



Cathodic delamination of unpigmented and pigmented epoxy coatings from mild steel



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ABSTRACT

Key factors affecting the cathodic delamination process of an unpigmented epoxy coating from mild steel have been systematically investigated. These are: film thickness, cation mobility and electrolyte concentration in the test solution, temperature, and specimen potential. The effect of addition of pigments has also been examined. Results show that cathodic delamination of unpigmented epoxy from mild steel follows parabolic kinetics and is only slightly slower with thicker coatings. Pigmented epoxy coatings, however, are best fitted to a linear, or parabolic equation. With alkali metal chlorides, the rate of delamination of unpigmented epoxy showed a strong dependence on cation mobility as seen previously, but potassium chloride did not fit the general trend. Increased concentration of NaCl solution results in a faster delamination rate. There is little difference between delamination rates at 40 °C and 50 °C but delamination is significantly faster than at either 20 °C or 30 °C (which is faster than 20 °C). Cathodic delamination rate increases with increasingly negative applied potentials, but the free corrosion potential falls to an essentially constant value after an initial induction period, so is not responsible for the decrease in delamination rate over time. It is proposed that ion transport along a coating/metal interfacial layer is the rate-determining process for cathodic delamination of unpigmented epoxy from mild steel. Scanning acoustic microscopy identified different patterns of blisters within the delaminated zone for pigmented or unpigmented coatings.

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1. Introduction

Organic coatings are frequently applied to protect steel structures from corrosion. Cathodic delamination is one of the most important mechanisms for failure of coated steel surfaces and has been studied extensively [1–9]. However, the mechanism is not yet fully understood, which is partly due to the variety of the results obtained when tested under different conditions. There are many factors that can affect the coating performance and several studies have been dedicated to the study of factors affecting cathodic delamination [10–13].

Leidheiser et al. [1] studied the mechanism of cathodic delamination of organic coatings from a metal surface and examined the route for water and oxygen transport. Effect of film thickness, effect of cations, and effect of temperature were also studied to identify the cathodic delamination mechanism. It was proposed that the major mechanism for cathodic delamination process is the solubilisation of the thin oxide coating at the interface between the organic

coating and the metal. Skar and Steinsmo [10,11] studied several factors affecting the cathodic delamination of an epoxy–polyamide coating on steel and found that the delamination rate decreased linearly with increasing dry film thickness and was dependent on the cation type in the electrolyte. It was suggested that the transport route for the cation species is through the part of the coating which has already delaminated. Sharman et al. [12] examined cathodic delamination of chlorinated rubber coatings from steel under free corrosion conditions in alkali metal chlorides solutions, the rate of delamination of unpigmented lacquer showed a strong dependence on cation mobility, whereas the same coating with pigment did not. Both were fitted to a parabolic rate law. Thus, it was proposed that the controlling process changed from ion transport along the interface to oxygen diffusion along the same path when pigment was added. Sørensen et al. [13,14] investigated the effects of several factors on cathodic delamination of epoxy coatings. Results show that cathodic delamination increased when air was replaced by pure oxygen and also with increasing concentration of potassium cations up to a certain point. Beyond this they suggest that the effect of ionic concentration on the solubility of dissolved oxygen became more important than the ionic concentration itself, and rates started to fall, implying that oxygen is involved in the rate-controlling process as suggested by Sharman et al. [12]. The rate

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of cathodic delamination increased linearly with applied polarisation potential under cathodic protection. They also showed that increasing the pigment loading and reducing the amide/epoxy ratio in the resin both reduced the rate of cathodic delamination. Tests in which a layer of aluminium foil blocked transport of all species through the intact coating around the defect lead to a dramatic reduction to delamination rate, which they attributed to the need for water and oxygen transport through the coating. Delamination rates decreased linearly with increasing thickness, but the rate is not inversely proportional to thickness, as they suggest.

In the present work, a systematic study of the effects of film thickness, cation mobility, electrolyte concentration, temperature, polarisation and open circuit potential on cathodic delamination of unpigmented epoxy coatings is reported. These tests provide a background for further studies by scanning acoustic microscopy to confirm that this system behaves as previously reported, and to provide results under normal full immersion conditions for comparison with the semi-immersion tests that simulate the partial immersion exposure used in many SKP studies. The tests with unpigmented coatings provide a context for tests on coatings with added pigments (inert or inhibitive).

Scanning acoustic microscopy is used to observe changes beneath the paint.

2. Experimental

Test specimens (7 cm × 5 cm) were cut from 0.8 mm thick mild steel Q panels, degreased using acetone then dried, then coated by the draw-down method with an unpigmented epoxy resin cured with a polyamide curing agent as used previously [9]. The coating thickness was measured with a SHEEN SS120 film thickness gauge. Samples with desired thickness ($45 \pm 5 \mu\text{m}$, except for film thickness tests) were selected. A wire was soldered onto some samples to allow electrochemical tests and the edges were protected with a hot beeswax–colophony mixture, further protected against damage by adhesive tape. A rectangular area of bare steel 10 mm × 1.5 mm was exposed at the centre of the sample using a 1.5 mm wide chisel-edged cutter. All these defects were inspected visually for cleanliness and uniformity using a binocular microscope.

Cathodic delamination was tested by both full-immersion in naturally aerated solutions and semi-immersion tests. The set-up for the semi-immersion tests is as follows: Panels were hung vertically in a covered beaker with the middle of the defect aligned horizontally at the water surface so that half the vertical panel was immersed in solution and half (the part above the defect) in moist air, as described in [9]. The distance of propagation normal to the edge of the defect (visible as a lighter patch) was measured at intervals for several positions on both edges by observation through an optical microscope. Samples were also examined using a scanning acoustic microscope [KSI WINSAM 100] at a frequency of 80 MHz while immersed briefly in distilled water.

2.1. Effect of film thickness

Panels coated with unpigmented epoxy films of different dry film thickness (DFT), $30 \pm 5 \mu\text{m}$, $45 \pm 5 \mu\text{m}$, $60 \pm 10 \mu\text{m}$, and $85 \pm 10 \mu\text{m}$ were prepared and tested at room temperature under full-immersion conditions (immersed horizontally in 3.5% NaCl solution contained in unsealed plastic boxes fitted with lids to reduce evaporation).

2.2. Effect of cation mobility

Four solutions were examined to assess the effect of cations on cathodic delamination; they were 0.5 M LiCl, NaCl, KCl and CsCl. The unpigmented epoxy coated mild steel panels were immersed

in these solutions for 7 days as above. If transport of cations were the rate-limiting factor for the cathodic delamination of the system studied, a linear relationship would be expected between the delamination rate constant ($\text{distance}^2/\text{time}$) and the cation mobility.

2.3. Effect of solution concentration

To study the effect of ionic strength on cathodic delamination, unpigmented epoxy samples were exposed to NaCl solutions of different concentrations: 0.1%, 1%, 3.5% and 5% (by weight).

2.4. Effect of potential

To conduct this investigation, a cell was set up with the unpigmented epoxy coated sample as the working electrode, a piece of platinised titanium as a counter electrode, and a saturated calomel electrode (SCE) as reference electrode. A Ministat potentiostat (H. B. Thompson & Associates) was used to maintain a constant potential. The coated samples were exposed to 3.5% NaCl solution for 7 days at room temperature at either -800 mV or -1000 mV (vs. SCE), with one sample of each pair fully immersed in solution and the other semi-immersed. Another pair of samples without potential control was tested with the free-corrosion potential continuously monitored on a PC via a Pico-Log system (ADC-16, Pico Technology) connected by a high impedance buffer amplifier to the SCE reference electrode to avoid polarisation. This provided information on the potential of samples without external polarisation for comparison.

2.5. Examination by scanning acoustic microscopy

Scanning acoustic microscopy (SAM) was used to examine blistering and cathodic delamination after full- and semi-immersion tests in 3.5% NaCl solution with potential of -800 mV (SCE) or -1000 mV (SCE) applied for 7 days. The SAM examination was conducted at 80 MHz with a KSI WINSAM 100 as described in the previous paper [9]; the samples were immersed in distilled water as coupling medium. The images were taken with the focus at, and the reflected signal gated at, the coating–metal interface.

2.6. Effect of temperature

Duplicate mild steel samples coated with unpigmented epoxy were fully immersed in 3.5% NaCl solutions at 22 °C, 30 °C, 40 °C and 50 °C as before. 22 °C was the room temperature. 30 °C and 40 °C tests were conducted in a temperature-controlled enclosure (self-designed: a 100 W light bulb as heater controlled by a digital thermostat (RS Components Ltd., accuracy: $\pm 1 \text{ }^\circ\text{C}$)) within a perspex box. 50 °C tests were carried out in enclosed boxes within a SUB Aqua 26 L water thermostat (Grant Instruments Ltd.).

2.7. Effect of pigment

Cathodic delamination of two pigmented epoxy coatings from mild steel was also studied: (epoxy with talc [ET] and epoxy with talc and zinc phosphate [ETZ]). Details of pigment content are shown in Table 1.

Distances of delamination were measured after different periods fully immersed in 3.5% NaCl solution.

Further tests were conducted with semi-immersed samples [9] with the linear defect positioned horizontally at the water line, so that only coating below the defect was immersed in the test solution. This was used to determine whether migration along or through the coating is the most significant mechanism.

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