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In situ capacitance measurements for in-plane water vapor transport in paint films

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ABSTRACT

A capacitance technique has been adapted to study in-plane water vapor transport in paint films. The technique requires an application of electrical contact materials on the paint film surface for capacitance measurements by electrochemical impedance spectroscopy (EIS). The capacitance obtained by EIS using Cu tape and Ag paste as the contact materials are presented. A direct comparison of capacitance and gravimetric measurements demonstrates that the change in the coating capacitance is quantitatively correlated with the total amount of in-plane water vapor transported in paint films. The water vapor diffusion coefficient derived from the capacitance technique agrees with one from the gravimetric method.

1. Introduction

The water-transport properties of paint films, both in the through-plane and in-plane directions, are believed to be key factors affecting the corrosion protection performance of paint films. The relevance of water-transport behavior related to a paint film's protective performance can be seen in the standard testing methods for coatings, such as the ASTM B117 salt spray test and the ASTM G85 series of cyclic corrosion tests.

A number of techniques have been developed to investigate water uptake and transport in coatings, including gravimetric [1], capacitance [2–5], and spectroscopic methods [6–9]. The gravimetric technique is the most straightforward method that measures the weight gain or loss of water in coatings. Spectroscopic techniques, although reported as having a number of important advantages, require a sophisticated infrared instrument system. Capacitance techniques have been widely used to assess water transport in coatings [3–5,9–12]. These techniques are based on the assumption that the change in capacitance is due entirely to the water uptake and transport into the film. Because of a large difference between the dielectric constant of water ($\varepsilon_w = 80$ at 25 °C) and that of the organic coating material (ε typically 3–4), when water penetrates into the coating, its dielectric constant increases resulting in an increase in the coating capacitance, hence, the coating capacitance can be used to understand the water transport in organic coatings. In-plane water transport properties are of special interest for paint and adhesive primer coatings. In the case of paint primers, certain failure modes such as undercutting and filiform attack are expected to be mediated by lateral water transport. In the case of adhesives and adhesive primers, through-plane water transport is generally not significant due to the geometry, and lateral water transport through the bondline is of primary importance. Unfortunately, the large majority of the literature on water transport in coatings has been limited to through-plane water absorption and transport, very little has been given to in-plane (lateral) water transport behavior in organic coatings [13], and there is no information on the isotropy of water transport in primer films.

In this paper, we propose a capacitance technique for measurement of in-plane water vapor transport behavior in commercially available aerospace paint primer films. The technique requires an application of electrical contact materials on the paint film surface for capacitance measurements. The effects of using Cu tape and Ag paste as the contact materials on capacitance measurements are discussed. The purpose of this work is to validate the capacitance technique for in-plane water vapor transport from both experimental and theoretical aspects.

2. Theoretical background

The capacitance technique is based on the assumption that the change in capacitance is due entirely to the water uptake and diffusion into the film. Two models were proposed to describe the

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effect of the water permeation in coatings on the capacitance measurements [14,15]. One is discrete model (DM) where the water is assumed uniformly distributed across the film, and the other is continuous model (CM) where a variable water distribution is present in the film.

For a cylindrical paint film like the one (inner diameter about 3.5 cm, outer diameter of 6.0 cm) used in this work, the water concentration distribution $C(r,t)$ is not uniform along the radial direction (Fig. 2(a)). According to the concept of CM model, the film can be divided in many parallel infinitesimal thick layers; each can be represented by a simple equivalent circuit consisting of a resistance dR, in parallel with a capacitance dC, as shown in Fig. 2.

The capacitance dC is given by:

$$dC = \frac{\varepsilon_0 \varepsilon(r,t) \times 2\pi r}{d} dr \tag{1}$$

The resistance dR is given by:

$$dR = \frac{\rho(r,t)}{2\pi r \times dr} d \tag{2}$$

where $\rho(r,t)$ and $\varepsilon(r,t)$ are the resistivity and dielectric constant of the paint film, respectively, ε_0 is the dielectric constant of vacuum (8.854×10^{-14} F/cm), d is the film thickness, and dr is the infinitesimal thickness.

The total capacitance of the coated film at time t, C_t, can be calculated by integrating Eq. (1) over the entire electrode areas of the film as follows:

$$C_t = \int_{r_0}^{R} dC(r,t) = 2\pi \int_{r_0}^{R} \frac{\varepsilon_0 \varepsilon(r,t)}{d} \times r dr = \frac{2\pi\varepsilon_0}{d} \int_{r_0}^{R} \varepsilon(r,t) \times r dr \tag{3}$$

The total resistance of the coated film, $R(t)$, can be computed by integrating Eq. (2) over the entire coated areas of the film, as follows:

$$\frac{1}{R(t)} = \frac{2\pi}{d} \int_{r_0}^{R} \frac{r}{\rho(r,t)} dr \tag{4}$$

In order to relate the dielectric constant of the paint film, $\varepsilon(r,t)$, to the water concentration profile $C(r,t)$, the Brasher–Kingsbury equation is used as follows:

$$\varepsilon(r,t) = \varepsilon_{dry} \times \varepsilon_w^{\phi(r,t)} \tag{5}$$

$$\phi(r,t) = \frac{C(r,t)}{\rho_w} = \frac{\ln[\varepsilon(r,t)/\varepsilon_{dry}]}{\ln \varepsilon_w} \tag{6}$$

$$\varepsilon(r,t) = \varepsilon_{dry} \exp[(\ln \varepsilon_w/\rho_w) \times C(r,t)] \tag{7}$$

where $\phi(r,t)$ is the local water volume fraction of each infinitesimal thick layer, ρ_w is the density of water in the film, ε_{dry} and ε_w are the dielectric constant of the dry film and of pure water, respectively.

By substituting Eq. (7) into Eq. (3), the total capacitance, $C(t)$, then becomes:

$$C_t = \frac{2\pi\varepsilon_0\varepsilon_{dry}}{d} \int_{r_0}^{R} r \times \exp\left[\frac{\ln \varepsilon_w}{\rho_w} C(r,t)\right] dr \tag{8}$$

Note that using expansion of the exponential term in a MacLaurin series, Eq. (8) becomes:

$$C_t = \frac{2\pi\varepsilon_0\varepsilon_{dry}}{d} \int_{r_0}^{R} r \times \{1 + \frac{\ln \varepsilon_w}{\rho_w} C(r,t) + \frac{1}{2}\left[\frac{\ln \varepsilon_w}{\rho_w} C(r,t)\right]^2 + \frac{1}{6}\left[\frac{\ln \varepsilon_w}{\rho_w} C(r.t)\right]^3 + \cdots\} dr \tag{8-1}$$

The total amount of water transported into the film at time t, $M(t)$, is given by:

$$M(t) = \int_{r_0}^{R} 2\pi r \times C(r,t) dr \tag{9}$$

By substituting Eq. (9) into Eq. (8-1), then

$$C_t = C_0 + \frac{\varepsilon_0\varepsilon_{dry} \ln \varepsilon_w}{2d\rho_w} M(t) + \frac{\pi\varepsilon_0\varepsilon_{dry}}{d}\left(\frac{\ln \varepsilon_w}{\rho_w}\right)^2 \int_{r_0}^{R} r[C(r,t)]^2 dr + \cdots \tag{8-2}$$

For the case $\ln \varepsilon/p_w \ll 1$, the second-order term of the series can be neglected, then:

$$\frac{C_t - C_0}{C_\infty - C_0} = \frac{M(t)}{M(\infty)} \tag{10}$$

Eq. (10) suggests that the normalized capacitance change from impedance measurements can be equally translated into the normalized mass change from gravimetric measurements.

2.1. Radial diffusion

Given the paint film specimen configuration as shown in Fig. 2(a), it is expected that the mass transport of water vapor in the in-plane direction is controlled by radial diffusion. For the problem of radial diffusion in an infinite medium, assuming that the in-plane water vapor transport follow Fick's second law:

$$\frac{\partial C(r,t)}{\partial t} = D\left[\frac{\partial^2 C(r,t)}{\partial r^2} + \frac{1}{r}\frac{\partial C(r,t)}{\partial r}\right] \tag{11}$$

For non-steady state, the water concentration $C(r,t)$ is given by [16]:

$$C(r,t) = C(r_0)\left[1 - \frac{2}{r_0}\sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t) J_0(r\alpha_n)}{\alpha_n J_1(r_0\alpha_n)}\right] \tag{12}$$

where $J_1(x)$ is the Bessel function of the first order and α is the root of the Bessel function of the first kind of order zero.

$$\frac{M(t)}{M(\infty)} = 1 - \sum_{n=1}^{\infty} \frac{4}{r_0^2\alpha_n^2} \exp(-D\alpha_n^2 t) \tag{13}$$

where $M(t)$ is the total amount of water vapor diffused into the film at time t, $M(\infty)$ the total amount of water vapor when the film is fully saturated with water vapor (steady state radial diffusion).

For a small value of time, we have [16]:

$$\frac{M(t)}{M(\infty)} = \frac{4}{\pi^{1/2}} \times \frac{(Dt)^{1/2}}{r_0} - \frac{Dt}{r_0^2} - \frac{1}{3\pi^{1/2}} \times \frac{(Dt)^{3/2}}{r_0^3} - \ldots \tag{14}$$

Combining Eqs. (14) and (10), for a short time approximation, we obtain:

$$\frac{C_t - C_0}{C_\infty - C_0} = \frac{M(t)}{M(\infty)} = \frac{4}{\pi^{1/2}} \times \frac{(Dt)^{1/2}}{r_0} - \frac{Dt}{r_0^2} - \frac{1}{3\pi^{1/2}} \times \frac{(Dt)^{3/2}}{r_0^3} - \ldots\ldots \tag{15}$$

Eq. (15) shows that the diffusivity D can be found by numerical analysis of experimental results from capacitive or gravimetric measurements.

It must be pointed out that in deriving Eq. (14), the diffusion is assumed as a non-steady state in an infinite medium, i.e. the outer radium of the paint film is infinite large. As will discussed later, for a finite radial diffusion where the outer radium of the circular