



Effects of accelerated ageing conditions on the mechanism of chemically-active antifouling coatings



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ABSTRACT

The accelerated ageing of chemically-active antifouling coatings was investigated by performing *in vitro* and *in situ* static/dynamic cycles. One of the main objectives of this study was to develop an ageing test able to predict long-term antifouling coating performances in less than one year with a mechanism which is representative to the natural ageing. One self-polishing copolymer (SPC)-based coating and one controlled depletion polymer (CDP)-based coating were selected because of their well-known distinct mechanisms of action. Five static artificial conditions were used in cycles and their influence on the ageing of two coatings was investigated. Comparison of two key parameters such as erosion of the coatings and formation of a leached layer or a depleted layer at the surface of the two coatings were investigated in accelerated and *in situ* tests. Results support the different mode of action of the two coatings. The static artificial conditions were shown to affect the residual antifouling efficiency differently. Deionized water buffered at pH = 8 with tris(hydroxymethyl)methylamine was the only static artificial condition that led to an acceleration of both the formation of a leached layer or a depleted layer at the surface of the two coatings and their erosion.

1. Introduction

The objective of accelerated ageing tests is to predict long-term performances and to determine whether or not a system is durable enough to satisfy the service life demand. The efficiency of chemically-active antifouling coatings is mainly based on the release of biocidal species from the coatings into the seawater [1]. The mechanism of action of chemically-active coatings is a complex one involving kinetics of dissolution of fillers and biocidal pigments and kinetics of hydrolysis/solubilization of the polymer matrix initiated by the diffusion of water within the coating. Seawater-soluble pigments dissolve near the surface of the coating creating voids in the upper coating layer. The distance from this dissolving front to the surface of the coating is termed as leached layer or depleted layer. Dissolved species diffuse out of the coating through the seawater-filled leached layer. The polymer matrix could be also sensitive to hydrolysis reaction or solubilization depending on its chemistry. For SPC coatings, when the polymer matrix hydrolysis proceeds, the polymer chains become more and more hydrophilic. The voids, filled of water, play a role in the kinetics of solubilization of the polymer matrix as the water/matrix interface area increases with time. At a certain extent of hydrolysis or depending on its hydrophilic character, the polymer begins to erode by moving seawater. Then, two moving fronts, the dissolving pigment front and the

erosion front, vary over time. A constant thickness of the leached layer with *in-service* time associated with a linear thickness loss of the coating is related to a self-polishing behavior of the coating. The integrity and the mechanical properties of the coating are therefore affected. The mechanism of action of a self-polishing copolymer (SPC)-based coating and a rosin-based ablative coating by simulating diffusion processes have been extensively studied [2–5]. Fayé et al. investigated microscopic, spectroscopic and indentation experiments to monitor the diffusion of biocidal species out of the coating and any variation in mechanical properties at the coating surface [6]. Each step of natural ageing processes is not so easy to simulate [7]. Therefore, long-term ageing tests in conditions as similar as possible as those encountered in service are crucial experimental inputs before launching a new coating formulation into the market.

There are two main ways for testing the AF performances of coatings in the marine environment: static and dynamic real-life tests. In case of *in situ* static immersions, tests are normally conducted for 1–5 years depending on the coating performances through assessing the percentage and the type of biofouling settled on coated panels [8]. Dynamic tests are currently used to expose coatings to shear stress, hence simulating exposure conditions experienced on ship hulls [9,10]. Such dynamic conditions are especially relevant for SPC or Controlled depleted polymer (CDP)-based coatings where erosion of the coatings is

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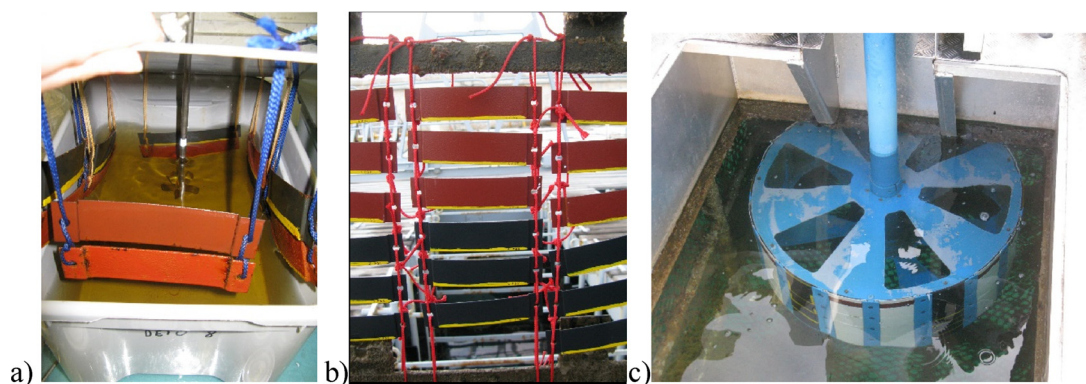


Fig. 1. a) Device used for the static phase of laboratory tests; b) Device used for the *in situ* static phase of cycling tests; c) Device used for the dynamic phase of tests: the rotating drum.

contributing to their long-time efficiency. Testing coatings on ship hulls is restricted to very promising coatings because of large financial investments involved and a lack of control over the test conditions. Field tests take a long time to be completed, therefore accelerated ageing tests have been widely used in the coating industry to save time and money at the stage of developing new products.

Accelerated ageing tests are currently used for assessing anticorrosive coatings for ship hulls or offshore marine protection [11,12]. Standards are available for thirty years. However, the correlation between the artificial ageing and the natural one is not obvious and requires a lot of input data. To accelerate the ageing of SPC and CDP coatings, at least during the screening stages, parameters which affect the polishing and biocide leaching rates have to be considered. Cycling static and dynamic exposures have been proposed in this work to approach the real-life use of antifouling systems. In this approach of accelerated ageing of chemically-active AF coatings, the effect of the (sea) water parameters on the mechanism of action was investigated through assessing the thickness of the surface layer depleted or leached from biocides and the thickness loss of the coating in the static phase of the static/dynamic cycles. The dynamic phase allowed studying the influence of shear stress on erosion or removal of the leached layer (LL) previously formed in static conditions. The static phase was performed in laboratory and the dynamic phase was performed by rotating the coated panels in natural seawater. Chemical reactions and diffusion phenomena are deeply affected by seawater conditions such as water temperature, salinity and pH [4,5,9,13–15]. The average salinity of the artificial seawater is currently taken around 35‰ and is known to affect the erosion of the coating and the dissolution of soluble contents [2]. A high temperature could increase the kinetics of the polymer matrix hydrolysis and of the dissolution of soluble contents in SPC coatings [4,5]. pH values of seawater vary from 7.5 to 8.5. Slightly different pH values could be found in strongly contaminated waters or locally within the coating due to the dissolution of some of the components of the AF coating (e.g. Cu_2O) [2]. As the swelling of coatings could affect the diffusion of water or soluble species, a polar organic solvent (not present in natural seawater) could also be used as ageing parameters. Two main parameters such as the thickness of the LL (SPC) or the depleted layer (CDP) and the erosion value of aged samples were assessed under various ageing conditions. Then, the residual AF efficiency of *in vitro* and *in situ* aged coatings were compared after 14 months of *in situ* static immersion on a raft.

2. Experimental

2.1. Materials

Two tin-free AF coatings (called SPC and CDP) have been furnished by International Paint Ltd. CDP and SPC coatings contain both Cu_2O

particles as the main biocidal. The amount of Cu_2O found in the safety data sheet is ranging from 30 to 60% for the SPC coating and from 25 to 50% for the CDP coating. The CDP coating contains from 2.5 to 10% of zineb as co-biocide. The SPC coating contains also copper pyrithione from 3 to 5% and CuO from 1 to 3% as co-biocides.

Artificial seawater was prepared from inorganic salts purchased from Sigma Aldrich according to ASTM D1141 – 90 (Table S1, supplementary information). Ethanol 99% was purchased from SODIPRO. Tris(hydroxymethyl)methylamine and sodium hydrogenocarbonate buffer solutions were purchased from Sigma Aldrich.

2.2. Coating application

80 μm of an epoxy vinyllic tie-coat (M121 from KOLORIAN, France) was first applied to protect steel panel substrates from corrosion. AF coatings were applied by airless spray at thicknesses recommended by the coating supplier for five years of efficiency (e.g. dry thicknesses of $2 \times 120 \mu\text{m}$ for SPC and $2 \times 85 \mu\text{m}$ for CDP).

A seawater insoluble acrylic coating was applied with a brush on selected parts of the AF coatings. This seawater insoluble coating was used to monitor the degree of polishing or erosion of the exposed antifouling coating to water with time *via* a destructive method. Small coating samples of 1 cm^2 were withdrawn from the coated panels and SEM images were taken to analyse the cross section [9,16].

2.3. Ageing devices

Coated steel panels of $150 \times 35 \times 1 \text{ mm}$ were both immersed in artificial (sea)water and *in situ* during the static phase of the ageing procedure. The immersion of specimen in artificial (sea)water was done in a plastic tank. Two strings allowed hanging up the panels to the lid of a plastic tank in order to keep them vertically immersed. The artificial (sea)water was homogenized by a mechanical stirrer (Fig.1a). The *in situ* static phase was performed by immersing specimen on a raft located in the Toulon Bay (GPS $43^\circ 06' 25'' \text{N} - 5^\circ 55' 41'' \text{E}$) (Fig. 1b). The *in situ* dynamic phase consists in using an *in situ* rotor test located in Mediterranean Sea ($43^\circ 06' 19.0'' \text{N} 5^\circ 53' 07.8'' \text{E}$) (Fig.1c). Coated panels were placed on the drum's peripheral surface which, through rotation, reaches predefined perimeter velocities up to 20 knots.

2.4. Ageing tests

Ageing tests combine water immersion under static conditions and dynamic exposures according to ASTM D4939-89 [17]. Artificial ageing tests were performed in laboratory and compared to natural ageing tests. Artificial ageing tests are composed of a 2 month-static exposure in laboratory (designated as "Lab") followed by an *in situ* dynamic phase on rotor for 15 days (designated as "rotor"). Five artificial static

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