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Fundamental investigation on the stability of the steel/coating interfaces contaminated by submicroscopic salt particles

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Abstract

It is known that the presence of hydrosoluble species, mainly chlorides and sulphates, at the metal/paint interface, promotes osmotic blistering of the coating and underfilm metallic corrosion when the concentration exceeds a critical level. However, since the interface is not easily accessible by experiment, not much is known about interfacial structure, reactions and the processes causing degradation. Scanning Kelvin Probe (SKP) is an ideal tool for the in situ monitoring of the degradation processes at the buried interface. In the present paper, a study of the fundamental aspects of the stability of the contaminated buried steel/coating interfaces, specially focused on the initial stages of blistering and underfilm corrosion, has been carried out. Results of the characterization study performed with a height-regulated SKP (HR-SKP) on coated steel contaminated at the interface by different salt concentrations with well-defined crystal size and distribution are shown. An effect of crystal size and distribution has been observed. While, small crystals or low density of salt spots do not show macroscopic blistering, bigger crystals or a local accumulation of them can cause significant de-adhesion and macroscopic blistering.

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1. Introduction

It is known that for painted metals the presence of hydrosoluble species within the layer of atmospheric corrosion products, mainly chlorides and sulphates, beneath the coating promotes osmotic blistering and underfilm metallic corrosion when the concentration of the soluble salts exceeds a critical level [1]. This situation occurs quite often in practice, especially when the metal surface has been exposed for some time prior to painting to an aggressive atmosphere (marine, industrial, etc.). Loss of adhesion, cathodic disbondment and scribe creep can be also consequences of the presence of soluble salts at the interface. These processes can lead to the deterioration of the paint system in a very short period of time.

Though this is a long-standing problem, it has recently come to receive greater attention from the protective coating industry to the point that much of the protective coatings industry currently requires testing of soluble salt levels and trends show these requirements are increasing. International Standards Organization (ISO) has for some time been trying to develop a standard for guidance levels of water-soluble salt contaminant before the application of paints and related products [2]. Numerous research studies have been carried out on this issue, especially on the determination of critical chloride and/or sulphate levels above which premature coating failure frequently occurs [3–17].

In an interesting review by Alblas and van Londen of studies carried out with chlorides as interfacial contamination [18], it is commented that despite the lack of consensus on precise contamination levels, all researchers agree that soluble salts have a dramatic effect on coating performance. However, it is difficult to set acceptable levels since each type of coating, film thickness, fillers, pigments, etc., also varies in susceptibility to soluble salt degradation, mainly due to different oxygen and water permeability [19,20]. It is known that coating degradation induced by the presence of soluble salts at the metal/paint interface strongly depends upon osmotic water migration through the coatings and obviously this will be affected by coating thickness and physical-chemical properties of the film [1]. Coating thickness will also affect the overall mechanical properties. It is clear that different coating systems can tolerate different levels of salt and the maximum tolerable salt level for specific coating sys-

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tems also varies depending on the exposure conditions [17] and the metallic substrate [21,22]. Although there are no references in the literature, it could be also expected that solubility of the salts into the coating during hardening could also affect to the breakdown level.

The topic is of utmost current interest for the coating and flat metal industry and as has been pointed out above, has been widely studied, but it is also a question of fundamental scientific importance. However, since the interface is not easily accessible by experiment, not much is known about interfacial structure, reactions and the processes causing degradation.

It was the intention of the present work to address the fundamental scientific aspects involved here. In particular, the focus is being on the question why there exists a critical or threshold value of salt contamination at the interface above which the stability of the paint coating is significantly affected, and below which the contamination level seems no danger for the coated system or has only a very low impact on the stability of the coating? Other interesting questions that should be addressed are for instance, why are there different thresholds for different metal/polymer interfaces? What are the initial stages of blistering? Have the crystals size and distribution any effect?

It has to be assumed that most contaminations are too small in size to cause macroscopic blistering immediately. Hence, at very early stages only the metal/polymer interface in the direct vicinity of the contaminations will be delaminated. The question is under which conditions this will turn in macroscopic delamination?

This delamination will be driven by a superposition of mechanical stress, caused by the formation of a small size droplet of electrolyte at the site of the salt contamination, and electrochemical attack, most likely dominated by cathodic delamination. The pressure caused by the increase in volume can exert a greater force than the paint adhesion and cohesion forces, giving rise to the formation of a blister. It has been calculated that the osmotic pressure in the interior of a blister can be as high as 2500 - 3000 kPa (25 - 30 atm), much higher than the yield strength of a paint coating, which is estimated to be of the order of 6 - 40 kPa (0.06 - 0.4 atm). It is believed that blisters do not form in one single step but in several successive steps of growth and release of pressure due to the viscoelastic and deformation response of paint coatings.

To answer this, the Height-Regulated Scanning Kelvin Probe (HR-SKP) method developed at MPIE is an ideal tool for the in situ monitoring of the degradation processes at the buried interface [23]. On the other hand, for an in-depth understanding it is important that the superposition of the effects of all different parameters involved can be disentangled. Hence, it has been important to design experiments focussing on individual aspects of the complex system. For that, is essential that different salt contamination morphologies of well-defined crystal size and distribution can be obtained for fundamental studies focused on whether there is a threshold for crystal size and quantity to initialise a two-dimensional delamination of the steel/coating interface or to cause a critical extent of localised de-adhered spots. Very low contamination level distribution can be prepared where the interface is not measurably destabilised by the salt, others where it is.

2. Experimental

Smoothly polished mild steel samples $(25 \text{ mm} \times 25 \text{ mm} \times 1 \text{ mm})$ were prepared. Afterwards, in order to achieve contamination morphologies of well-defined crystal size and distribution three laboratory contamination methods have been investigated: (i) the so-called "impactor" method, resulting in submicroscopic or microscopic salt crystals, (ii) the "droplet" method, a novel developed method where a droplet of salt solution is spread

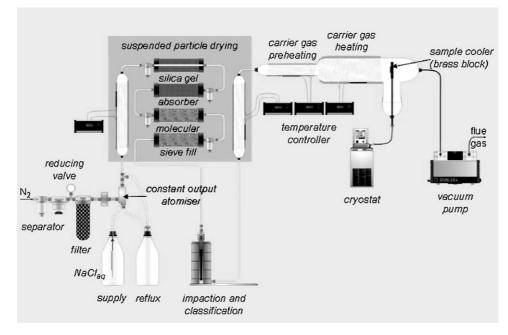


Fig. 1. Sketch of the impactor set-up.

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