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Cathodic delamination of seawater-immersed anticorrosive coatings: Mapping of parameters affecting the rate

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ABSTRACT

Cathodic delamination is one of the major modes of failure for organic coatings immersed in seawater and refers to the weakening or loss of adhesion between the coating and the substrate. The diminished adhesion is the result of electrochemical reactions occurring at the coating–steel interface, where solid iron is oxidized to ferrous ions and oxygen is reduced to hydroxyl ions. In this work, the effects of various parameters on cathodic delamination have been investigated. The parameters are: permeability of the coating, concentration of dissolved oxygen and cations, polarization potential, type of binder, degree of curing, and pigment loading, shape and type. The results show that cathodic delamination increases with increasing concentration of cations up to the point where the concentration of dissolved oxygen becomes insufficient to maintain the corrosion rate. The rate of cathodic delamination is inversely proportional to the magnitude of polarization potential when ions can penetrate the coating, while cathodic polarization does not affect cathodic delamination when the ionic transport is restricted to the coating–steel interface. Increasing the pigment loading or partial replacement of spherical pigments with flake-shaped micaceous iron oxide or aluminium pigments reduces the rate of cathodic delamination. Finally, binders with an increasing amount of secondary hydroxyl groups in the polymer backbone reduce the rate of cathodic delamination while increasing the initial molar ratio of amide to epoxide increases cathodic delamination.

1. Introduction

The rapid oxidation of steel in aqueous environments necessitates the use of anticorrosive coatings to retard corrosion [1]. Organic barrier coatings are used to protect immersed structures from corrosion by preventing direct contact between corrosive species and the steel surface. In addition to adequate adhesion, these coatings must have a low permeability towards corrosive species because the protective action of barrier coatings relies on their high resistance towards ionic transport [2–4].

Long-term protection against corrosion can be challenging, especially for coatings which have been physically damaged during service because the defect region cannot retard corrosion. The corrosion processes will cause further degradation of the coating in terms of so-called “cathodic delamination”, which refers to the weakening or loss of adhesion, developing from the defect and caused by the cathodic activity underneath the coating [5–7].

The electrochemical reactions occurring at the defect involve an anodic reaction in which solid steel is dissolved and a cathodic reaction in which oxygen is reduced to hydroxyl ions, respectively Reactions (1) and (2):

$$\mathrm{Fe(s)} \rightarrow \mathrm{Fe^{2+}(aq)} + 2\mathrm{e^-} \qquad (1)$$

$$4\mathrm{e^-} + 2\mathrm{O_2(aq)} + 2\mathrm{H_2O(l)} \rightarrow 4\mathrm{OH^-(aq)} \qquad (2)$$

The hydroxyl ions, which are formed underneath the delaminated coating, will destabilize the local charge neutrality and thereby create an electrical field, which will facilitate the transport of cations to the cathodic areas. The cations will primarily be sodium ions because the major salt component in seawater is sodium chloride. Consequently, a highly alkaline environment will arise underneath the coating [8]. In addition, several reactive intermediates such as peroxides and free radicals, which may be more destructive than sodium hydroxide, can also be formed by the cathodic reaction [9–11]. The combined destructive action of an alkaline environment, peroxides, and free radicals leads to a delamination front advancing from the defect and into the intact coating regions. The front moves with a velocity around 6 mm/month, the exact value being dependent on coating formulation and seawater conditions. An idealized scheme of the mechanism of cathodic delamination is illustrated in Fig. 1.

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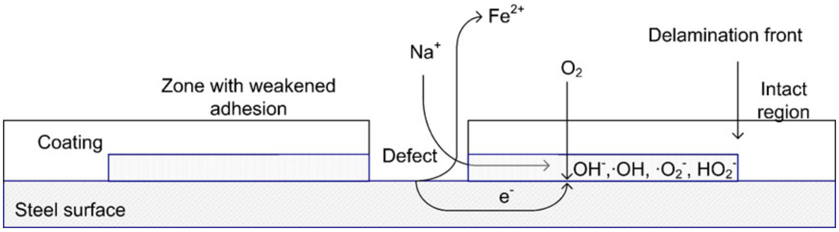

Fig. 1. Idealized sketch of cathodic delamination. Solid iron is transformed into ferrous iron at the defect and oxygen is reduced to hydroxyl ions at the cathodic sites underneath the delaminated coating. Sodium ions must migrate along the coating–steel interface to neutralize the charge of the hydroxyl ions. The presence of a highly alkaline environment and reactive intermediate products weakens the adhesion between the coating and the substrate, resulting in delamination of the coating.

The rate-determining step for cathodic delamination is generally believed to be the transport of cations along the coating–steel interface to the delamination front, where they will serve as charge carriers and enable oxygen to be reduced on the oxidized steel surface. This is consistent with the fact that the rate of cathodic delamination is a direct function of the ionic mobility of the cations [5,12–14] and the apparent interfacial diffusion coefficients of sodium ions along coating–steel interfaces [15]. Furthermore, the transport of water and oxygen through typical anticorrosive coatings is sufficient to balance the amounts consumed by the cathodic reactions [16–18].

Mapping of parameters affecting the rate of cathodic delamination may provide important information about the detailed mechanism of cathodic delamination and help optimizing coating formulation towards cathodic delamination.

2. Strategy of investigations

The purpose of this paper is to investigate how the various parameters illustrated in Fig. 2 affect the rate of cathodic delamination and apply the knowledge to improve the understanding of cathodic delamination and the interactions occurring at the coating–steel interface.

The activities at the interface between the coating and the steel surface, after a damage has occurred, are important for the mechanism of cathodic delamination. The interactions take place on top of a thin layer of ferrous oxide because steel surfaces prepared by abrasive blasting are oxidized instantaneously upon contact with the atmosphere. The layer of ferrous oxide is typically 1–5 nm thick [19,20] and contains single, divalent and trivalent ferrous ions. The majority of the iron groups at the surface are in the trivalent state and have associated hydroxyl groups originating from dissociated water molecules present on the high energy oxide surface. The hydroxyl groups can participate in acid–base interactions with cations in the aqueous environment to which the steel is exposed [21]. It is well-established that the bonding of a polymer to ferrous oxide/hydroxide surfaces primarily occurs through acid–base interactions (e.g. hydrogen bonds [22]) between the basic epoxy coating [23] and the acidic steel surface. The concept of hydrogen bonds is in accordance with monolayer studies of model epoxy compounds, which have shown that adhesion between epoxy resins and the substrate is strongly dependent on the content of hydroxyl group in the resin [24]. In addition, the adhesion strength was independent of the epoxy group content, molecular weight and hydrocarbon group content of the resin. The bond energy between epoxy resins and steel surfaces is in the range of 10–40 kJ/mol [25]. This is within the range of typical bond ener-

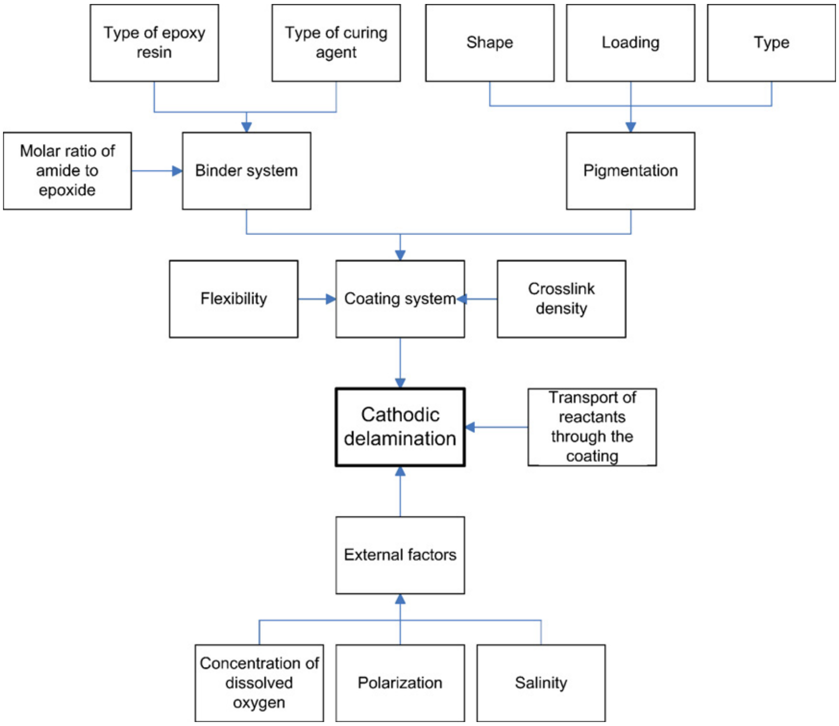

Fig. 2. Overview of parameters investigated, which affect the rate of cathodic delamination of polyamide/polyepoxide-based anticorrosive coatings.