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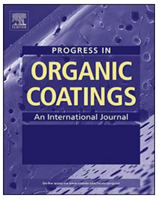

Review

Developments in smart anticorrosive coatings with multifunctional characteristics

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ABSTRACT

Smart coatings are innovative coatings that can react spontaneously, due to inbuilt stimuli-responsive mechanisms. The functionality obtained from these class of coatings at the metal-solution interface in aggressive environments has led to advances in anticorrosion studies and applications. This review emphasizes the effects of corrosion sensing, self-healing, anti-fouling, and self-cleaning coatings for corrosion inhibition of metallic materials. However, in keeping with the theme, novel coating designs with anticorrosive characteristics that outweigh the limitations in the use of conventional coatings have been discussed. Noting that the presence of high-quality nanoparticles in coating formulations has outweighed the effects of the microparticles. These have triggered unprecedented functionalities in the smart coatings. The smart coatings respond to single/multiple external stimuli such as light, dirt, pH changes, temperature, aggressive liquids, bio-foulant, impact, fatigue etc; and have demonstrated outstanding, barrier properties with scratch resistance, in-situ healing, super-hydrophobicity, superoleophilicity, high optical transmission, thermal stability, and resistance to strong acids etc., resulting in extended service life of the coatings and the protected metallic materials. The utilization of smart coatings in complex, real-time conditions, effectively controls the triggers of metallic degradation, structural failures, and resource depletion.

1. Introduction

Coatings for corrosion inhibition purposes are usually applied as functional barriers in various environments such as continuous immersion in water, buried in soils, exposed in industrial areas and faced with ultraviolet radiation, hot corrosive liquids, and air pollution. Specifically, coatings in industrial areas are constantly exposed to chemicals and acid rain while coatings on soil buried structures or in water encounter micro-organisms and humidity. The categories of coatings frequently used are metallic, inorganic, organic and hybrid coatings. While substrate preparations, primer, and topcoat selection are the three pertinent factors to note when considering the application of any of these categories of coatings. Nevertheless, failure is inevitable if no appropriate considerations of the aforementioned are met [1–4]. Coatings most importantly provide barrier protection to materials amongst other functions and generally experience atmospheric elements, wide temperature ranges, and electromagnetic radiations. These effects have the tendency to degrade coating matrices of industrial facilities and products on exposure resulting in initially unseen micro cracks. With time, these cracks degenerate into actual fractures which can be seen and due to their position of occurrence eventually give rise to coating failure. This encourages cost intensive damages alongside severe corrosion reactions on the metallic substrate. A reliable coating should, therefore, be cost effective and exhibit the following characteristics: low moisture penetration, impact resistance, durability, chemical resistance, good substrate adhesion, good surface morphology, environmentally friendly, and flexible asides from being easy to apply [5–8].

In corrosion resistance, we look forward to one or more of the following to protect the metal substrate: (i) utilizing corrosion inhibitors that can provide a resistive film on the substrate during application, (ii) a coating that can provide an impermeable barrier to moisture and corrosive species. The single layer polymer only coatings referred to as intrinsically conducting polymer coatings has been reported [4–9]. For enhanced barrier efficiency of coating systems, the inhibitors are often included in surface pretreatments and primers and usually at low concentration levels [10]. Some stand-alone single–layered barrier coatings have been tried and some others are more complex multi-layered coating formulations. Single-layered barrier coatings consisting of the necessary inhibitors mixed therein for their improved

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performance have been reported [11,12] and there has been obvious degradation of some of the polymeric matrices used alongside deactivation of the inhibitors therein [13]. Some of these coatings were as thick as 250–400 μm and presented some limiting factors like low mechanical strength and inability to withstand temperatures beyond 150 °C [12]. For significant corrosion protection, a single layer of coating is not sufficient, a more robust coating system consisting of surface pretreatments, primers, undercoats, and topcoats is mostly used. These multi-layered coatings are multifunctional because the pretreatment layer and primer layer enhance adhesion and provide corrosion inhibition to the substrate metal, undercoat layers enhance durability, and topcoats provide aesthetics with added environmental resistance. Furthermore, environmental compliance is a key requirement for an acceptable coating alongside impermeability and inhibition. This is where the inorganic zinc-based primers are good examples. They are the industry-standard chromium alternatives that act as cathodically protective pigments [14]. However, there should be compatibility between the different layers and a synergy is required to enhance overall corrosion protection. The wrong combination of coating materials possibly will result in premature failure [10].

The notable inhibiting products of the coatings industry are the smart coat category. These smart coatings consist of inhibitors alongside other additives and reflect the advancements in corrosion inhibition process of metallic materials, with their multifunctional and eco-friendly properties. The considerations in this review highlight a critical examination of corrosion resistant effects and some interrelated functionalities of smart coatings. It examines corrosion sensing, self-healing, anti-fouling, and self-cleaning functionalities of smart coatings and their contribution to corrosion protection of metals. The review also includes some limitations encountered during fabrication and applications. All aspects within the scope of our consideration cannot be completely covered in this active area of research but we present the examinations carried out by the last one and a half decade on corrosion protection with these materials.

2. Smart coatings

Depending on the formulation, smart coatings are special films that exhibit auto-responsive characteristics, when in contact with an aggressive environment. Smart coatings provide feedback responses during corrosion processes, which enhance durability [10]. Thus, smart coatings are innovatively formulated for diverse applications and can react spontaneously due to predefined stimuli-responsive mechanisms. This creative concept has initiated interesting research in its direction to determine how active and functional these coatings are. The multifunctional qualities in smart coatings observed so far when applied to extend the life of metallic substrates and equipment have greatly improved the value of anticorrosive coatings. The smart coatings respond to the aggressive changes caused as a result of a change in pH, temperature, pressure, surface tension, ionic strength, electrical or magnetic fields, acoustics, light, mechanical forces including abrasions etc. resulting in certain photochemical, acid-base, complexation, bond formation/breakage, electrochemical reactions etc. [15]. The majority of these class of coatings are formulated in synergy with inhibitors, to ensure that anticorrosive properties are improved as other additional properties are sought for. Application of corrosion inhibitor loaded coating varies, depending on the mixture, thickness, and particular functional purpose. The layers of coating importance are pre-treatment, primer, and topcoat [16]. With the advent of smart coatings, the primer layer can also be used as a pre-treatment layer but loaded with inhibitors in combination with the relevant pigments for corrosion protection and subsequent healing effects [17,18]. With the use of smart coatings, modified optical properties, modified electromagnetic properties, self-destructive abilities, substrate adhesion, surface functionality etc. have been experienced. These features were observed based on the coating composition and morphology of molecular (bulk) or nanometer scale additives, corrosion inhibitors and polymers that make up the coating systems [15].

The idea of nanoparticles within a polymer resin has been well received as an important eco-friendly step expected to bring satisfaction, with respect to toughness and reliability of the coating. This is because polymeric nanocomposite coatings have been designed in such a way that combined effects of water resistance and elasticity; permeability and hardness of both the organic polymers and inorganic nanomaterials have been achieved [19]. The fine nanoparticles within fills the cavities in the organic coating, that results in crack bridging. Disaggregation during curing is thus encouraged with a reduced tendency for the coating to blister or delaminate. This experimental observation of nanoparticle/capsules reported has yielded better features than that of the bulk corrosion inhibitors; corrosion inhibitors only in a coating or microcapsules loaded with corrosion inhibitors in coatings [11]. Particle behavior along with spatial distribution are greatly influenced by the interaction between ligands within the polymer molecules and the nanoparticles attached to them. These nanoparticles are also attached by electrostatic interactions and strong covalent bonds within the polymer molecules [20]. Examples of smart coatings include the following, but not limited to: thermochromic coatings, photochromic coatings, smart coatings for window, paints with pressures sensing capability, self-cleaning coatings and superhydrophobic systems, electrochromic coatings, antimicrobial coatings, self-healing coatings, anti-fogging coatings, corrosion sensing coatings, pH-responsive coatings, intumescent fire-retardant coatings, antifouling coatings, radio frequency identification coatings, anti-friction, anti-icing coatings etc. When applied to the surfaces of the respective products they also account for decoration in their functionality. These chemically active smart coatings exhibit their functionality either on film–substrate interfaces, air–film interfaces or in the bulk of the film [5–8]. Table 1 [21] presents a summary of multifunctionality of various smart coatings containing nano-additives for mostly automotive and construction sectors.

Specifically, in the industrial sector multifunctionality of smart coatings is an advantage. Triggers for smart responses come from both internal and external stimuli. Fig. 1 illustrates a smart coat response to external stimuli. Therefore, when a stimulus is initiated, the signal is received by the material and a physical or chemical process is induced by this signal. Signals that trigger responses within coatings and modify bulk properties of the coatings are referred to as internal stimuli. This can be observed in corrosion sensing and self-healing coatings. While external stimuli are from signals whose responses alter the surface characteristics of the coatings in relation to its environment, as seen in self-cleaning and anti-fogging coatings. Enhanced performances can be seen when both active and passive components are embedded in the smart coatings. This provides fast responses from changes, like scratches and cracks occurring in the coating or changes in temperature, pH, and salinity [1–5,7]. Due to the complex nature of the coating–metallic substrate systems in use, high performances of some coatings is observed to be reduced during service. Coating achievement and durability desired is dependent on the substrate type, substrate pretreatment, coating thickness, curing time, environmental factors as well as adhesion of coating on the substrate [2]. Also, coating structure and morphology will experience changes depending on composition. Coatings with outstanding properties to delay the onset of corrosion, provide corrosion sensing indications alongside crack repairs are preferred. This category of coatings exhibits their functions including conservation of energy and resources. These ‘defensive coatings’ ensure there is a lasting protective effect as well as a restrictive effect, and subsequent corrosion deterrence once the protective barrier is broken [5,22]. For the purpose of these considerations, our focus is only on corrosion sensing, self-healing, anti-fouling and self-cleaning coatings. These four categories of smart coatings with notable anticorrosive qualities are discussed with some schematics and surface morphological references to aid explanations.