Progress in Organic Coatings 102 (2017) 60–65

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Effect of inhibitor-loaded halloysites and mesoporous silica nanocontainers on corrosion protection of powder coatings

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ARTICLE INFO

Article history:
Received 25 February 2016
Received in revised form 31 March 2016
Accepted 19 April 2016
Available online 20 May 2016

Keywords:
Nanocontainer
Self-healing
Halloysite
Mesoporous silica
Salt spray test
Anticorrosion

ABSTRACT

We carried out the comparative study of the effect of inhibitor-loaded nanocontainers on the corrosion protection performance of polyester powder coatings by neutral salt-spray test (5% NaCl, 35 °C, different time). Halloysites and mesoporous silica particles loaded with corrosion inhibitor 8-hydroxyquinoline were homogeneously distributed in powder coating effectively reducing corrosion of the metal substrate over 1000 h of salt-spray test. Addition of only 2 wt.% of inhibitor encapsulated either in halloysites or in mesoporous silica particles to the powder coating is sufficient to decrease the delamination effect by >4 times and to suppress the formation of the blisters on the low carbon steel substrates.

1. Introduction

Self-healing activity of the materials is based on their feedback action. The trigger for feedback action can be an external signal applied to the material (light, mechanical force) or changes of the internal properties (like local pH-changes during corrosion process) and overall material integrity [1]. The output of the trigger is the restored functionality of the initial material, in our case corrosion protection ability of the coatings. First simple approach for providing self-healing to the organic coatings is to directly introduce corrosion inhibitors in the pretreatment, primer or topcoat layer of the coatings [2]. The idea behind is the response to the coating damage by diffusive or stimuli-induced release of the inhibitor from the coating matrix. Direct introduction of the inhibitor into the coating matrix showed successful results for some classes of the inhibitors (like phosphate pigments); however, there are difficulties with application of inhibitors with very high or low solubility in paints [3,4]. Very low solubility of inhibitor leads to its deficit in the damaged area. In case of too high solubility, metal substrate can be protected for only a relatively short time due to rapid spontaneous leaching of inhibitor from the coating [5]. Another drawback, which can appear due to high solubility, is the osmotic pressure initiating blistering and, finally, delamination of the coating [6,7].

The new and promising solution to avoid interaction between inhibitor and coating matrix is to encapsulate the inhibitor into stimuli-responsive capsules [6,8]. Capsules or nanocontainers can isolate encapsulated corrosion inhibitor from coating matrix, prevent spontaneous leakage of inhibitor and, at the same time, provide controlled release of the inhibitor directly into the corroded area. There are several approaches demonstrated so far for the design of nanocontainer systems: (i) polymer containers [9], (ii) halloysites [10], (iii) nanocontainers with polyelectrolyte shell [11], (iv) layered double hydroxides [12], (v) ion-exchange organic resins [13], (vi) conductive polymer matrixes [14] and (vii) mesoporous inorganic materials [15]. Depending on the selected approach, the size of the containers can be varied from 20 nm to 50 μm and, besides permeability control, the shell can have other functionalities (magnetic, catalytic, conductive, targeting, etc.).

The current level of the development of nanocontainer-based self-healing coatings shows large number of the highly-efficient examples on the laboratory scale [16,17]. However, there are two main difficulties for the transfer of the research to commercial applications: (i) the costs of the nanocontainers and (ii) lack of valid industrial test results (mostly salt-spray tests). The first problem requires the search for cheap nanocontainer hosts which can be available in large-scale quantities. Halloysites and mesoporous sil-

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http://dx.doi.org/10.1016/j.porgcoat.2016.04.031
0300-9440/

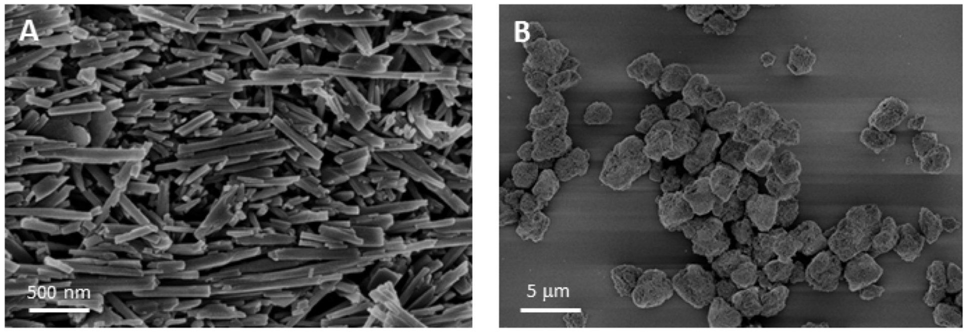

Fig. 1. SEM images of halloysite nanotubes and mesoporous SiO_2 particles used for encapsulation of corrosion inhibitor.

ica particles can be perfect candidates here. They are much cheaper comparing to the other types of nanocontainers and commercially available in large quantities [18]. Additional interest of using inorganic nanocontainers is mechanical and thermal stability, which allow their utilization in different coating layers (pre-treatment, primer, topcoat) subjected to high mechanical loads or significant thermal stresses.

Halloysites are defined as two-layered natural aluminosilicates chemically similar to kaolin, which have a predominantly hollow tubular structure in the submicrometer range [19]. Efficient self-healing properties of the benzotriazole and 8-hydroxyquinoline loaded halloysite nanotubes were demonstrated in zirconia-silica sol-gel coatings deposited on the surface of aluminium alloy A2024 [10]. To prevent undesirable leakage of the loaded inhibitor from the halloysite interior at neutral pH, the outer surface of the halloysite nanotubes can be modified by deposition of alternating polyelectrolyte multilayers (poly(allylamine hydrochloride)/poly(styrene sulfonate)) [20].

Another type of the nanocontainers with inorganic scaffold is mesoporous silica. It is inert to the most of the corrosion inhibitors and has high specific surface area (>1000 m^2/g) [21]. The incorporation of inhibitor-loaded mesoporous nanocontainers into inorganic sol-gel coatings improved significantly the coating corrosion resistance [22]. On one hand, the coating barrier properties were enhanced by reinforcement of the coating matrix caused by introduction of mechanically stable, robust silica nanoparticles. On the other hand, the large amount of encapsulated inhibitor (up to 80 wt.%) and its controlled release upon corrosion attack provided superior corrosion inhibition. Additional advantage of the silica nanocontainers is the possibility to tailor hydrophobic surface functionality for solvent-born coatings. Mesoporous SiO_2 functionalized with octyl groups and loaded with benzotriazole showed tenfold greater corrosion protection performance in polyester-based commercial coatings than for the coating without nanocontainers [23].

Despite large number of the papers devoted to the nanocontainer-based self-healing coatings, most of them use lab-scale analytical methods for characterisation of their self-healing performance: EIS, polarisation, SVET and various adapted electrochemical techniques. Only a few papers [24] analysed the efficiency of the nanocontainer-based coatings using industrial methods. Here, we attempt to decrease this "transfer gap" and present comparative analysis, done by industrial neutral salt-spray test (ISO 9227), of the corrosion protection performance of 8-hydroxyquinoline (8-HQ) loaded halloysites and mesoporous silica particles impregnated into polyester powder coating. Coatings with and without nanocontainers were tested on bare low carbon steel substrates.

2. Experimental procedure

2.1. Materials

Corrosion inhibitor 8-hydroxyquinoline, ethanol, acetone, HCl, NaOH and NaCl were purchased from Sigma-Aldrich and used without further purification. Halloysites were provided by Atlas Mining Company (Dragon mine deposit, Utah, USA) and mesoporous silica particles were purchased from Grace, USA (SYLOID® C803 silica). Halloysites are naturally occurring layered kaolin aluminosilicates with hollow tubular structure. The aluminium hydroxide and the silicon oxide layers are bond covalently with each other. The bilayer rolls up to a tube, i.e. a hollow cylinder with alumina layer inside and silica layer outside [25].

Halloysite nanotubes from Dragon Mine deposit have elongated form with average length around 1 μm with outer diameter around 50 nm and inner lumen of 15–20 nm diameter (Fig. 1a). Mesoporous SYLOID® C803 silica particles have irregular shape and average size of 3–4 μm (Fig. 1b). BET analysis demonstrated specific surface area of 60 m^2/g with pore volume of 0.2 cm^3/g for halloysites and 285 m^2/g with pore volume of 1.4 cm^3/g for mesoporous SiO_2.

Powder coatings were prepared on the basis of polyester resin Crylcoat 2698-3 provided by Cytec Industries Inc., USA. Cold rolled low carbon steel plates for neutral salt spray tests were purchased from Rocholl GmbH (Germany) and had dimensions $L \times W \times T = 150 \times 75 \times 2$ mm and surface cleanliness grade SA2.5.

2.2. Preparation of the coatings

Loading of the nanocontainers with 8-hydroxyquinoline was performed from 33 wt.% acetone solution under reduced pressure. 50 ml of 33 wt.% 8-HQ were mixed with 5 g of empty nanocontainers (halloysites or mesoporous silica particles) and then introduced into a desiccator with reduced pressure. As the air goes out from the nanocontainer inner volume, the solution containing corrosion inhibitor fills all pores. The loading was performed three times followed by centrifugation of the nanocontainers suspended in water at 5000 rpm each time. The loading capacity was measured by TGA analysis of the prepared nanocontainers. The maximum 8-HQ loading inside halloysite nanotubes was 20 ± 3 wt.% while loading capacity reached 77 ± 4 wt.% for mesoporous SiO_2.

On the next stage, 8-HQ loaded nanocontainers (10 wt.% of halloysites or 2.6 wt.% of SiO_2) were mixed with the powder coating composition using a laboratory extruder in order to achieve the same concentration of inhibitor in the final coating for both halloysites and mesoporous silica (2 wt.%). The coating was deposited on the metal substrate and cured for 10 min at 190 °C object temperature. The final coating thickness was 85 ± 5 μm for all samples.