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An historical perspective on the corrosion protection by paints

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ABSTRACT

Corrosion protection by organic coatings or paints dates back to the beginning of recorded history. Since this time, the technology has advanced through the understanding of the corrosion process and the physics and chemistry of paints. Throughout this history four themes persist: role of electrical properties, role of coating homogeneity, role of adhesion and the role of the paint as a carrier for inhibiting pigments. The aim of this paper is not to provide a comprehensive review of the state of the science but rather to outline the main themes of the research with examples illustrating these themes. To some extent this paper compliments two other reviews in this special issue viz those by Jamali et al. and Lyon et al.

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1. Introduction

The use of protective pigmented organic layers, paints, for protecting metals against corrosion dates back to ancient times. Pliny the Elder in 77 AD referred to the rust preventing properties of a mixture of "ceruse" (a white lead carbonate), gypsum and tar (paint) as useful for protecting iron against rust [1].

Corrosion occurs when the corroding metal loses electrons in an anodic reaction leading to metal loss. The electrons move through the metal the metal to sites of cathodic reduction of an oxidant. To balance this charge transfer, ions in the corrosive environment must move between these sites of oxidation and reduction. This model of the electrochemical nature of corrosion has been first attributed to an anonymous paper by L.J. Thénard and R. Mallet appearing in 1819. H. Davy also recognized the electrochemical aspect of corrosion suggesting galvanic protection of copper sheathing of canal boats as early 1824. Davy's student, M. Faraday was also an early proponent of the electrochemical aspect of corrosion [2].

2. Themes

Over the years a number of themes have persisted in the conceptual understanding of the nature of corrosion protection by paints. Early conjectures on the important properties of paint by Newman included suggestions that paint should be perfectly homogeneous and adhere tightly to the bare iron or steel surface while maintaining its elasticity [3]. He went on to suggest that paint prevents the galvanic action by being an insulator of electricity [3].

The authors, with some ninety years of experience of studying anti-corrosive paints between them, believe that the four most important themes which need to be addressed relating to understanding the corrosion protective properties of paints are as follows:

(1) Electrical properties
(2) Coating heterogeneity
(3) Role of corrosion and corrosion Induced adhesion loss
(4) Paints as a platform for release of Inhibitors

These themes are covered in the following four sections of this paper.

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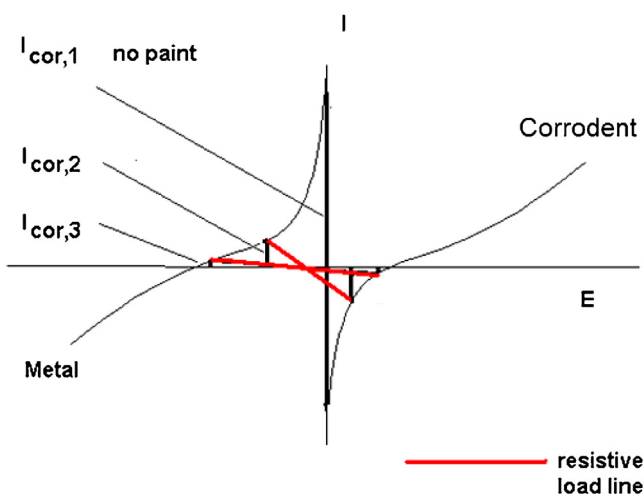   E-mail address: Martin.Kendig@Verizon.net (M. Kendig).

Fig. 1. A schematic for electrochemical kinetics illustrating the role played by resistivity of paint.

2.1. Electrical properties

As an introduction to the discussion of the importance of the electrical properties (specifically ionic resistance) of paint in protecting metal from corrosion, we consider the hypothesis of Dr J.E.O Mayne. Mayne observed that paints and organic coatings generally transport sufficient water and oxygen to maintain corrosion of the steel substrate. This leads to the hypothesis that adhesion of the paint inhibits electrochemical reactions though the formation of high resistance pathways between micro and macro anodes and cathodes [4].

For corrosion to take place, electrons must be transferred between anodic and cathodic sites on the metallic surface while ions must be transferred through the solution or corrosive environment. Fig. 1 illustrates schematically that a highly resistive pathway placed between anodic and cathodic sites can significantly slow corrosion. With no effective resistance between the respective half

cells, a significant corrosion rate will occur. The presence of a resistive layer adds a load line between the two processes effectively slowing the rate (Fig. 1). Well adhering non-conducting paints provide such a resistance. In Fig. 1, $i_{cor,1}$ represents the corrosion rate with no coating while $i_{cor,2}$ and $i_{cor,3}$ represent the corrosion rates for the material with a resistive paint and a more resistive paint, respectively.

Wolstenholme [5] citing the work of Clay [6] suggested that the when the polarization resistance of the corrosion process exceeds the coating resistance then the coating has broken down and is not the rate limiting process. A good example of this occurs for paint primers incorporating partially soluble Cr(VI) inhibiting pigments which dramatically increase the polarization resistance of the underlying metal while contributing to a highly conducting coating.

Other electrical properties also relate to paint integrity. For example, a relatively un-damaged paint can be considered as a dielectric giving a capacitive electrochemical response. The broad frequency response of the impedance of the film exhibits an inverse frequency and capacitance dependence. Brasher and Kingsbury [7] related the change in capacitance due to the water taken up by the coating through the equation:

$$v = (\log(C_t/C_o)/\log \varepsilon, \tag{1}$$

where v is the volume fraction of water, C_t, the coating capacitance after immersion in water, C_o, the dry coating capacitance, and ε is the relative dielectric constant of water.

Fig. 2 shows the water uptake for a coating as determined by a gravimetric method and the more accurate capacitance evaluation [8].

In 1965, Clay [6] used both ac and dc methods to evaluate coating performance. Menges and Schneider [9] expressed results in terms of ac resistance. Using bridges such as the one shown in Fig. 3 (Lehigh University) [11]. Early use of frequency response analyzer methods [10] significantly streamlined the process of gathering broad frequency response of polymer coated steel [10–13].

While most data were expressed in terms of complex impedance Z as a function of frequency, Kendig and Leidheiser [11] expressed
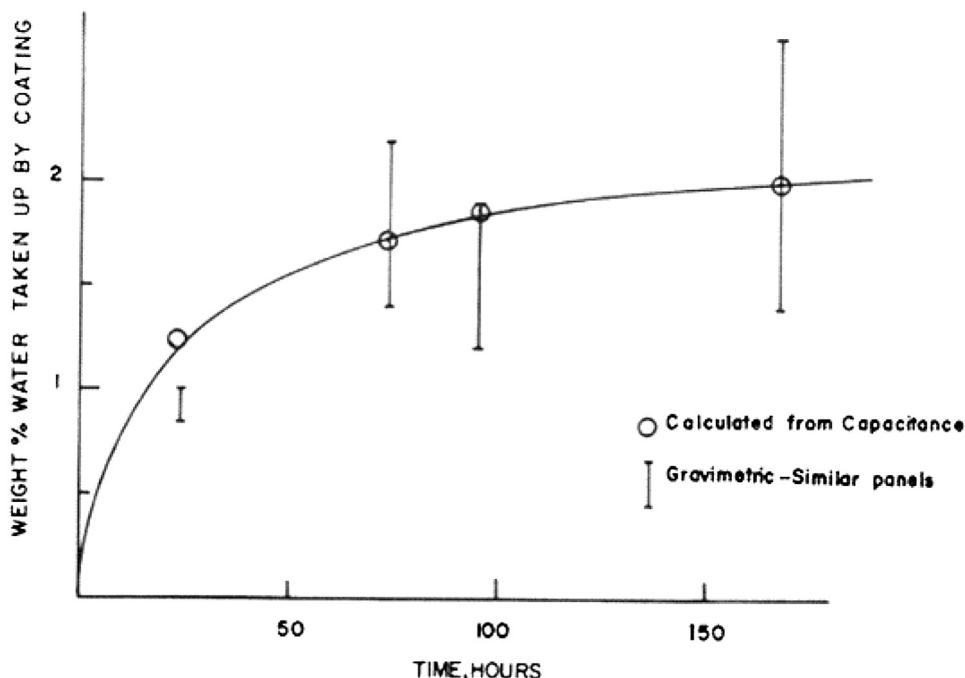

Fig. 2. Water uptake for a coating as determined by mass uptake as compared to that calculated from capacitance (Kendig and Leidheiser Jr. [11]).