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Nanocoating of Carbon Steel for Anti-Corrosion: A Review

Nurul Nabila Mohd Din[1], Norhasnidawani Johari[2,*], Mohd Aidy Faizal Johari[1], Noor Azlina Hassan[3], Abd Halim Md Ali[4]

[1] Engineering Materials and Structures (EMaSt), Malaysia-Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia (UTM), Jalan Sultan Yahya Petra, 54100, Kuala Lumpur, Malaysia
[2] Department of Mechanical Precision Engineering (MPE), Malaysia-Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia (UTM), Jalan Sultan Yahya Petra, 54100, Kuala Lumpur, Malaysia
[3] Department of Manufacturing and Materials Engineering, Faculty of Engineering, International Islamic University Malaysia (IIUM), Jalan Gombak, 53100, Kuala Lumpur, Malaysia
[4] Malaysia-Japan Advanced Research Centre (MJARC), Malaysia-Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia (UTM), Jalan Sultan Yahya Petra, 54100, Kuala Lumpur, Malaysia

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ABSTRACT

Corrosion is gradual degradation process of metal through chemical reaction. Mostly happen by electrochemical and reaction with the surrounding environment. It affects material properties. Paint industry continuously working on the growing demand on modern coating and strives to improve their products especially to meet requirement in petrochemical industries. Over the past years nanotechnology has become more and more important in the development of coatings. Nanocoatings offer great potential for various applications due to their superior characteristics that are not typically found in conventional coatings. This paper reviews $ZnO-SiO_2$ and $CaCO_3$ as nanopowder in paint formulation as the agent for new and improved corrosion resistant coating by sol-gel method. Focusing more on epoxy as matrix and carbon steel on medium type as common substrate in nanocoating industry.

1. Introduction

Corrosion is always the major reason of energy and material loss. It was reported that 1/5 of energy globally and average 4.2% of gross national product (GNP) is lost each year due to corrosion behaviour and the economic impact of corrosion is estimated to be greater than $1billion/year in the United States alone [1-6]. This cost includes the application of protective coatings (paint, surface treatment, etc.), inspection and repair of corroded surfaces and structures, and disposal of hazardous waste materials. Atmospheric corrosion and under insulation corrosion are two major reasons of corrosion problems in different industries especially oil, gas and petrochemical industries. The solution is by introducing nanocoatings technology that significantly may yield large savings for the industry and nation; with the potential energy savings of 105 trillion Btu/year and potential cost

* *Corresponding author.*
E-mail address: norhasnidawani@utm.my

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savings of $1.74 billion/year. The large saving issues have led the project to study and formulate the anti-corrosion nanocoating. One of the study before was the investigation of compatibility between metal oxide nanoparticles and epoxy to as nanocoating materials. The sols will be prepared through copolymerization of epoxy resin hardener and with the incorporation of metal oxide nanoparticles, Zinc Oxide (ZnO) and Silica (SiO_2). Epoxy hardener will act as host while the metal oxide nanoparticles will act as guest components [7,8].

2. Nanocoating Industries

According to the research study by Thomas [1], the nanocoatings market is envisaged to grow over the next 5 to 10 years across all market segments. This is attributed to growing need for better facilities and advances in nanocoating technology. This industry is segmented by type of future markets that includes anti-bacterial, anti-fouling, anti-fingerprint, easy to maintain and self-cleaning nanocoatings. In addition, the anti-corrosive nanocoatings market is expected to grow on the strength of demand from oil and gas industries for protection of pipeline surfaces [10-12]. The schematic diagram of nanocoating as showed in Figure 1.

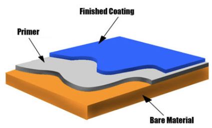

Fig. 1. Schematic diagram of nanocoating

2.1 Nanoparticles as Fillers

Adding nanoparticles into nanocoating industries giving a large impact into nanocoating industries. Nanoparticles reduced contact tension, moisture penetration and surface roughness. On the other hand, nanoparticles increased surface area, enhanced physical, chemical, mechanical, optical and magnetic properties. Nanoparticles also absorb more resins, reduced free surface. So, the transport path of corrosive species increased and enhanced the properties and performance of nanocoating. In conventional nanocoating, when there was a drop of water on the surface of nanocoating, the contact tension was normal and the moisture can penetrate through the surface surface rougnhess much more compared to nanocoating [13,19-21].

2.2 Carbon Steel

Steel is the important material that is widely used for construction especially in heavy industries such as in the petrochemical, marine, and its surface that can lead to corrosion. The properties of carbon steel depend primarily on the amount of it carbon contents. Most carbon steel has a carbon content of less than 1%. Carbon steels are use in wide range of products, including structural beams, car bodies, kitchen appliances, and cans. In fact, there are 3 types of plain carbon steel and they are low carbon steel, medium carbon steel, high carbon steel, and as their names suggests all these types of plain carbon steel differs in the amount of carbon they contain. Indeed, it is good to precise that plain carbon steel is a type of steel having a maximum carbon content of 1.5% along with small percentages of silica, sulphur, phosphorus and manganese [22,25,36,38-40].

2.3 Corrosion

According to Cabrera-Sierra *et al.*, [2] plants have suffered from continuous economic loss and human casualties due to metallic materials corrosion. Applying coating nanomaterial on the steel surfaces can prevent corrosion. Corrosion is the gradual degradation of a metal by a chemical, often electrochemical and reaction with the surrounding environment. It impacts material properties such as mechanical strength, appearance, and impermeability to liquids and gases. Factors such as the chemical environment, pH, temperature, surface finish, product design, fabrication method, contamination, and maintenance procedures can all affect the corrosion behavior of steel. There are two types of corrosions, which are wet corrosion and high temperature corrosion. Wet corrosion refers to corrosion in liquids or moist environments and includes atmospheric corrosion. It is an electrochemical process that involves an anode and a cathode, connected by an electrolyte. The metal oxidizes (corrodes) at the anode, forming rust or some other corrosion product. At the cathode, a reduction reaction takes place typically the reduction of oxygen or hydrogen evolution. Preventing corrosion involves stopping these reactions taking place [2,3,41-45].

2.4 Mechanism of Corrosion

Corrosion can be classified into three categories based on the mechanism of their reactions and these are chemical, physical and electrochemical. Chemical corrosion is purely subjected to the basic laws of chemical kinetics of heterogeneous reactions. The physical mechanism of corrosion is typified in the metallic corrosion of solid metals in contact with liquid metal. Electrochemical reactions can be divided into anodic and cathodic reactions. While anodic reaction involves anodic dissolution, at the cathode there is consumption of all the electrons released at the anode. It also depends on the environment and the cathodic reactions include metal reduction, metal deposition, oxygen consumption, or hydrogen evolution. In some corrosion reactions the oxidation reaction occurs uniformly on the surface, while in other cases it is localized and occurs at specific areas [8,50]. Schematic diagram of corrosion as showed in figure 2.

$Fe \dashrightarrow Fe^{n+} + n$ electrons (1)

$O_2 + 2H_2O + 4e \dashrightarrow 4OH^-$ (2)

$Fe + O_2 + 2H_2O \dashrightarrow 2Fe(OH)_2$ (3)

Iron + water with oxygen dissolved in it -----> Iron hydroxide

$4Fe(OH)_2 + O_2 \dashrightarrow 2H_2O + 2Fe_2O_3.H_2O$ (4)

Iron hydroxide + oxygen -----> water + hydrated Iron oxide (brown rust)

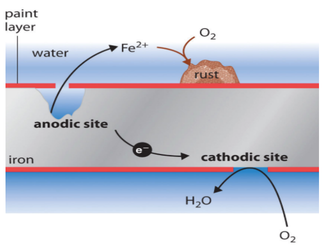

Fig. 2. Schematic diagram of corrosion process

2.5 Anti-Corrosion

Anti-corrosion refers to the protection of metal surfaces from corroding in high-risk (corrosive) environments. When metallic materials are put into corrosive environments, they tend to have chemical reactions with the air and or water. The effects of corrosion become evident on the surfaces of these materials [6,55,58]. Metal equipment lacking any preventive (anti-corrosive) measures, may become rusted both inside and out, depending upon atmospheric conditions and how much of that equipment is exposed to the air. There are a number of methods for preventing corrosion, especially in marine applications. Anti-corrosion measures are of particular importance in environments where high humidity, mist, and salt are factors [60,71].

2.6 Mechanism of Anti-Corrosion Coatings

There are so many mechanism of anti-corrosion coatings but generally, mechanism of coating can be differentiated into three, namely; barrier creation between substrate materials and environments, inhibition of the corrosion processes, and coating acting as sacrificial materials. However, recently one of the newest approaches is what is called “active-passive”. This involved the coating acting as barrier layers, which will not aloe permeation of corrosive agents to the metal surface (passive). While the active approach allows the formation of effective passive layer and this will impedes the corrosion half reactions leading to Schottky barrier at the interface resulting in depletion of electrons [6, 75, 78,91-95].

2.7 Parameter of Anti-Corrosion

a. Thickness of coating
b. Time of immersion
c. Concentration of salt water
d. Percent surface exposure

3. Epoxy

Epoxy (organic) coating is a type of common organic coatings used to protect metals against corrosion. Research by Armelin [3, 144,145,146] reported that the benzene rings in epoxy giving good properties such as resistance to chemicals, good mechanical properties, thermal stability and good adhesion make it is widely used for protective coatings. The epoxy contains ring-opening polymerization during curing time. The hydrophobic and hydrophilic group in epoxy structure increases the adhesion properties. The epoxy molecule is combined with a hardener material and effect crosslinking during curing or hardening. Epoxy is thermosetting resin, which contains low molecular weight, can either monomers or oligomers and having functional groups for cross-linking reaction. An epoxy coating is suitable to use under all different conditions [3, 96-98] such as for internal lining as well as for external coatings such as on pipelines. Epoxy increased the properties by addition of nanoparticles. The epoxy increased cross-linking density and prevent epoxy disaggregation that makes more homogeneous in coating. Nanoparticles also giving significance barrier properties for corrosion protection and reduced the coating from blister or delaminate.

3.1 Sol-gel Hybrid Coatings

Sol-gel hybrid coatings of organic and inorganic materials can combine the mechanical toughness and flexibility of organic components with the thermal stability and hardness of inorganic components [4,143]. Study by Atik and Aegerter [5] showed that by using sol gel method, metal oxides (ZrO_2) coatings provided corrosion protection of metal substrates. According to Robert [6], additives containing alumina, silica, ceria and zinc oxide nanoparticles can provide improved wear and UV resistance for UV coatings. Dispersed nanoparticles (alumina, zinc oxide and silica) can also improve corrosion resistance due to the large surface area, nanoparticles are often more efficient than micro particles, resulting in lower concentration necessary to obtain good results. The nano silica and alumina particles not only offer scratch resistance but can provide greater wear resistance, better adhesion and anti-staining because the nanoparticles create a denser, more compact film structure.

3.2 Zinc Oxide (ZnO)

Zinc oxide nanoparticles can stop solar degradation by absorption of the UV radiation. They absorb UV light and transfer it into vibration and heat. By transferring the UV light, the level of energy is lowered and does not destroy the polymer matrix. This absorption method also protects the substrate by not allowing UV radiation to penetrate through the coating. Inorganic UV absorbers do not suffer from UV light, resulting in long-term protection. Typically, low dosages of nanoparticles, 0.5-2.0%, provide significant and long-term scratch, mar, wear, corrosion and UV resistance without adversely affecting gloss, color, clarity or other physical properties of the coatings [8,117,126,143].

3.2 Silica (SiO_2)

The nano silica particles not only offer scratch resistance but can provide greater wear resistance, better adhesion and anti-staining because the nanoparticles create a denser, more compact film structure. Nanoparticle being able to improve the life cycle of coating. Nanoparticles are uniformly distributed throughout the coating, thus providing the resin or coating with a continuous, solid and protective network layer. The nanoparticles also form a unique elastomeric structure within the coating, and create a denser, more compact structure. Nanoparticles have a large amount of electrons on their surface, which can create this sacrificial anode [7,101-105].

3.3 Calcium Carbonate ($CaCO_3$)

Calcium carbonate is a non-toxic, odorless, non-irritating white powder, and it is one of the most widely used inorganic fillers. Calcium carbonate is neutral, basically insoluble in water but soluble in acid. It can improve the strength, water resistance, dryness and scrub resistance of the paint film [147].

3.4 Hybrid ZnO and SiO_2

Inorganic materials, which are SiO_2 and ZnO, will be used as nanoparticles to enhance the life cycles of coatings. ZnO material has anti-corrosion characteristics due to improve UV blocking coatings and having wavelength between 280-400nm [8,115,119,123-127]. Oxidation and acidic resistance metal can be improved by using silica oxide (SiO_2) due to its high heat and chemical resistance. In addition, carbon steel act as active material having negative value electromotive force (emf), which is -0.44V. ZnO and silica having a positif value +0.763V and +0.896V respectively and act as passive. As a result in will prevent the carbon steel from corrosion [8, 87]. The inorganic components (nanoparticle) contribute to increase the scratch and adhesion resistance on metallic substrate. The organic component (active site) increases the density and flexibility of the coating, and enhances functional compatibility with organic paint systems. Silica improves the oxidation, corrosion resistance having better mechanical properties, provide hardness, scratch and abrasion resistance and also gloss, transparency and flexibility remains unchanged [9,112]. Meanwhile, least research had been done to investigate the performance of ZnO against the corrosion but according to [10,141-143] study, ZnO was better in alkaline and salt resistance.

3.5 Hybrid ZnO and $CaCO_3$

Inorganic materials which are $CaCO_3$ and ZnO are widely use because of their low abundance and functional properties in coating. In particular, nanosized ZnO is an ideal candidate for applications that require good chemical stability and specific physicochemical properties, such as antibacterial, anti-corrosion, high photocatalytic activity, and ultraviolet absorption potentially in self-cleaning coatings,photovoltaic cells, biomedical, and cosmetic and photocatalytic surfaces [148-151]. While $CaCO_3$, the nanoparticles form a denser, more compact film structure, they offer improved adhesion, wear resistance, and anti-staining properties. $CaCO_3$ binds the aggregates and matrix more effectively, which results in reducing porosity and increases the compressive strength [152]. The ability of nanoparticles to extend the coating's life cycle.

4. Properties

Properties on selected materials in sol-gel process as stated in table 1 for ZnO and table 2 for SiO_2 below;

Table 1
Selected physical properties of ZnO [5]

Properties (Unit)	Zinc Acetate Dehydrate	Sodium Hydroxide	Ethanol
Molar mass (g/mol)	219.50	39.997	46.07
Density (g/cm^3)	1.735	2.13	0.789
Melting point (ºC)	237	0.789	114
Appearance	White Solid	White, opaque crystal	Colourless liquid

Table 2
Selected physical properties of SiO_2 [5]

Properties (Unit)	Tetraethyl Orthosilicate	Acetic acid	Distilled water
Molar mass (g/mol)	208.33	60.05	18.02
Density (g/cm^3)	0.933	1.049	1
Melting point (ºC)	-77	16-17	98-99
Appearance	Colourless liquid	Colourless liquid	Colourless liquid

5. Conclusions

Addition of nanoparticles into epoxy coating increases the performance of coating. Based on literatures, it can be concluded that inorganic nanoparticles have been used as alternative to improve corrosion resistance, which is TiO_2, Al_2O_3, V_2O_3, ZrO_2, CeO_2, ZnO and SiO_2 to improve the corrosion properties of carbon steels, by using sol gel technique [8-146]. Moreover, the nanocoating has attracted a lot of attention due to simple and cost-effective method for the enhancement of coating properties by addition of a small amount into coatings. Therefore, nanoparticles improve the corrosion properties of carbon steels by using sol gel technique. Nanocoating was expected to have the significant effect on nanocoating industry.

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