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Assessment of steel corrosion and deadhesion of epoxy barrier paint by scanning Kelvin probe

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ABSTRACT

Marine paints are complex polymeric systems containing layers of different nature that significantly delay the corrosion failures. In order to obtain a rapid ranking in the corrosion protection provided by the paints, it is important to apply sensitive and non-invasive methods for early detection of under paint corrosion. Scanning Kelvin Probe (SKP) was used to determine the mechanism(s) of corrosion and paint de-adhesion. This technique is sensitive to the metal-polymer interface and gives a quick assessment of cathodic delamination or anodic undermining. Depending on the type of exposure the mode of corrosion de-adhesion was evaluated and compared with SKP data obtained under polarization experiments by impressed current in aqueous electrolyte. After exposure, pull off test and Scanning Electron Microscopy – Energy Dispersive X ray Spectrometry (SEM-EDX technique) were applied to determine the paint adhesion stability around the defect and to analyse the steel-paint interface.

1. Introduction

Electrochemical processes occurring at the metal-polymer interface and leading to corrosion driving coating deadhesion are not fully understood. This is particularly true for industrial systems like thick and highly resistive marine paints. At the beginning of the exposure, the corrosion rate underneath an intact coating is generally very small and it is mainly determined by the stability of the metal-polymer interface to hydrolyse [1,2]. A coating failure normally initiates at a local defect, which can be the result of chemical heterogeneities in the resin or other defects such as bubbles, under film deposits or pinholes.

Corrosion of steel in a defect can lead to cathodic delamination of the surrounding coating. It is the result of the formation of a macro galvanic couple across the corroding metal and the intact polymeric coating [3]. The primary pre-requisite for this form of failure is that the substrate should support a cathodic reaction. Considering a coated steel substrate immersed in an electrolyte at near neutral pH, the half-cell reaction responsible for the delamination process is generally agreed to be the oxygen reduction [3]. This reaction generates hydroxide ions or peroxide species at the cathodic sites leading to the formation of an alkaline environment at the delamination front. The elements required for this process to proceed are water, oxygen and free electrons. Additionally, in order to maintain electro neutrality, some forms of counter ions like alkali cations are required [3]. After weakening of the interface due to cathodic disbonding, residual stresses concentrate at the metal-polymer interface and thus can cause peeling of the coating [4]. The rate of delamination decreases for thicker coatings and systems with decreased diffusion rate of cations across the interface [3,5,6]. Thus, increasing the pigment loading or partly replacing spherical pigments with flake-shaped micaceous iron oxide or aluminium pigments may reduce the rate of cathodic delamination [5]. A pre-treatment like for instance phosphating is able to improve the adhesion by inhibiting the cathodic reduction of oxygen at the interface. The rate of delamination increases significantly in the case of cathodic polarization of the steel at the defect [3].

In opposite to cathodic delamination which is taking place under immersions conditions, anodic undermining or filiform corrosion usually takes place under atmospheric corrosion exposures [7–10]. In this case, the anodic front propagates from the defect [8]. The galvanic cell consists in the cathodic area (e.g. defect or tail of the filament) and the anodic location (head). Generally, it is agreed that differential aeration cells are created and maintained [10].

Several techniques have been developed for the investigation of the formation of galvanic cells and corrosion de-adhesion of polymeric coatings. Among these techniques, the Scanning Kelvin Probe (SKP) has emerged as a powerful tool to understand the mechanisms of corrosion [10–19]. SKP is a local electrochemical technique that can be used to determine the distribution of the electrochemical potential across a metal surface and/or a metal-polymer interface. It has been applied to study the cathodic delamination of organic coatings on steel starting

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from a defect [11,12]. It has been shown that the potential difference between the active iron surface in the defect (e.g. $-0.4\ V_{SHE}$) and that of the passive iron beneath the polymer ($0.1\ V_{SHE}$) acts as the driving force of the cathodic delamination of the coating around the defected area. The anodic reaction proceeds in the defect filled by the electrolyte and the cathodic process takes place under the coating.

SKP showed that anodic undermining of polymeric coatings could also be due to macro galvanic cells or cells of different aeration [9,10,13]. In humid air conditions, a thin electrolyte layer covers the area of the defect that is well aerated and works mostly as a cathode where oxygen reduction can take place, while anodic reaction occurs underneath the coating and the anodic undermining front spreads from the defect [13,14]. The change of the polarity of the galvanic cell depends upon the electrolyte thickness in the defect or the formation corrosion products. This was shown by SKP and by measurements of galvanic currents for model galvanic couples containing bare steel/painted steel electrodes [14–16].

SKP was mainly applied to analyse model thin coatings that are not practically used for corrosion protection of the steel in aggressive environments such as seawater. From technical systems, SKP was previously used to study corrosion/de-adhesion of coil coatings [17], cataphoretic water-borne coatings [13] and marine paint systems [18]. The aim of the present work is to determine in details the mechanisms of corrosion/deadhesion of thick highly resistive marine paints as a function of exposure conditions. SKP was used for a quick assessment of the paint performance and for a better understanding of the mechanisms of deadhesion. The metal-paint interface was analysed using SEM-EDX.

2. Experimental

2.1. Samples and exposure conditions

The samples were prepared using 4 mm thick plates of structural steel S355MC often used for shipbuilding applications. The chemical composition of the steel is given in Table 1. Before painting, the plates were degreased in acetone, washed with de-ionized water and blasted to grade Sa 2 ½ according to ISO 8501-1. The dust was removed by pressured air. The paint was applied by airless spraying. After completion, the paint was allowed to cure during 21 days, temperature between 20 and 25 °C, humidity between 40 and 60%.

Normally, the corrosion protection used for marine applications consists in at least three layers of polymeric coatings of different nature with a total thickness higher that 400 µm. In this report, the degradation of epoxy mastic painted steel with a coating thickness at about 300 µm was studied. This layer is normally applied as a part of the full protection system for marine paints. The role of this layer is to improve the barrier properties. The high content of inorganic pigments delays the diffusion of oxygen, water and ions from the electrolyte to the steel-paint interface.

Painted samples of dimensions 50 × 50 mm were scribed down to the metal surface with a vertical scribe of 30 × 1 or 10 × 0.5 mm. The samples were then edge protected and exposed in different accelerated corrosion tests. Three different test conditions were used. In the first test namely ACT1, scribed samples were immersed in 3 wt% NaCl for 33 days at 22 °C and 35 °C. The second test ACT2 was a cyclic corrosion test according to Volvo STD423-0014 (see Fig. 1). The relative humidity was cycled in the range of 50–95% and the temperature was cycled in the range of 35–45°C. The duration of one cycle was 12 h and a 1 wt% NaCl solution was sprayed 2 times a week. In the third accelerated corrosion test namely ACT3, the same relative humidity cycle as for Volvo STD 423-0014 was used but the temperature was set constant at 45 °C during the whole duration of the test. The samples were sprayed by 1% NaCl water solution three times per week instead of 2 times for the Volvo STD423-0014 as displayed in Fig. 1. This study is part of a larger project and the testing conditions that are used in this work were applied to a larger body of different paint systems. Indeed the tests used in this work revealed to mimic rather well the behaviour of marine paint under atmospheric conditions. This work has been published elsewhere [19].

Table 1
Composition of the structural steel.

Grade	C%	Mn%	P%	S%	Si%
S355	0.23 max	1.6 max.	0.05 max.	0.05 max.	0.05 max.

Both cyclic tests ACT2 and ACT3 were carried out during 6 weeks and SKP measurements were performed at regular time intervals. Pull off tests according to ISO 4624 were performed in the scribed area at the end of the test and the pull off strength was measured. “Elcometer” pull-off device PAT GM 01 was used.

2.2. Scanning electron microscopy (SEM)

A Scanning Electron Microscope (SEM) Hitachi SU3500 connected to an Energy Dispersive X-Ray Spectrometer (EDX) Thermo-Scientific Ultra dry NSS 312 SEM/EDX was used for analysing the metal-paint interface in delaminated locations or cross sections of the samples after cutting and embedding the steel-paint joints into an epoxy resin holder.

2.3. Electrochemical experiments

To evaluate the mechanisms of under paint corrosion, painted steel samples with a linear defect of 10 × 0.5 mm were polarized by impressed *dc* current in 3% NaCl. A potentiostat “Gamry reference 600” was used to polarize the defect in the painted steel sample (working electrode) by impressed current. Platinum wire and saturated calomel electrode (SCE) were used as counter and reference electrodes respectively. It was found that anodic polarization of steel in the defect was more damaging for metal/paint interface relatively cathodic one. To get softer conditions of de-adhesion, decreased anodic current density relatively cathodic one was applied: $20\ \mu A/mm^2$ and $-40\ \mu A/mm^2$ correspondingly. After the electrochemical polarization, the metal-paint interface was analysed by SKP and SEM-EDX techniques.

2.4. Scanning Kelvin probe

SKP is non-contact and non-destructive technique for measuring the Volta potential difference between a sample and a probe vibrating above the surface in air. The two surfaces create a capacitor in which, due to the vibration and the variation of the distance, an *ac* current is generated. The current amplitude is proportional to the Volta potential difference. The potential of the probe was calibrated which makes it possible to determine the potential of the working electrode. SKP is able to determine the potential of free or polymer coated metallic or semiconducting surfaces [11,12]. In corrosive environments, the Volta potential of a metal is related to the corrosion potential [20]. In the case of the intact metal-paint interface, the potential is mainly corresponding to the passive steel surface [21]. Degradation of the interface including loss of adhesion, activation of the steel surface and formation of corrosion products changes the Volta potential that is measured by SKP. This makes possible to characterize the processes at a very early stage of corrosion even under very thick paints [14,18]. Measurements can be carrying out in situ in air (or nitrogen) at different humidity or under electrolyte films.

In this study, a UBM Mestechnik instrument and height – controlled SKP instrument from Wicinski & Wicinski GbR were used. The reference electrode was a Ni-Cr alloy needle with a tip diameter of 100 or 150 µm and the distance to the working electrode surface was close to 50 µm. The potential of the probe was calibrated relatively to $Cu/CuSO_4$ electrode. All potentials are given versus the standard hydrogen