



Galvanic function of zinc-rich coatings facilitated by percolating structure of the carbon nanotubes. Part II: Protection properties and mechanism of the hybrid coatings

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ABSTRACT

Innovative zinc-rich hybrid paint coatings were developed using nano-size particles composed of alumina hydrate modified with polystyrene-sulfonate (PSS) doped polypyrrole (PPy) and either purified or functionalised multi-walled carbon nanotubes (MWCNTs). General properties of the particles and their dispersions were characterised in 1st part of the work. Corrosion protection characteristics of the hybrids were examined on low-carbon steel panels by immersion and salt-spray chamber tests. Immersion tests were monitored by electrochemical impedance spectroscopy (EIS). Primers were analysed by glow-discharge optical emission spectroscopy (GD OES) and surface of the steel substrates was investigated by X-ray photoelectron (XPS) and FT-Raman spectroscopy. Improved barrier and galvanic function of the hybrids over traditional zinc-rich paints (ZRPs) were evidenced by performance metrics. Optimal protection characteristics were found when content of the particles was close to the statistical and kinetic percolation thresholds. Advanced protection mechanism of the hybrids is discussed on function of the nano-size filler benefiting the utilisation of sacrificial current output of the anodic zinc along with taking into account aspects of the multiple percolation theory. The interpretation given in this work is intended to facilitate design of next generation of corrosion protecting metal-rich coatings.

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1. Introduction

Besides the investigation of corrosion prevention mechanism [1] with modified compositions [2], recent development of conventional ZRPs incorporates the application of hybrid binder [3] and hybrid pigment based paint formulations. To lower excessive anodic currents and to obviate premature cathodic delamination, hybrid composition of the ZRPs with intrinsic conducting polymers (ICPs), i.e., polyaniline [4,5] and polypyrrole [6,7] has been invented. CPVC is based on geometrical, or more exactly statistical percolation of the solid particles, resulting in electrical percolation of the primers. Otherwise, environmental and economical considerations urge paint industry to develop new products having reduced zinc content while keeping mind the relevance and inevitable impact of the critical pigment volume concentration (CPVC) [8] which is always a priority to provide reliable thermodynamic protection

[9]. Accordingly, the role of ICPs as semi-conducting particles is to lower metallic grain contents and increase barrier nature of the coatings (similarly to carbon black) [10] as well as to inhibit surplus sacrificial galvanic and self-corrosion of the anodic pigments. Regarding the improvement of the fillers, both free-standing [4,5] and core-shell particles [11,12] have been introduced. Salt and base forms of polyaniline (Pani) have been favourably used in powder coatings [4] and liquid paints, respectively [5]. However, in zinc-rich composition, only clay supported Pani was applied with hybrid, i.e., ethyl silicate binder [13]. From all types of carriers, carbon nanotubes (CNTs) are exotic agents to support ICPs, e.g., PPy and thereby improve protection characteristics in cases of stand-alone polymer films [14] and organic binder composited paint coatings [15]. Nevertheless, relatively small number of studies has been pursued to examine and construe the role of ICPs in ZRPs and the absence of CNT application in these works is obvious. The latter is partly explained by negative effects of the CNTs on corrosion resistance of metals [16–19]. The causes are well known as micro-galvanic action between CNTs and metallic components, and catalytic activity of the CNTs towards accelerated oxygen

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reduction because of depolarised interfacial charge-transfer kinetics, as a result of the efficient cathodic function [20,21]. This behaviour hinders the utilisation of CNTs despite their otherwise preferable properties which are highly anticipated to be exploited even in the field of corrosion protecting composites. In spite of these findings, there was a successful attempt by tackling some of the shortcomings [22]. On the other hand, some articles showed positive results of corrosion inhibition – anodic protection by applying CNTs in stand-alone PPy film [17] and organic binder composited coatings [18]. In addition, one study was devoted to investigate the potential of vehicle composited nano-size alumina monohydrate supported PPy for corrosion inhibition of aluminium alloy [23]. Furthermore, siloxane–polymethyl methacrylate matrix based coatings with functionalised multiwall carbon nanotubes (MWCNTs) provided better protection characteristics compared to CNT-free alternatives as a consequence of good barrier nature of the coating by high covalent bonding through siloxane end groups [24].

Therefore, in this paper we analyse the corrosion protection features of paint coatings formulated with PPy-coated CNT particles described in the first part of this contribution [25]. Our formulation consists of zinc particles at reduced weight fraction (70%) supplemented by a fixed weight fraction of the inhibitor particles; as relative fraction of the nanotubes varies between the different particle types, we are able to determine the preferable amount of the CNTs so that we can explore the effect on electrical percolation based galvanic corrosion prevention function of the hybrid ZRPs. The ratios of PPy coated alumina and the nanotubes in a zinc-rich composition are also to be probed. Thus we can disclose the relevance of different particle assemblies with their percolating or non-interacting structure both in the coatings and the binder matrix. The entire range of the active/passive protection characteristics is analysed as a function of composition of the particles, particle dispersions and the hybrid paints to draw conclusion on the importance of submicron-scale distribution and interaction of the nano-size additives as well as the nanotubes themselves. Based on observations, we delineate conditions of application of the MWCNTs in metal-rich paints with the purpose to propose simple modelling so as to facilitate future prosperous engineering of cathodic type galvanic protecting paint coatings.

2. Experimental

2.1. Preparation of paint coatings

The substrates of low-carbon steel panels (RS type CRS, roughness; 25–65 μm , complying with ASTM A1008.1010, A-109 and QQS-698 standards) were used as received (Q-Lab, Ltd., USA). Particles were dispersed after 20 min mortar grinding and milling in dissolved epoxy (at polymer conc. of 50 wt.%). The organic solvent was composed of 80:10:10 volume% of xylene (Fluka), 1-methoxy-2-propanol (Fluka) and 2-butanone (Aldrich). Powdered samples were applied in quantities to give primer coatings with relative amount of the particles at 3.21 wt.%. Suspensions of the particles were mixed with component A; stabilised zinc-rich masterbatch (HZO Farbenzinkstaub, Norzinco GmbH) in epoxy (Epoxidharz CHS141, bisphenol-A epoxy resin, Prochema). Component B; poly(amido amine) cross-linking agent (Durepoxy H15VP, USNER), was added to the suspensions, stirred to homogenise and diluted to get desired wet-concentration. Primer coatings were roll-blade casted on steel panels in 90 μm wet thickness ($35 \pm 5 \mu\text{m}$ dry thickness) and let cure for a week at $25 \pm 3^\circ\text{C}$. Top-coatings were layered on hardened epoxy in overall wet thickness of 120 μm ($80 \pm 5 \mu\text{m}$ dry thickness) with Macrynal SM 2810/75BAC hydroxyacrylic resin (CYTEC Industries, Inc.) cured with hexamethylene

diisocyanate (Desmodur[®] N75MPA/X, Bayer Material-Science LLC) which was dissolved in the mixture of n-butyl acetate, xylene and isobutanol (2:2:1). Coatings were dried and cured for 3 weeks at $25 \pm 3^\circ\text{C}$. Scribes were made by a blade as X-cuts. Composition of the paint coatings are summarised in Table 1. Volume ratio of the micron-size isotropic zinc content was aimed at keeping considerably low (~ 0.27) less than half of the traditional ZRP type Z (~ 0.58). At such a low volume ratio, auxiliary fillers must be present in the vehicles at contents to provide the necessary electrical percolation but remaining fully enclosed by the organic binder not to increase electrolyte diffusion, permeation through the primer. This sets an upper limit in contents of the nano-size fillers as they feature high volume exclusion effect because of their high interacting surface if they are well dispersed, wetted and activated. In our case, the lower particle content limit was estimated by relying on rheological characterisation results indicating the impact of both the geometrical (statistical) and kinetic percolation thresholds using various measurement methods. On the other hand, our extensive results with anodic protecting paint coatings [15] furnished us to make assessment of the recommended particle content range in the epoxy resin too. So, relative amount of the nano-size particles in the epoxy was set based on content of the binder as it would be a metal-free neat coating. Furthermore, the utmost difference between the investigated systems lays on the various nanotube contents of the particles which translate into different amounts of carbon, spatial density of the nanotubes and their filaments. As for the spatial density differences, estimations were based on the average diameters of the applied nanotube samples.

2.2. Immersion and salt-spray chamber type accelerated corrosion tests

Immersion tests were carried out for 254 days with 1 M sodium chloride solution at room temperature, changing the electrolyte in every 42-day period. Corrosion tests were performed by a spray/prohesion/humidity cabinet (SF/MP/AB100, C+W Specialist Equipment, Ltd., UK) installed with a Jun-Air oil-free compressor (OF302, Gast Manufacturing, Inc., USA). The 45 min cycles were divided into two phases. In the first 25 min, samples were exposed to salt fog combined with prohesion. Dosage rate of the sodium chloride solution (5 wt.%) was $7 \text{ cm}^3 \text{ min}^{-1}$. Temperature of the chamber was set to 35°C and the salt solution was heated up to $45 \pm 3^\circ\text{C}$. In the second phase, the temperature was held at 35°C for 20 min without application of salt mist. Test cycles were repeated for 142 days. Assessment of both types of corrosion propagated samples was performed according to the EN ISO 4628:2005 standard.

2.3. Investigation of corrosion propagated paint coatings

2.3.1. Electrochemical impedance spectroscopy

A platinum spiral, SCE and glass-tube-fitted paint coatings covered steel panels ($A = 5.3 \text{ cm}^2$) were used as counter, reference and working electrodes, respectively. Immersion tests were performed with an electrochemical cell configuration proposed by Kendig et al. [26] which is known as “Rapid Electrochemical Assessment of Paints” method. The electrochemical cell and the Zahner IM6eX potentiostat–frequency analyzer (Zahner-elektrik GmbH and Co., Germany) were placed into two grounded Faraday cages wired to each other. OCPs were measured in an open cell configuration. Then impedance measurements were carried out in the frequency range of 10 kHz and 20 mHz applying sinusoidal perturbation of 20 mV. The most probable electrical circuits with the lowest number of discrete elements were used for modelling. In all cases, resistance of the electrolyte solution ($R_s = 25 \text{ ohm}$) was assumed to be the same

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