatings cannot be applied using conventional techniques [5, 10, 12].

These coatings can be processed under mild conditions, but are permeable for aggressive anions. The permeability can be decreased by sealing with inorganic polymeric sols. Despite their low thickness, the resulting coatings show remarkable protective properties. With decreasing particles size the sintering temperature decreases [13 14, 15].

Tiny particles with proper dispersion at low viscosity result the defect-free thin film transparent coatings. Thicker and crack-free coatings can be achieved by multiple coating applications (up to 5 layers). The coating resistance (R_{po}) increases with each additional layer and localized corrosion becomes inhibited [16, 17, 19].

Zeolite: Zeolites are microporous, aluminosilicates minerals, commonly used as commercial adsorbents. Zeolite was originally observed when rapidly heating the material; it produces large amounts of steam from water that had been adsorbing by the required material. Based on this practice, it has been called the zeolite; from the Greek meaning boiling stone. About 194 unique zeolite frameworks have been identified, and over 40 naturally occurring zeolite frameworks are known. Zeolites are widely used in industry for water purification as catalysts, and in nuclear reprocessing. Their biggest use is in the production of laundry detergents. They are also used in medicine and in agriculture. Zeolites have a porous structure that can accommodate a wide variety of cations, such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. An example mineral formula of zeolite is: $Na_2Al_2Si_3O_{10} \cdot 2H_2O$ [18, 19, 21].

II. MATERIALS AND METHODS

In order to carry out the present research work, few objectives have been framed. First of all, problems have been identified and developed an experimental set up accordingly. Next step

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was to select different nano particles compositions for proper dispersion in coating system and their proper application techniques.

Nano particles modified surface coatings have been formulated with different approach (pigment compositions are mentioned in Table 1) and applied to protect various types of metals and alloys from corrosion and other degradation. For this purpose, epoxy-zeolite self-cleaning super hydrophobic and antimicrobial corrosion resistant coatings have been formulated to protect metals and alloys from corrosion. The corrosion protection efficiency has been improved when nanoparticles have been incorporated and dispersed into paint media.

Purely inorganic transparent coatings have been developed for the corrosion protection of magnesium alloys based on commercially available aqueous SiO₂ nano dispersions in resins media. Commercial silica dispersion with suitable sintering additives was applied onto surfaces (grinded, degreased with acetone and activated with natal solution) by dip-coating process.

Zeolite molecular sieves: Zeolite molecular sieves have been characterized by the following properties:

- Selective adsorption due to the uniform pore size of the zeolite structure.
- High adsorption capacity for polar substances at low concentrations.

Epoxy resin alongwith pigments, solvents and required additives have been blended and used as coating materials to protect the steel reinforcement structures because of its outstanding process ability, excellent chemical resistance, good electrical insulating properties, strong adhesion and affinity to heterogeneous materials surfaces [14,15, 16].

III. RESULTS AND DISCUSSION

Influences of nanoparticles on anti corrosion and mechanical properties of epoxy coatings:

Epoxy coatings generally reduce the corrosion of a metallic substrate subject to an electrolyte in two ways. First, they act as a physical barrier layer to control the ingress of harmful species. Second, they can serve as a reservoir for corrosion inhibitors to assist the steel surface in resisting the attack by aggressive species such as chloride anions. However, the successful application of epoxy coatings is often hampered by their susceptibility to damage by surface abrasion and wear [17, 18]. They also show poor resistance to the initiation and propagation of cracks [19, 20]. Such processes introduce localized defects in the coating and impair their appearance and mechanical strength. The defects can also act as pathways for accelerating the ingress of water, oxygen and aggressive species onto the metallic substrate, resulting as the localized corrosion. Furthermore, being hydrophilic in nature, epoxy coatings experience large volume shrinkage upon curing and can absorb water from surroundings [20, 21, 22]. The pores in

the cured epoxy coating can assist in the migration of absorbed water and other species to the epoxy-metal interface, leading to the initiation of corrosion of the metallic substrate and to de-lamination and blistering to the coating films. The barrier protection property of epoxy coatings can be enhanced by the incorporation of a second phase of curing resin and nano pigment compatible with the epoxy polymer by decreasing the porosity and zigzag nature of the diffusion path of harmful species [23, 24].

For illustration, inorganic filler particles at nanometer scale can be dispersed within the epoxy resin matrix to form an epoxy nano composite. The incorporation of nanoparticles into epoxy resins offers environmentally benign solutions to enhancing the integrity and durability of coatings, since the fine particles dispersed in coatings can fill cavities [22, 23] and cause crack bridging, crack deflection and crack bowing [24]. Nanoparticles can also prevent epoxy disaggregation during curing, resulting in a more homogenous coating. Nanoparticles tend to occupy small hole defects formed from local shrinkage during curing of the epoxy resin and act as a bridge interconnecting more molecules [25, 26].

Table 1. Performance test observations of coatings w.r.t. different compositions (weight % ratio) of micron & nano sized pigments in different paint formulations

Micron sized TiO ₂ Wt.% Ratio	Nano ZnO Wt.% Ratio	Zeolite wt. % Ratio (1:1)	Cross cut Adhesion Test	Gloss at 60° angle	Aging Test at 80°C for 48 hours	Salt spray Test: Passed hours
23.0	-	-	99/100 (99%)	95%	5% change in gloss	700 hours Passed
22.0	1.0	-	100/100 (100%)	98%	No change	1400
21.5	1.5	-	100/100	99%	No change	1800
21.0	2.0	-	100/100	100 %	No change	2200
22.0	-	1.0	100/100	97%	No change	1400
21.5	-	1.5	100/100	97%	No change	1800
21.0	-	2.0	100/100	97%	No change	2200
21.0	0.5	1.5	100/100	97%	No change	2600
21.0	1.0	1.0	100/100	98%	No change	3000
21.0	1.5	0.5	100/100	99%	No change	3200

Zeolite coatings

Zeolites are microporous crystalline aluminosilicates with uniform and molecular sized pores. They are non-toxic and have been explored for medical and industrial applications. The application of zeolite films as chromium-free protective coatings on aluminum alloys have been investigated. It has been shown that synthesized high-silica-zeolite (HSZ) coatings are non-porous and have excellent corrosion resistance in strong acids, bases, and pitting aggressive media. High silica coatings are very good corrosion resistant

coatings. The crystallized coating deposition process can coat surfaces of complex shapes and in confined spaces. Beving et al successfully expanded their investigations to include other aluminum alloys (6061-T4, 5052-H32, 7075-T6) and steels (SS304-2b, S1008, S4130). They were able to use one simple pretreatment and a single zeolite formulation on all aluminum alloys and steel to formulate coatings. Corrosion protection was measured by DC polarization in several corrosive media. DC polarization in 5 wt% NaCl was used as a screening diagnostic prior to salt-spray testing. Salt fog accelerated weathering tests were performed according to ASTM B-117 on scribed and non-scribed coated panels. The non-scribed HSZ MFI coated 2024-T3 panels had no observable corrosion after more than 3200 hours in continuous salt fog exposure. The scribed HSZ-MFI coated 2024-T3 panels exhibited no de-lamination of the zeolite coating after 1400 hours continuous salt fog exposure and corrosion was limited to the scribe. The compatibility between zeolite coatings with primer and top-coat systems has been investigated. A coating system of zeolite-primer (chromated) and then topcoat passed 3200 hours continuous salt spray exposure with no observable corrosion and de-lamination [1, 2, 23]. This results in a reduced total free volume as well as an increase in the cross-linking density [25, 26].

In addition to this, epoxy coatings containing nanoparticles offer significant barrier properties for corrosion protection and reduce the trend for the coating to blister and de-lamination. Homogeneous epoxy coatings containing nanoparticles of SiO₂, and ZnO were successfully prepared and applied in coatings at room-temperature-curing of completely mixed epoxy slurry diluted by acetone. The surface morphology and mechanical properties of these coatings were characterized by scanning electron microscopy [27, 28, 30,].

The effect of incorporation of various nanoparticles on the corrosion resistance of epoxy-coated steel was investigated by potentiodynamic polarization. The electrochemical monitoring of the coated steel over the required days of immersion in both 0.3-3 weight % NaCl solutions suggested the beneficial role of nanoparticles in significantly improving the corrosion resistance of the coated steel, with the ZnO nanoparticles being the best [29-31].

Corrosion resistant zeolite coatings

For over one hundred years, hexavalent chromium compounds, mainly chromates, have been widely used as a corrosion inhibitor to protect high strength Al-alloys used in aerospace and defense applications, as well as other materials in a wide range of applications [3-5]. Chromate can be applied to a surface as a chromate-conversion coating or added to paint as a pigment. Unfortunately, chromate has become stringently regulated because it is highly toxic and carcinogenic; hence, a chromium-free alternative with equivalent or superior corrosion performance is critically needed.

Zeolites are a class of crystalline oxides with uniform channels and cages ranging from 0.3 to 2 nm. They are extensively used as adsorbents, catalysts, and ion exchange

agents. The idea of corrosion-resistant zeolite coatings takes advantages of several well-known facts about zeolite.

- i) Most zeolites are non-toxic, and some compositions are even used in food and drug applications.
- ii) High-silica and pure-silica zeolites are thermally and chemically stable. For example, many high-silica zeolites (HSZ) are thermally stable up to 1000⁰C, and pure-silica zeolites are stable in all mineral acids except hydrofluoric acid. Thus, the framework of zeolites contains the needed corrosion resistance. (As used herein, HSZs have a Si/Al ratio greater than 50, while the ratio for low-silica zeolite (LSZ) is less than 2.).
- iii) Most HSZ syntheses use structure-directing agent (SDA) molecules, which are eventually trapped inside the zeolite pores.

The SiO₂ nanoparticles were found to significantly improve the microstructure of the coating matrix and thus enhanced both the anticorrosive performance and Young's modulus of the epoxy coating. In addition to enhance the coating-barrier performance, at least another mechanism was at work to account for the role of the nanoparticles in improving the anticorrosive performance of these epoxy coatings [29, 30, 31]. Zeolite is based on TO₄ tetra-hedra like most silicates, where T is an aluminium or silicon atom (phosphorus in aluminophosphates). The vast three dimensional networks are a result of all four corners for the tetra-hedra being shared, producing low density micro porous materials.

Discussion on structure of zeolite and its properties

Zeolite structures can be thought to exist of finite or infinite (chains, layers etc) component units. An important class of materials is the pentasil zeolite, named so because they are constructed of five membered rings. The most important example is that of ZSM-5, which is shown in Fig. 1, 2, and 3. ZSM-5 is used in a variety of catalytic applications, including the catalysis of methanol into fuel hydrocarbons. The individual pentasil units are shown in Figure 1. They combine to form long chains (Figure 2), which then join together to form layers (Figure 3).

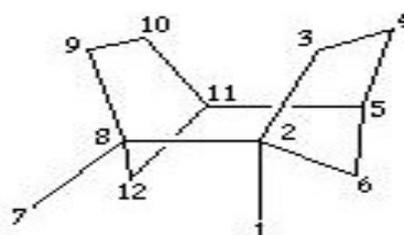


Figure 1. Secondary building units (SBU) in pentasil zeolite

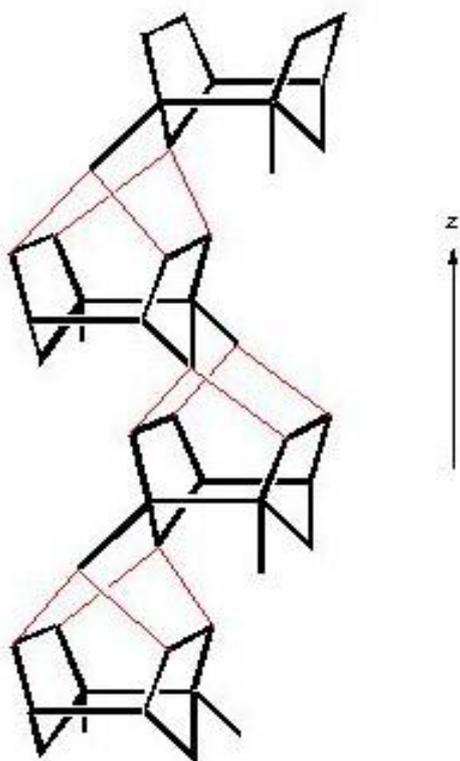


Figure 2. SBU linked chains

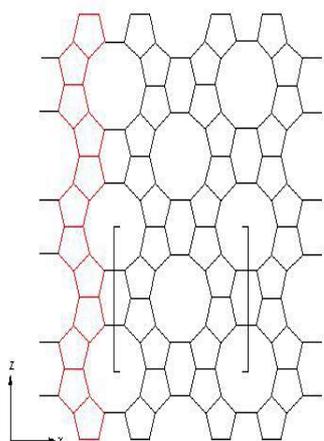


Figure 3. Layer formed from linked chains in ZSM-5 structures

Zeolite molecular sieves are crystalline, highly porous materials, which belong to the class of aluminosilicates. These crystals are characterized by a three-dimensional pore system with pores of precisely defined diameter. The corresponding crystallographic structure is formed by tetrahedras of (AlO_4) and (SiO_4) . These tetrahedras are the basic building blocks for various zeolite structures, such as zeolites (Fig 4 and Fig 5), the most common commercial adsorbents.



Figure 4. Molecular Sieve Type A



Figure 5. Molecular sieve type-X

Due to the presence of alumina, zeolites exhibit a negatively charged framework, which is counter-balanced by positive cations resulting in a strong electrostatic field on the internal surface. These cations can be exchanged to fine tune the pore size or the adsorption characteristics. For instance, the sodium form of zeolite-A has a pore opening of approximately 4 Angstrom ($4 \times 10^{-10} \text{ m}$), called 4\AA molecular sieve. If the sodium ion is exchanged with the larger potassium ion, the pore opening is reduced to approximately 3 Angstrom (3\AA molecular sieve). On ion exchange with calcium, one calcium ion replaces two sodium ions. Thus, the pore opening increases to approximately 5 Angstrom (5\AA molecular sieve).

Ion exchange with other cations is sometimes used for particular separation purposes. The pore opening of the sodium form of zeolite-X is approximately 8 Angstrom. The ability to adjust the pores to precisely determined uniform openings allows for molecules smaller than its pore diameter to be adsorbed whilst excluding larger molecules, hence the name “molecular sieve”. The different pore sizes of synthetic

zeolite open up a wide range of possibilities in terms of “sieving” molecules of different size or shape from gases and liquids.

For separation and catalysis applications, these molecules are normally removed before use. However, for anticorrosion applications, it is better to retain the SDA since it was recognized that defect-free as-synthesized zeolite can be gastight, and some SDA molecules, such as amines, have already been used as corrosion inhibitors. These facts all suggest that as-synthesized zeolite films can be corrosion resistant. Recent technological advances of Zeolite corrosion resistant coatings have been reported [9-12].

Nano Particle incorporated self-cleaning coatings and biocidal coatings

There is a great interest in the design and development of surfaces that not only provide biocidal activity but are also easy to clean and even self-cleaning. Most of such coatings acquire their biocidal/self-cleaning capacity by incorporating specific nanoparticles: basically silver (Ag) and rutile titanium dioxide (TiO₂) [29, 30, 31]. Nano TiO₂ is used for developing self-cleaning, UV-rays-resistant, and anti-bacterial paints. This possesses self-cleaning hydrophobic properties, which causes water droplets to bead-off of a fully cured surface picking up dirt and other surface contaminants along the way. This self-cleaning action helps clean and maintain important surfaces and to accelerate drying, and leaving the surface with minimal spotting. A recent study by Cai et al, utilizes corona treatment technique, inert sol-gel coating and anatase TiO₂ layer. With the corona treatment, an organic surface was activated to allow a uniform TiO₂ sol-gel coating. Nanoparticles of surface-treated Al₂O₃ molecules help increase hydrophobicity and increase scratch resistance.

Microbial evolution on a wide variety of surfaces can cause corrosion, dirt accumulation, bad odor and even serious hygiene and health problems. Advanced Nanostructured Surfaces for the Control of Bio-fouling (ANSCB), a European Union Research Project has been investigating that how to prevent the build-up of organisms on surfaces under marine conditions to avoid bio-fouling. The project aims to use nano-structuring to significantly reduce the adhesion of organisms to surfaces in aquatic environments, and thus control the fouling process without the use of toxic biocides such as copper and Chlorine compounds that prevent fouling by killing organisms. Nano-structuring of the surface alters the wetting properties and is intended to signal that the site is not suitable for the organisms to settle. The project aims to synthesize new nanostructured polymers that are stable under marine conditions. Although no alternatives to the use of biocides are available at present, creation of nanostructured surfaces could offer an innovative and environment friendly solution to the problem of biofouling [31, 32]. Research has developed new biocidal coating systems that prolong biocidal activity by immobilizing such additives on nanoparticles; the embedded biocides are designed to be released into the environment only when needed, thus extending the lifetime of the biocidal activity [32, 33, 34].

Nanoparticle based antimicrobial corrosion coatings

Marine-microbiological corruptions are responsible for considerable damages to all devices and vessels immersed in or contact with seawater, and this induces serious economic problem to maritime activities. Coating is the most convenient method for preventing the corrosion/fouling of steel surfaces, storage tanks, ship-bottoms and their super structures. Employing effective antifouling marine paints, containing booster biocides at non-toxic levels is one approach to solve the issue of fouling [38, 39, 40]. Copper and its oxides are common biocides in a large number of commercial antifouling marine paints. Commercially available antifouling coatings have cuprous oxide (Cu₂O) as the primary biocide, which typically varies from 20% to 76% copper content [39, 40].

However, recent reports have shown that 26% sampling locations per year in UK exceeded the concentration of current Environmental Quality Standard: EQS (5 micro gram per Litre) [40-43] for copper and marine micro algae were able to take up copper very quickly in natural coastal seawater [41-43]. These data suggest that monitoring of concentrations of copper is important so as not to cause ecological damage in marinas. Besides Cu, other metals such as zinc and silver exhibit antifungal and antibacterial properties, which have been widely utilized in advanced coating technologies [40-43]. Especially, silver has long been known to have strong inhibitory and bactericidal effects as well as a broad spectrum of antimicrobial activities, even at low concentrations in the ppb range. Meanwhile, silver has a remarkably low toxicity compared to other heavy metal ions, which make it possible to be more environmentally friendly antimicrobial painting additives instead of copper [40-43].

One important function of paints containing biocides or inhibitors is to obtain optimal release rate of the actual active substance into the sea. The leaching rate of biocides should not be too fast, resulting in rapid and premature depletion of the antifouling activity of marine coatings and unnecessarily high concentration in the sea. However, the release rate should not be too slow since this would undoubtedly result in fouling. In order to deal with both issues, application of core-shell structured materials should be one of the best alternatives since the shells offer protection to the cores and introducing new properties to the hybrid structures [41, 42]. Up to date, there are only some reports exploring the marine corrosion protection based on core shell structures. White et al. demonstrated the application of micrometer scale capsules loaded with oligomers for self-healing of the cracks in polymer coatings, Shchukin et al developed corrosion protection coatings with halloysite nanotubes as nano containers loaded with the corrosion inhibitors [39-41]. However, there are still challenges such as stability of core-shell particles, uniform dispersion in a matrix, and control of the release rate. Ke et al., have successfully prepared mono-dispersed Ag-SiO₂ core-shell nanoparticles with facile pathway. Ag-SiO₂ core-shell nanoparticles within the size of 50-60 nm were applied in marine antimicrobial corrosion coatings.

XRD results indicated silver was completely covered by silica and its crystal form was not affected after coated by silica. Effects of Ag-SiO₂ nanoparticles in the microbial corrosion of acrylic-coated steel were studied by means of electrochemical noise analysis (ENA). ENA results reveal that 1 wt% Ag-SiO₂ nanoparticles exhibit better antimicrobial corrosion activity

than that of conventional 30 wt % Cu₂O biocides. Inductively coupled plasma optical emission spectrometry (ICP) showed very lower amount of Ag-ions leaching from the resin-matrix, whereas a higher amount of copper ion leaching from the resin in the same period. It was concluded Ag-SiO₂ core-shell nanoparticles could enhance long-term corrosion protection in comparison with the copper biocides. This composite has a strong potential use in environmentally friendly antimicrobial coatings [40-43].

IV. REVIEW

Main advantages of nano coatings have been found:

- Better surface appearance.
- Good chemical resistance.
- Decrease in permeability to corrosive environment and hence better corrosion resistance properties.
- Optical clarity.
- Easy to clean surface.
- Anti-skinning, anti-fogging, anti-fouling and anti-graffiti properties.
- Better retention of gloss and other mechanical properties like scratch resistance.
- Anti-reflective in nature
- Chromate and lead free coating.
- Good adherence on different type of materials-surfaces.

V. CONCLUSION

Incorporation and optimum dispersion of appropriate nanoparticles in paint formulation enhance the corrosion protection efficiency and adhesion property of polymeric surface coatings. Both theoretical and experimental analysis show enhancement in the overall performances of the surface coatings. Therefore, it is recommended that the rutile TiO₂ with nano TiO₂, nano ZnO and zeolite as pigment particles can be used in paint formulations for the purpose of overall improvement in coating properties. Both theoretical and experimental analysis show enhancement in the performance of the coatings:

- Dispersion capacity of nano particles in resins media has been expected to enhance the performance of coatings.
- Nano coatings show a positive influence on the application property.
- Nano coatings may be cost effective in long run.

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