

## In situ measurement of water at the organic coating/substrate interface

Tinh Nguyen, Eric Byrd, Dale Bentz, Changjian Lin<sup>1</sup>

*National Institute of Standards and Technology, Gaithersburg, MD 20899, USA*

Received 17 October 1994; revised 26 September 1995

### Abstract

In situ and quantitative information on the water layer at the organic coating/substrate interface is crucial for understanding and preventing the failure of organic coating systems. A technique, based on a two-layer model derived rigorously from internal reflection theory, has been developed for measuring in situ the thickness and amount of the water layer at the organic coating/substrate interface. The technique gives new insight into the processes by which water degrades the coating/substrate bonds. In this technique, a transparent or an opaque organic coating of sufficient thickness is applied to an internal reflection element (IRE) with or without a thin metallic film, which is used as the substrate. A water chamber is attached to the organic-coated specimen. After adding water to the chamber, Fourier transform infrared-multiple internal reflection (FTIR-MIR) spectra are taken automatically at specified time intervals without disturbing the specimens or the instrument. Water uptake in the coating and FTIR-MIR spectra of water on the coating-free substrate are also used for the analysis. Examples of clear and pigmented coatings on untreated and treated substrate surfaces are given to demonstrate the technique. Results of water accumulation at the coating/iron interface with and without applied electrical potentials are given. In addition to measuring water at the coating/substrate interface, the technique provides a means for studying the transport of water through a coating adhered to a substrate. Information on water at the interface and its transport properties through coatings applied to a substrate is valuable for interpreting corrosion, blistering and delamination of organic coating systems, and for developing models for use in predicting the service lives of protective coatings.

*Keywords:* Organic coating/substrate interface; Water measurement

### 1. Introduction

Water at the organic coating/substrate interface is often the main cause of degradation of an organic coating system. Probably the most severe effect of water at the organic coating/substrate interface is the cathodic delamination and blistering that occur near a defect when an organic-coated steel panel is exposed to electrolytes [1–6]. The detrimental effects of water and water vapor on the adhesion of organic-coated substrates [7–10], adhesive bondings [11] and paved asphalts [12] are well documented. And finally, water at the interface is essential for corrosion to occur and spread on a metal surface under an organic protective coating. In situ measurement of water at the organic film/substrate interface is the subject of great interest in many industries including organic coatings and adhesives. Water and hydroxyl groups on surfaces can be studied effectively by a number of spectroscopic methods [13–15]. Similarly, techniques for studying in situ

chemical reactions at an aqueous electrolyte/electrode interface have been developed [16,17]. A technique for measuring the viscosity of thin films of aqueous solutions between two closely spaced mica or silica surfaces has been reported [18,19]. However, until recent research at the National Institute of Standards and Technology (NIST), no technique has been available for measuring in situ water at the organic coating/substrate interface. Previously, Funke and Haagen [20] have suggested using the 'crossover' point, that point in time where a coated metal sorbs more water than the free film, to indicate when water starts to accumulate in substantial amounts at the coating/metal interface. Leidheiser and Funke [9], in a critical review of water disbondment of coated metals, have suggested the use of sensors placed at the coating/metal interface to follow the thickness of the water layer at that location.

We have developed a technique based on Fourier transform infrared-multiple internal reflection (FTIR-MIR) spectroscopy for measuring in situ water at the organic coating/substrate interface [21,22]. In this technique, an organic coating is applied to the surface of an

<sup>1</sup> Present address: Xiamen University, China.

internal reflection element (IRE), which serves as the substrate. A water chamber is attached to the organic-coated substrate and FTIR-MIR spectra of the exposed specimen are collected at specified time intervals without disturbing the specimen, the conditions of the experiment, or the optical alignment of the instrument. In situ information on water accumulation in the coating/substrate interfacial region is obtained from the FTIR-MIR intensity change of the water detected in the specimen. The theoretical basis for quantifying water at the coating/substrate interface using FTIR-MIR spectroscopy has been described in detail elsewhere [22]. The use of this technique for studying water at the interface between a coating and an iron layer has been illustrated [23]. The applications of this technique for measuring the diffusion coefficient of water through a polymer film adhered to a substrate [24], characterizing the water layer at the organic film/SiO<sub>2</sub> interface [25,26] and studying the effects of silane coupling agents on the water layer at the polymer/SiO<sub>2</sub> substrate interface [27] have been demonstrated. An attempt to correlate interfacial water obtained by this technique with the adhesion loss due to water exposure of organic-coated substrates and polymer/fibre composites has also been presented [27,28].

This paper presents a summary on three aspects of this work: (i) principle of the FTIR-MIR technique for measuring in situ water at the polymer coating/substrate interface; (ii) examples to demonstrate the capability of this technique for characterizing and quantifying water at the coating/substrate interface; (iii) discussion on the presence of the water layer at the coating/hydroxylated oxide interface and the effect of this layer on the adhesion of polymer-coated substrates exposed to water. Quantitative and in situ information on water at the organic coating/substrate interface will enhance our understanding of the mechanisms of adhesion loss, delamination and corrosion of organic-coated and adhesive-bonded materials. Such information is needed for the development of improved models for predicting the service life of protective coatings and adhesive bondings.

FTIR-internal reflection spectroscopy offers a number of advantages for studying water at the organic coating/substrate interface: (i) it is sensitive toward molecular water, its dissociated OH group and its degrees of hydrogen bonding; (ii) it can be used at ambient conditions, and thus, is suitable for in situ measurement; (iii) it detects water from the substrate side, therefore, preventing the interference of water from the environment.

Fourier transform infrared-internal reflection, commonly known as FTIR-ATR (attenuated total reflection), spectroscopy is a powerful technique to provide qualitative, as well as quantitative, information on complex molecules at surfaces and interfaces. In inter-

nal reflection, the evanescent electric field (produced on total reflection at the IRE surfaces) penetrates the surface of the sample to a depth generally in the order of one wavelength of the radiation. The evanescent field, which decays exponentially with distance in the sample, interacts with the material of interest and causes an attenuation of the reflection of the propagating beam. Detection of the attenuated radiation at the exit of the substrate yields an IR spectrum of the sample. Thus, when an organic-coated IRE specimen is exposed to water, water will eventually enter the coating/substrate interfacial region and interact with the evanescent wave and be detected. This unique mode of interaction between the evanescent wave and material has made possible a large number of applications. Also new applications are being developed each year. These applications take advantage of the technique's ability to probe the near surface layers of solids and liquids. Harrick [29,30] has developed the quantitative aspects of the internal reflection spectroscopy. The quantitative capability of this technique has been verified by experimental data from a variety of applications [31–34]. The uses of this technique for the studies of adsorbed species, ultrathin organic films, and single-monolayer Langmuir–Blodgett films on substrates have been reviewed [35–40].

## 2. In situ measurement of water at the organic coating/substrate interface

### 2.1. Organic coating/internal reflection element substrate system

Three specimens of organic coatings applied to three different surfaces were used to demonstrate the applicability of the FTIR-MIR technique for characterizing and quantifying water at the coating/substrate interface. These were: a water-reducible epoxy applied to a germanium (Ge) substrate, a clear epoxy on a silicon (Si) substrate, and the same epoxy on a silane-treated Si substrate. The Ge and Si substrates were 50 × 10 × 3 mm spectroscopic grade, 45° parallelogram internal reflection element (IRE). When received, each IRE was wrapped in a soft cloth and hermetically sealed in a plastic envelope inside a rigid box containing desiccant. The substrates were employed immediately after unwrapping without surface cleaning or treatment. The Si IRE surfaces had a 2.25 nm SiO<sub>2</sub> layer (as measured by an ellipsometer), which was covered with silanol (SiOH) groups and adsorbed water [26]. Thus, the chemical functional groups on the surfaces of this substrate are similar to those on steel or aluminum, which are, under normal conditions, covered by hydroxylated oxide [41]. The hydroxyl-rich oxide surface adsorbs and strongly retains several

monolayers of bound water. The silane-treated surfaces were prepared by immersing the Si IRE in an acidified (pH = 4) water solution containing 0.1% aminoethyl-aminopropyltrimethoxysilane for 30 min. The treated substrates were dried at 110 °C for 10 min before use. Although the surfaces of the Ge substrate were not characterized, they were probably also covered with adsorbed water before applying the coating because this material and its oxide are highly energetic.

The clear epoxy was a stoichiometric mixture of a low molecular weight diglycidyl ether of bisphenol A and a polyethertriamine. There was no solvent in this coating. The 15% titanium dioxide pigmented, water-reducible epoxy coating was a stoichiometric mixture of a water-reducible epoxy resin and an amine adduct as the curing agent. The resin contained 47% solvent, which was a mixture (by volume) of 83% water and 17% 2-propoxyethanol. The curing agent contained 40% solvent, comprised of 95.5% of 2-propoxyethanol and 4.5% glacial acetic acid. The chemical structures of the resin and curing agent were unknown.

The coatings were applied to the untreated and silane-treated substrates by the draw-down technique using the procedures described previously [21,22]. The thickness of the coating films was controlled by the thickness of the masking tape strips placed along the length of the substrates. The quality of all three coated specimens was good and no visible pinholes or air bubbles were observed (by the naked eye) on the specimens' surfaces. After curing, a water chamber was attached to each organic-coated specimen. The specimen with the water chamber attached was placed vertically in an ATR accessory holder and in situ measurements of water were carried out using an FTIR

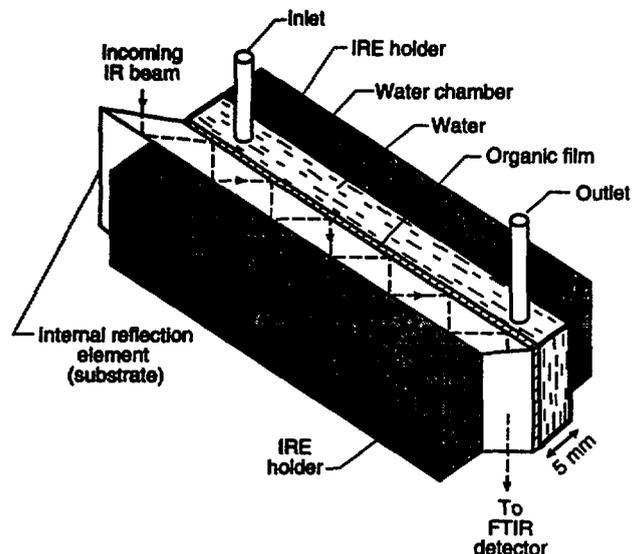


Fig. 1. Experimental setup for in situ measurement of water at the organic coating/substrate interface.

spectrometer with a variable angle ATR accessory. FTIR-MIR spectra of the water-exposed specimens were taken automatically every 15 min without disturbance to the spectrometer or to the specimens throughout the measurements, until the experiment was complete. All spectra were taken using unpolarized radiation at an angle of incidence of 45° and purged dry air. Fig. 1 illustrates the specimen configuration and experimental setup for in situ measurement of water at the organic coating/substrate interface. With this configuration, the only pathway for water migration from the environment to the coating/substrate interface is through the thickness of the coating film within the walls of the chamber.

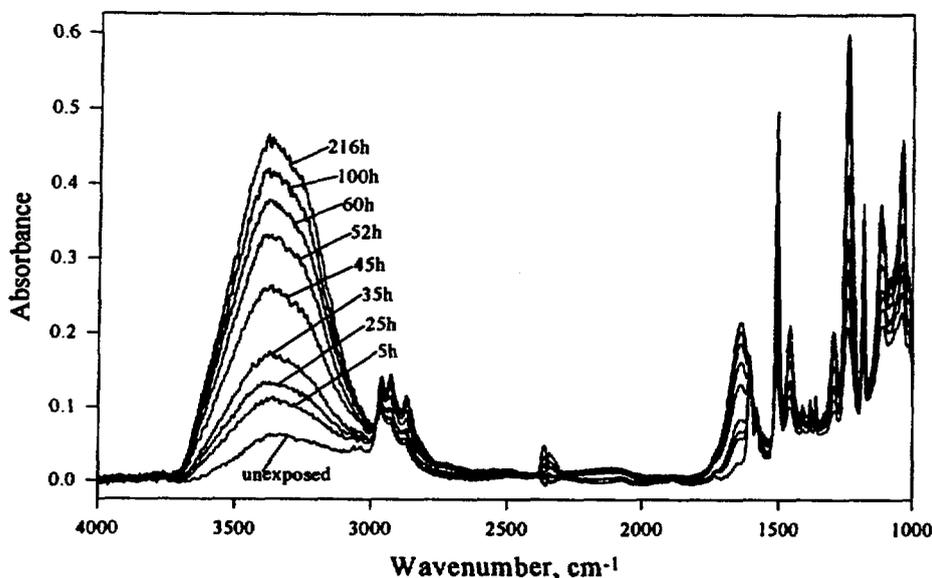


Fig. 2. Typical unprocessed FTIR-MIR spectra for several exposure times of an in situ measurement of water at the organic coating/substrate interface.

Fig. 2 presents typical unprocessed FTIR-MIR spectra in the  $1000\text{--}4000\text{ cm}^{-1}$  region for an organic-coated specimen before and during exposure to water for different time intervals. Each spectrum was obtained by ratioing the spectrum of the exposed specimen against the corresponding background spectrum. Although the effects of water are evident in the  $3000\text{--}3650$  and  $1625\text{--}1645\text{ cm}^{-1}$  regions, these spectra still contain the absorption bands of the coatings. To accentuate the effects of water in the organic-coated specimens, difference spectra were acquired by subtracting the spectra collected before exposure to water from those obtained at different exposure times. Fig. 3 presents the difference spectra for three specimens in the  $2800\text{--}3800$  and  $1400\text{--}1800\text{ cm}^{-1}$  regions. The coating thickness of the water-reducible/Ge, clear epoxy/untreated Si, and clear epoxy/silane-treated Si was  $430 \pm 15$ ,  $140 \pm 9$  and  $130 \pm 10\ \mu\text{m}$ , respectively. The thickness values were the average of five measurements, determined using a micrometer on the dried, free films removed from the substrates after the conclusion of the experiment. As emphasized earlier, there were no mirror or sample adjustments throughout the measurements. If there were no effect due to water exposure, all difference spectra would be straight lines with the exception of the intensity fluctuations of the  $\text{CO}_2$  bands from the air in the spectrometer. Bands above or below the baseline of a difference spectrum indicate an increase or a decrease, respectively, of the concentration of a chemical functional group as a result of water exposure.

Difference spectra displayed in Fig. 3 clearly show the effects of water on the organic-coated specimens. The intensity of the water bands at  $1640\text{ cm}^{-1}$  and in the  $3000\text{--}3650\text{ cm}^{-1}$  region increased, while the intensity of the coating bands, e.g. at  $1507\text{ cm}^{-1}$ , decreased with time of exposure to water. These changes are the result of water entering the coating/substrate interfacial region and interacting with the evanescent wave. Interfacial region is defined here as the probing depth of the evanescent wave in the sample. This depth is controlled by the refractive indices of the substrate and the sample, the angle of incidence, and the radiation wavelength. At the OH stretching of water ( $3400\text{ cm}^{-1}$ ,  $2.94\ \mu\text{m}$ ), this depth is  $<0.75\ \mu\text{m}$  for the Si and Ge substrates [22]. The bands peaking near  $1640$  and  $3400\text{ cm}^{-1}$  in the spectra of Fig. 3(a)–(c) are due to OH bending and stretching modes, respectively, of molecular water, as verified previously [21,22]. The intensity, expressed as peak height, of the  $3400\text{ cm}^{-1}$  band has been chosen for the quantitative analysis of water at the coating/substrate interface, because the water OH bending mode at  $1640\text{ cm}^{-1}$  is not sensitive to low water concentrations [26].

Fig. 4 depicts the intensity change of the  $3400\text{ cm}^{-1}$  band, which is proportional to the total amount of water detected, as a function of exposure time for the

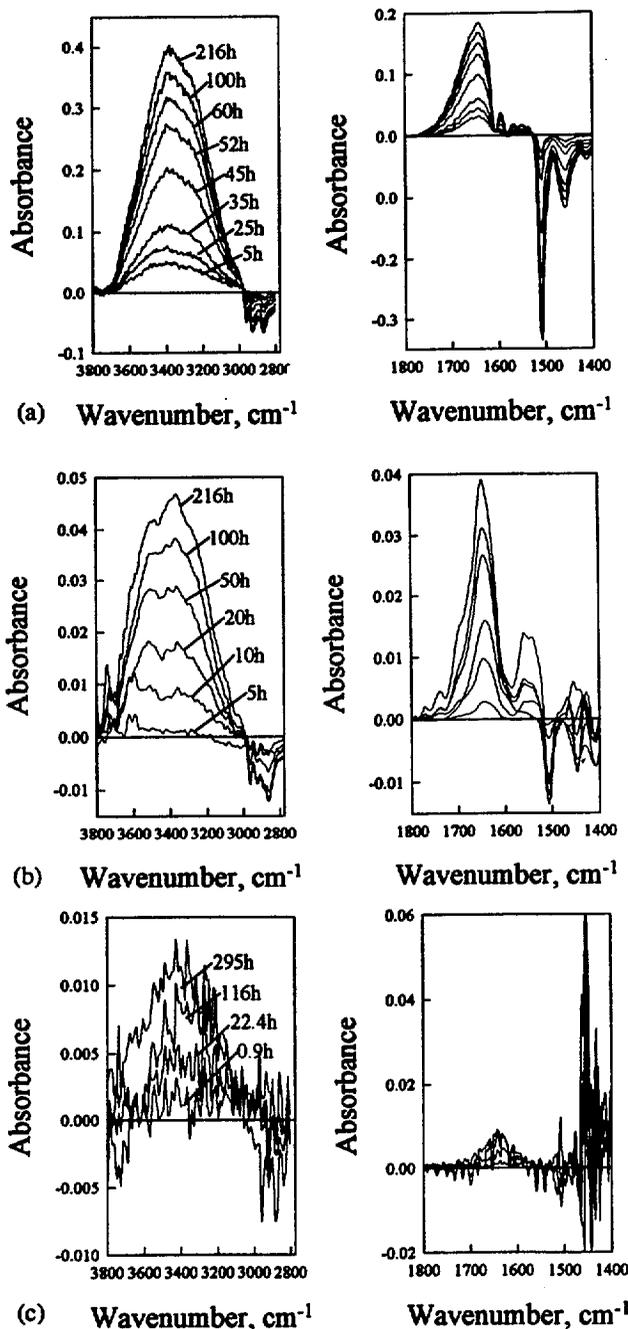


Fig. 3. FTIR-MIR difference spectra in the  $2800\text{--}3800$  and  $1400\text{--}1800\text{ cm}^{-1}$  regions for different times exposed to water for three specimens: (a) water-reducible epoxy/Ge; (b) clear epoxy/untreated Si; (c) clear epoxy/silane-treated Si.

three specimens. Fig. 4 shows that the processes and the rates at which water entered the interfacial region were different for the three coating systems. The rate for the clear epoxy/silane-treated specimen was smallest and that for the water-reducible/Ge system was greatest. The absorbance intensity at each exposure time displayed in Fig. 4 represents the total amount of water detected. This water comprised water at the coating/substrate interface and water in the coating film within

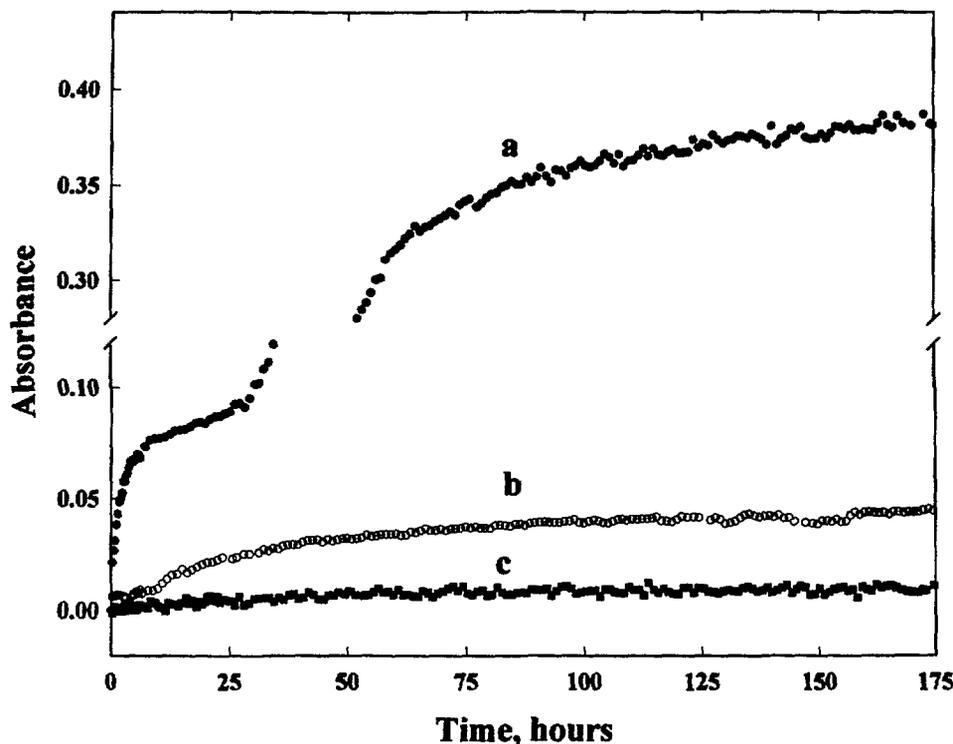


Fig. 4. Intensity changes of the water OH stretching band as a function of time exposed to water for three specimens: (a) water-reducible epoxy/Ge; (b) clear epoxy/untreated Si; (c) clear epoxy/silane-treated Si (each dot represents a data point).

the probing depth of the evanescent wave [21,22]. The contribution of the latter may be significant for relatively pure organic coatings, in which the total amount of water detected is small [22,26,42]. However, for most commercial organic coatings studied, the total amount of water detected is mainly from the water layer at the coating/substrate interface [22,24–26,42].

In addition to the intensity of the water bands, the intensities of the organic coating bands also decreased with exposure time. These changes for several common bands of a pigmented alkyd and a pigmented epoxy on a Ge substrate are illustrated in Fig. 5. The results reveal that the decrease was different for different bands. The largest decreases were for the strongest absorption bands, e.g. at  $1739\text{ cm}^{-1}$  for the alkyd and  $1507\text{ cm}^{-1}$  for the epoxy. The intensity decreases of the coating bands, together with the intensity increases of the water bands as a function of exposure, may only be explained by the water entering the coating/substrate interface. This is because the probing depths of the evanescent wave in the water-saturated and water-free coatings are essentially the same. As the thickness of the water at the interface increased, the amount of the organic material within the probing depth decreased because the coating film was pushed further away from the substrate surface.

Obviously, this technique is useful for studying the effects of a number of factors, e.g. temperature, electrolyte concentration and substrate surface contamina-

tion, on water accumulation at the coating/substrate interface. One interesting example is given in Fig. 6, which shows the effect of multiple layers (coats) on the water accumulation in the organic coating/substrate interfacial region. Curves a, b and c are plots of the OH stretching of the total water detected as a function of exposure time for one, two and three layers, respectively, of a water-reducible epoxy coating applied to a Ge substrate. The two-coat and three-coat films were prepared by allowing the preceding layer to cure 4 h before applying the next coat of the same thickness. The thickness of each layer was controlled by the thickness of the masking tape spacer (used in the draw-down technique). The thicknesses of the one-, two- and three-coat films were  $141 \pm 12$ ,  $208 \pm 19$  and  $242 \pm 20\ \mu\text{m}$ , respectively. It should be noted that the probing depth of the evanescent wave in the organic coating on a Ge substrate was only a small fraction of the thickness of the first layer of the multi-coat films ( $< 0.6\ \mu\text{m}$  for the probing depth as compared to  $\sim 105\ \mu\text{m}$  for the two-coat and  $\sim 120\ \mu\text{m}$  for the three-coat). Thus, the layering process should not affect the chemical and morphological characteristics in the probing depth region of the three specimens.

Fig. 6 reveals several interesting features. The process of water accumulation in the coating/substrate interfacial region of all three specimens apparently took place in four stages. The rates of increase of the first and third stages were quite rapid, while those for the second

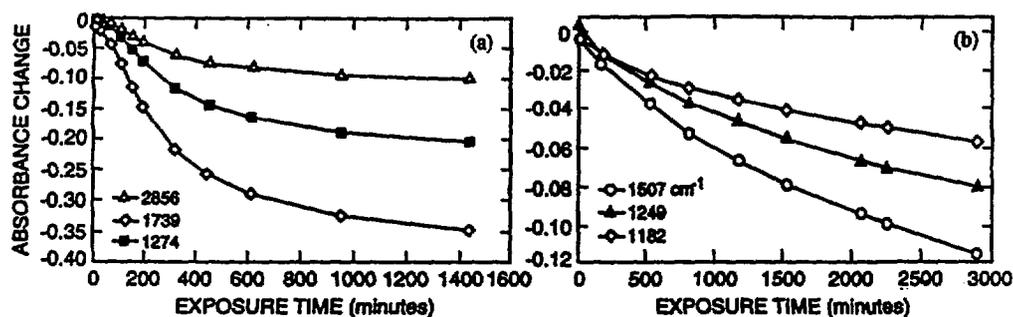


Fig. 5. Intensity changes of the coating bands as a function of time exposed to water: (a) alkyd/Ge; (b) epoxy/Ge [21].

and fourth were much slower. The effects of multiple coats may be seen in the slopes of the first and third stages and the time spans in the second stage. The rates of increase in the first and third stages decreased, and the time spans in the second stage increased, with an increasing number of coats. Differences in thicknesses between the specimens cannot explain these results because film thickness generally only affects the time required for water from the outside to reach the coating/substrate interface (time-lag). The time-lag is determined by the intersection between the first-stage line and the horizontal axis. The results suggest that layering has probably changed the water transport pathways in the coatings and that such change can be detected spectroscopically by this technique.

## 2.2. Organic coating/iron system

In this section, we present two examples to demonstrate the application of the FTIR-MIR technique for in situ measurement of water in the interfacial region between an organic coating and an iron film. The measurement was conducted using the specimen configuration shown in Fig. 7. In this case, the iron layer (obtained by a high-vacuum evaporation technique) was between the organic coating and the substrate. The presence of a poorly-reflective metal, such as iron, greatly decreases the signal-to-noise ratio of the FTIR-MIR spectrum. This is primarily due to the reflectivity loss, which increases by a factor of  $N$  for an  $N$ -reflection IRE, and is a function of the absorption coefficient of the metal [30]. Thus, for this kind of configuration, too many reflections may not be desirable, particularly, for low reflective metals. Indeed, we found that the signal-to-noise ratio improved with decreasing length of the iron film on the 50 mm substrate. Although good quality spectra were obtained with iron covering only 1/4 of the substrate length, for ease of handling, we used half-length, iron-coated substrates for this study (Fig. 7). Fig. 8 presents the FTIR-MIR difference spectra in the 1380–3910  $\text{cm}^{-1}$  region of the  $\text{TiO}_2$  pigmented epoxy coating on an iron-coated KRS-5 (thallium bromide iodide) substrate exposed to dis-

tilled water for various exposure times. The thickness of the iron layer was  $8.5 \pm 0.5$  nm (measured by ellipsometry) and that of the epoxy was  $92 \pm 7$   $\mu\text{m}$ . Fig. 8 shows an increase in the intensity of the OH stretching in the 3000–3650  $\text{cm}^{-1}$  region and the H–O–H bending at 1640  $\text{cm}^{-1}$  of water accumulation in the coating/iron interfacial region as exposure time increased.

Electrical potential, applied intentionally or unintentionally, accelerates blistering and delamination of coated steel [43]. Using the FTIR-MIR technique, we investigated the effects of applied electrical potential on the water accumulated in the organic coating/iron interfacial region. The study was conducted using the specimen configuration similar to that shown in Fig. 7, except that a platinum counter electrode and a platinum reference electrode were placed in the chamber containing 3.0% NaCl in water. The iron layer served as the working electrode. The electrodes were connected to a potentiostat and FTIR-MIR spectra of the organic coating/iron/KRS-5 system at open,  $-1.0$ ,  $-1.5$  and  $-2.0$  V (versus Pt reference electrode) were collected as a function of exposure time. Fig. 9 presents FTIR-MIR results in the 1000–4000  $\text{cm}^{-1}$  region for a polyurethane coating/iron/KRS-5 system. The thickness of the iron layer was approximately  $10 \pm 0.5$  nm and that of the polyurethane was  $110 \pm 10$   $\mu\text{m}$ . The same specimen was used for all potentials. The spectra were taken after 1 h of exposure at open potential (no applied potential), then scanned for 10 min at  $-1.0$  V, 10 min at  $-1.5$  V and 10 min at  $-2.0$  V. The bands at 1640  $\text{cm}^{-1}$  and in the 3000–3650  $\text{cm}^{-1}$  region are due to molecular water, as stated earlier. Fig. 9 shows that the amount of water detected increased with increasing applied potential. Leidheiser [43] reported an order magnitude increase in the rate of water transported through an alkyd coating on a steel substrate when the applied potential was increased from open potential (no applied potential) to  $-0.8$  V (versus SCE). He suggested that, under a cathodic potential,  $\text{H}_3\text{O}^+$  may be an important diffusing species. The results of Figs. 8 and 9 indicated that the FTIR-MIR technique can be used successfully to measure in situ water accumulation in the interfacial region be-

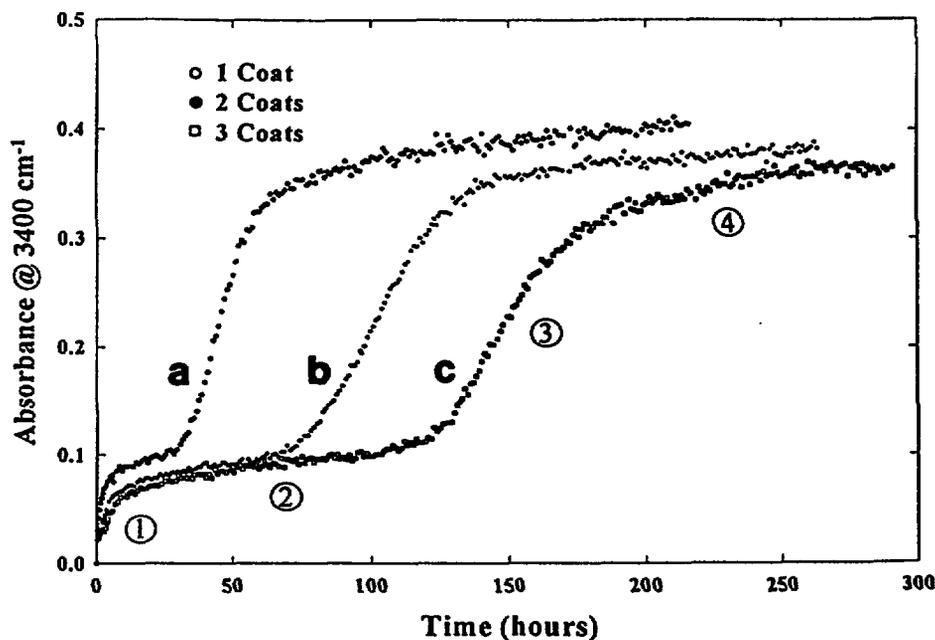


Fig. 6. Effect of multiple coats on FTIR-MIR intensity of the water OH stretching band as a function of time exposed to water for a water-reducible epoxy coating on a Ge substrate (each dot represents a data point).

tween an organic coating and a thin film of an industrial metal.

### 3. Quantification of water at the organic coating/substrate interface

This section summarizes the quantification of water at the coating/substrate interface using the FTIR-MIR technique for an organic coating/IRE system (Fig. 1). Quantitative aspects of the water layer at the coating/iron interface for the organic coating/iron/IRE arrangement (Fig. 7) have not been investigated. The theoretical basis of the technique for quantifying water at the organic coating/IRE substrate interface is derived from the penetration depth concept of internal reflection spectroscopy developed for thin and thick films. The model, in which the thickness and amount of water at the coating/IRE substrate interface are determined by the FTIR-MIR technique, is illustrated in Fig. 10 [22]. The substrate in this case is an IRE having a

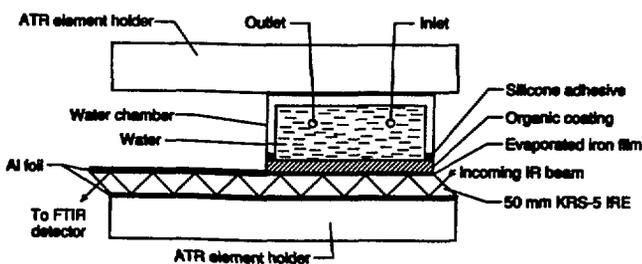


Fig. 7. Experimental setup for measuring water at the organic coating/iron substrate interface.

refractive index greater than those of organic coatings and water. The problem is treated as a two-layered sample model. The first layer consists of a water layer having thickness,  $l$ , in contact with the substrate. The second layer contains the water in the coating that is detected by the evanescent wave.

The water detected is the sum of the amounts in the layer at the coating/substrate interface and in the coating layer probed by the evanescent wave. Using IR absorbance to express the amounts of water, this statement may be written as [22]

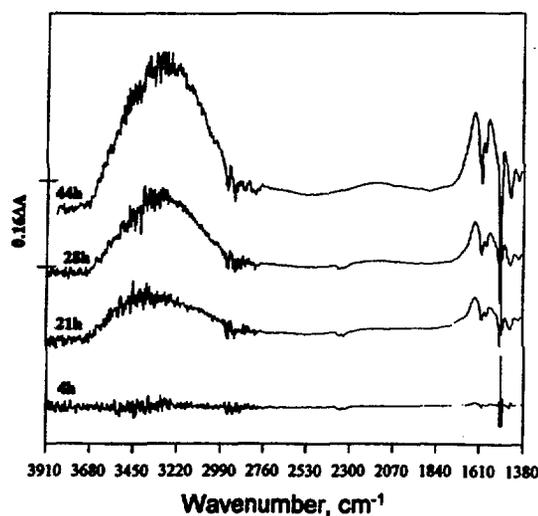


Fig. 8. FTIR-MIR difference spectra in the  $3910\text{--}1380\text{ cm}^{-1}$  region for different times exposed to water for a polyurethane/iron/KRS-5 specimen.

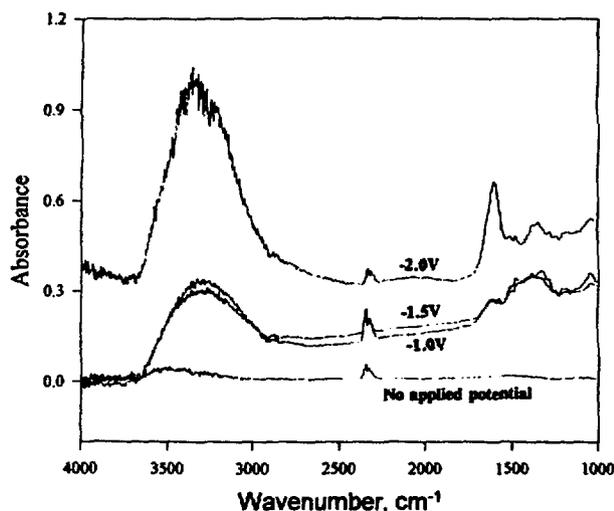


Fig. 9. Effect of applied electrical potential on the intensity of the water OH bands for a polyurethane/iron/KRS-5 specimen exposed to 3.0% NaCl solution.

$$A = \frac{n_2 \alpha_2 E_0^2}{n_1 \cos \theta} \int_0^l \exp\left(\frac{-2z}{d_{pw}}\right) dz + \frac{c_w n_3 \alpha_3 E_0^2}{n_1 \cos \theta} \times \exp\left(\frac{-2l}{d_{pw}}\right) \int_l^\infty \exp\left(\frac{-2z}{d_{pc}}\right) dz \quad (1)$$

where  $\theta$  is the incident angle,  $z$  is the depth from the interface,  $E_0$  is the amplitude of the evanescent wave at the surface,  $n_1$  is the refractive index of the substrate,  $n_2$  and  $\alpha_2$  are the refractive index and absorption coefficient of water at the coating/substrate interface,  $n_3$  and  $\alpha_3$  are the refractive index and absorption coefficient of water sorbed in the coatings,  $l$  is the thickness of the water layer at the coating/substrate interface,  $d_{pw}$  and  $d_{pc}$  are the penetration depths of the evanescent wave in water and coating, respectively,  $c_w$  is the fraction of water sorbed in the coating within the probing depth. The first term of Eq. (1) is the absorbance (FTIR) corresponding to the amount of water at the coating/substrate interface. The second term represents the amount of water in the coatings within the probing depth of the evanescent wave.  $d_{pw}$  and  $d_{pc}$  can be obtained from [30]

$$d_p = \frac{\gamma}{2\pi n_1 \left[ \sin^2 \theta - \left( \frac{n_2}{n_1} \right)^2 \right]^{1/2}} \quad (2)$$

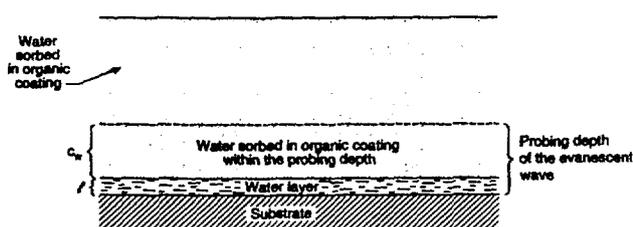


Fig. 10. Two-layer model used for quantifying water at the organic coating/substrate interface (not to scale).

where  $\gamma$  is the wavelength of the IR radiation in the vacuum.  $d_p$ , commonly defined as the penetration depth of the evanescent wave, is the depth at which the amplitude of the evanescent field has decreased to  $1/e$  of its value at the surface. Although the probing depth could be up to three times of  $d_p$  [32], due to the rapid decay of the evanescent wave, more than 85% of the total absorption intensity of a band is from one  $d_p$  [33,34]. Thus, the majority of water detected in the organic-coated specimen may be assumed to be within one  $d_p$ . Eq. (2) explicitly indicates that the penetration depth of the evanescent wave in the sample is a function of the angle of incidence, the wavelength of the radiation, and the refractive indices of the substrate and the sample. Eq. (2) is generally valid for non-absorbing or weakly-absorbing materials. For absorbing functional groups, Muller et al. [44] have derived a more exact equation for  $d_p$ , which uses the complex refractive index  $n_2/n_1(1 + i\kappa)$  ( $\kappa$  is the extinction coefficient) in place of the simple refractive index  $n_2/n_1$ . Further, due to the rapid change in the magnitude of  $n_2$  around the center of an absorption band (dispersion effect),  $d_p$  in the vicinity of the peak maximum may be different from that at or away from it, particularly for low  $n_1$  and low  $\theta$ , as demonstrated by simulation recently [45]. However, analysis by Nguyen et al. [22] has shown that the effect of absorption on  $d_p$  is negligible at the OH stretching of water and epoxy resins. Thus, at the band of interest (OH stretching) and for the materials used in this study, Eq. (2) is valid for calculating  $d_p$ .

Assuming that the refractive index and absorption coefficient of water at the coating/substrate interface are the same as those for water sorbed in the coating, i.e.  $n_2 = n_3$  and  $\alpha_2 = \alpha_3$  (a reasonable assumption), integrating and rearranging Eq. (1) yields an expression for calculating the thickness of the water layer at the coating/substrate interface,  $l$ :

$$l = \frac{d_{pw}}{2} \left[ -\ln \frac{1 - \frac{A}{A_\infty}}{1 - c_w \frac{d_{pc}}{d_{pw}}} \right] \quad (3)$$

where

$$A_\infty = \frac{n_2 \alpha_2 E_0^2 d_{pw}}{2n_1 \cos \theta} \quad (4)$$

and  $A_\infty$  is the IR absorbance when the water layer at the coating/substrate interface is very thick ( $l \rightarrow \infty$ , i.e.  $l > d_{pw}$ ). Physically, this means that the water layer at the interface is so thick that the amplitude of the evanescent wave decays to a negligible value within it. In this instance, only the first term of Eq. (1) remains. Eq. (3) is still valid for the case where the water layer at the coating/substrate interface is not continuous, e.g. discrete droplets, provided that the height of the droplet is not greater than the probing depth of the evanescent wave in water.

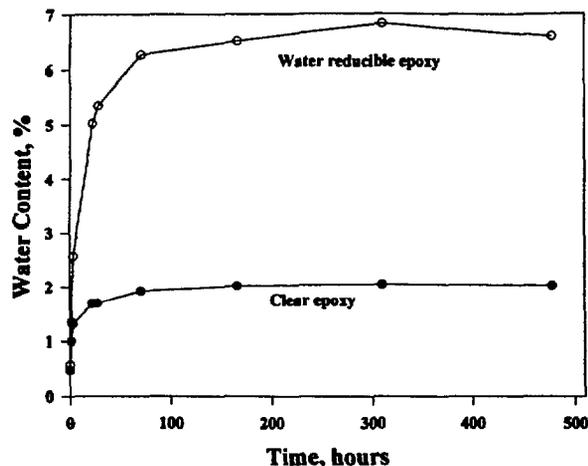


Fig. 11. Water uptake in water-reducible and clear epoxy free films as a function of time.

Assuming water is uniformly distributed over the entire surface area of the specimen, the amount of water at the coating/substrate interface,  $Q_i$ , will be given by

$$Q_i = l\rho \quad (5)$$

where  $a$  is the area in contact with water and  $\rho$  is the density of water at the interface.

To obtain the thickness  $l$  and amount  $Q_i$  of water at the coating/substrate interface using Eqs. (3) and (5),  $A$ ,  $A_\infty$ ,  $c_w$ ,  $d_{pc}$  and  $d_{pw}$  must be known.  $A$ ,  $A_\infty$ ,  $c_w$  are obtained from three separate experiments: (i) FTIR-MIR in situ measurement of organic-coated specimens exposed to water; (ii) FTIR-MIR analysis of water in contact with the coating-free substrates; (iii) water uptake in the free films, respectively. In this study,  $A$ , the FTIR-MIR absorbance corresponding to the total amount of water detected at a given exposure time, was taken directly from Fig. 4. Values of  $A_\infty$ , the FTIR-MIR maximum absorbance of liquid water, for the coating-free Ge and Si substrates were taken from Ref. [22]. Values of  $d_{pc}$  and  $d_{pw}$ , the penetration depths in coatings and water, respectively, were calculated from Eq. (2) using  $45^\circ$  incident angle, and the refractive indices of the substrates, coatings and water given previously [22]. At  $3400\text{ cm}^{-1}$ ,  $d_{pc}$  on Si and Ge substrates was  $0.24$  and  $0.20\ \mu\text{m}$ , respectively, and  $d_{pw}$  on the same substrates was  $0.22$  and  $0.19\ \mu\text{m}$ , respectively.

The mass fraction of water sorbed in the coating within the probing depth,  $c_w$ , was taken from the water uptake in the free films of the two epoxies (Fig. 11). The procedures for preparing the free films and recording the water uptakes in these specimens are given elsewhere [24].

The mass fractions of water sorbed in the coatings within the evanescent probing depth at a given exposure time ( $c_w$  in Eq. (3)) were linearly interpolated from the results of Fig. 11 after multiplying the time scale

(horizontal axis) by two. Time scale doubling was used to provide a rough correction for the difference between the water sorption process in the FTIR-MIR measurement and that in the water uptake in coating free films. Water sorption in the former (Fig. 1) was from one face of the coating while that in the latter took place on both faces of the films. The interpolation was made assuming that at steady state, all sorption sites in the coating films must be occupied by the same amount of water before the next layer of water was sorbed. This means that after a steady state was reached, the concentration of water remained constant at all points in the films. This assumption is analogous to that used in the derivation of the diffusion equations of materials in polymers based on the permeation approach [46]. We also made the analysis of water at the coating/substrate interface for the case where water was allowed to saturate the coating films before reaching the interface. The results showed essentially no difference in the amounts and thicknesses of the water layer at the interface between the two cases [26].

The thickness of the water layer at the organic coating/substrate interface was determined by substituting in Eq. (3) the values given above for  $A$ ,  $A_\infty$ ,  $c_w$ ,  $d_{pc}$  and  $d_{pw}$ . The amount of water at the interface,  $Q_i$ , was then calculated using Eq. (5) and an area value of  $329\text{ mm}^2$ , the surface area of the coated substrate within the water chamber, and a density of water at the coating/substrate interface of  $1\text{ Mg/m}^3$ . Fig. 12 displays plots of the thickness and the amount of the water layer at the coating/substrate interface as a function of exposure time for the three specimens. It can be seen that, for a given exposure time, a larger quantity of water was accumulated at the interface of the water-reducible epoxy/Ge specimen than that at the interface of the clear epoxy/Si specimens. Fig. 12 further shows that,

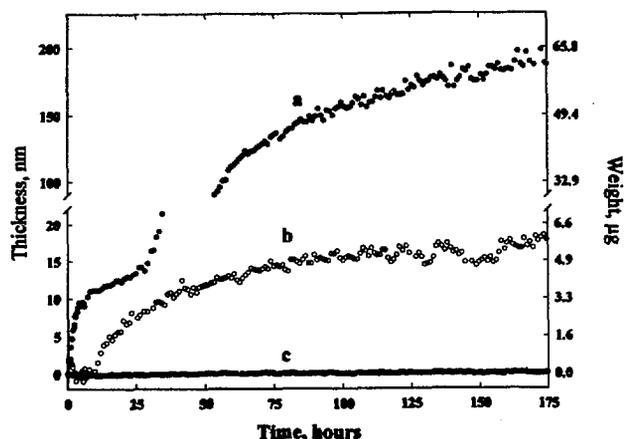


Fig. 12. Thickness and amount of water at the coating/substrate interface as a function of exposure time of water-reducible epoxy/Ge (curve a), clear epoxy/untreated Si (curve b), and clear epoxy/silane-treated Si (curve c) (each dot represents a data point).

essentially, no or little water had entered the interface of the silane-treated specimen, but more than 50 monolayers of water (one monolayer of water is approximately 0.3 nm) had built up at the clear epoxy/untreated Si sample after 100 h exposure. The rates of increase of the water layer for the clear epoxy specimens were also substantially lower than those of the water-reducible epoxy specimen. The results suggest that, for the specimens studied, the clear epoxy/Si system was more resistant to water displacement than the water-reducible epoxy/Ge system.

The results on water at the interface for the silane-treated specimen (Fig. 12(c)) suggest that the bond strengths between the treated surface and epoxy resin were stronger than those between the treated surface and water. Therefore, water molecules could not displace these bonds and thus little or no water entered the interface. These results are supported by the adhesion data [27], which showed that silane-treated specimens lost less than 20% of their bonding strength after more than 600 h exposure to 24 °C water, while untreated samples lost most of their adhesion in less than 50 h of exposure under the same conditions. The results are also consistent with the chemical bonding theory, which has been proposed as an explanation for the interfacial reinforcement mechanism and enhanced hydrolytic stability of composites made with silane-treated fibers [47]. It is noted that water/oxide bonds are relatively weak, <65 kJ/mol [15], and thus incapable of replacing stronger chemical interactions between the silane and the siliceous surface or between the silane and the epoxy resin.

It is important to point out here that the results of Fig. 12 (curve c) provide the first evidence that Eq. (3) is valid for quantifying water at the organic coating/substrate interface. This equation was derived based on a model consisting of the water layer at the interface and water sorbed in the coating film within the FTIR-MIR probing depth. If no water were at the interface, the total water detected (e.g. FTIR absorbance given in Fig. 4) would be due to only water in the organic coating layer near the interface. This is the case for the silane-treated specimen. This specimen had a hydrolytically stable interface, as evidenced by the small reduction in the adhesion after prolonged exposure and corroborated by the well-established mechanism of silane coupling agents on glass fibers. Such an interface should allow little or no water to enter this region. This is in good agreement with the results given in Fig. 12(c), which were calculated from Eq. (3).

#### 4. Discussion

It is evident from Fig. 12 that, at long exposure times, many monolayers of water have accumulated at

the interface of organic-coated untreated substrates. Indeed, this was the case because we observed (with the naked eye) substantial amounts of liquid water beneath the water-reducible coating specimens as they were slowly peeled from substrates at the conclusion of the experiments. The presence of water under the clear epoxy/untreated Si specimens was also evidenced by the wetness, which disappeared instantaneously, on the substrates at the peeling front. The accumulation of a substantial amount of water at the coating/substrate interface is also supported by other studies. For example, Leidheiser and Funke [9], in an extensive review on the water disbondment of organic coatings on metals, gave examples of, and cited references to, evidence of the presence of multilayers of water at the coating/metal interface. Further evidence is provided by comparative studies of water uptake in free films and films applied to a substrate (applied film) [20,48]; they showed that the water uptake in applied films is higher than that in the corresponding free films. Funke and Haagen [20] attributed the extra amount of water in the applied film to water accumulated at the coating/metal interface.

The amount of water at the coating/substrate interface is greatly increased if osmotic driving forces exist between the interface and the outside [9], or when the interface also contains hydrophilic contaminants. One example of the latter case is from the work of Bowden and Throssell [49] who found that, even at a relative humidity of 50%, a metal surface contaminated with  $10^{-7}$  g/cm<sup>2</sup> of potassium hydroxide would sorb the equivalent of five monolayers of water. It should be noted that, in the presence of salt contamination, a liquid phase of water at the interface can be formed at humidities far below the saturation point of water (humidity of liquification). For some salts, this humidity of liquification is quite low. For example, the humidities of liquification of LiCl and CaCl<sub>2</sub> are only 15 and 32%, respectively [50]. Thus, if the interface is contaminated with these salts, it is likely to hold molecular water even at low relative humidities. Unfortunately, water soluble inorganic and organic salts are almost ubiquitous contaminants at the organic film/substrate interface, either present before the film application or migrated during the exposure. Hydrophilic materials may also have migrated from the film to the interface during the coating application, curing process, or in service. Such a migration would likely result in the formation of a water-sensitive layer at the organic film/substrate interface. The presence of such a layer has been documented [7].

When the thickness of the water layer at the coating/substrate interface increases to tens of monolayers, there should not be any residual adhesion between the coating and the substrate. The loss of adhesion due to water can be substantiated by the fact that there was

little residual bond strength on the untreated specimens at the end of the experiment. This is consistent with the view expressed by Leidheiser and Funke [9] that the main mechanism responsible for the disbondment of organic-coated metals is the formation of a water film many layers thick at the coating/substrate interface. Similarly, Lefebvre et al. [51], in an intensive study on the mechanism of adhesion loss of epoxy/inorganic systems in humid environments, believed that water 'condensation' on the hydroxyl groups of the polymer at the polymer/substrate interface is the main cause of the sudden loss of the adhesion in high relative humidities. Further evidence of the effect of water in causing adhesion loss of organic-coated substrates comes from extensive data on the durability of organic coatings on metals [7-10], adhesive bonds [11] and asphalt pavements [12]. These studies all showed that the bond strength of an organic film/untreated, high-energy substrate system decreases significantly after exposure to water and high humidities. These results and the data presented in this paper suggest that changes in the FTIR-MIR intensity of water and of the coatings during exposure to humid environments may be related to the adhesion loss of the coatings on the substrate. If further work confirms that such a relationship exists, the technique may be useful for studying 'wet adhesion' (adhesion in the presence of water) non-destructively at the molecular level. Funke [52] has discussed the importance of wet adhesion in the corrosion control of organic coatings on metals.

Thermodynamic analyses by Kinloch [53] and others [54-56] revealed that interfacial bonds between an organic film and a high-energy, untreated substrate in the presence of an aqueous liquid are not stable and that water is capable of displacing the organic film from the substrate. This means that water is likely to enter the interface when an organic film/inorganic substrate system is exposed to a humid environment. The magnitude of the chemical bonds which water forms with metal and oxide surfaces is typically in the range of 40 to 65 kJ/mol [15]. Thus, compared with adsorbates such as CO or O<sub>2</sub>, water is a weakly-sorbed species. The fact that water entered the interface and that most of the bonding strength between the organic coatings and the substrates was lost during water exposure indicated that the organic coating/untreated substrate bonds are weak (<65 kJ/mol). These results suggest that, except for a few special cases where the organic coatings contain strong acidic groups, either present initially [57] or formed during oxidative curing [58], the majority of organic films interact with the untreated metal and inorganic oxide surfaces by means of secondary forces. These weak interactions are mainly due to the fact that most common metals are considerably more electropositive than the carbon atoms in organic compounds [59]. Consequently, the electron density on the

oxygen atom in the oxide surface group (-MOH, where M is the metal) is considerably greater than that on the oxygen in water or in most organic compounds. In general, therefore, covalently-bonded interfaces rarely exist in organic film/metal (oxide) systems, and the secondary-force bonds that do occur are too weak to resist the affinity of water to the polar, high-energy substrate. Thus, if the high-energy substrate surfaces are not modified, water is likely to form a layer at the interface when the system is exposed to water or high relative humidities. This will, in turn, lead to one or more of disbondment, corrosion and blistering of the system.

Water can reach the interface by a number of pathways, by diffusing through the matrix organic material, and by migrating through pinholes, pores, defects and local inhomogeneities in the films. Mayne and co-workers [60,61] have demonstrated experimentally the inhomogeneity of organic coatings. By the use of selective resistance and microhardness measurement techniques, they identified areas of poor- and high-crosslink density in a variety of polymer coatings. This type of 'cellular' structure has been used to explain the sharp drop in the d.c. resistance with little mass gain of epoxy/glass fiber composite exposed to water [62]. Even unpigmented polymer films are not homogeneous either but consist of micelles or granules of high-density polymer separated by narrow boundary regions of lower molecular weight material [63]. Bascom [64] surmised that this low molecular weight material may exist as a thin, continuous film or as channels between micelles at the interface and that the low-density regions provide pathways for easy entry of water to the film/substrate interface. For some coatings, the interface of the polymer with the fillers and pigments also serves as the transport pathways for water from the environment to the interface [65]. The transport through the organic films greatly increases if the swelling stresses in the films are high. In this case, the diffusion is much quicker—a linear function of time instead of a square root of time [66]. The transport also increases if there is an osmotic force between the outside environment and the interface [9]. Once entering the interface, water can transport along the film/substrate interface. For untreated substrate surface, the transport of water along the interface has been found to be much faster than that through the film [67].

Since the technique described here measures the amount of water at the organic film/substrate interface after water has penetrated through the thickness of the film, it can be used for measuring the diffusion of water through a film that is still adhered to a substrate, as recently demonstrated [24]. Data on water transport through a film adhered to a substrate better represents the transport of water in organic coatings in actual practice than do the values obtained for water

transport through a detached film. Thus, information on transport of water through a film applied to a substrate should be used for interpreting water disbondment and corrosion of organic-coated metals, and not that of the free film. Finally, although the method was developed for liquid water, it should be equally applicable for quantifying organic and inorganic compounds and ions at the organic films/substrate interface, or measuring their transport through a film still adhered to a substrate.

#### 4. Conclusions

Exposure to water causes disbondment of a coating from an organic-coated metal and may cause corrosion of the metal. Quantitative information on the water layer at the coating/substrate interface is crucial for understanding and preventing the failure of organic-coated substrates. A technique for determining the amount and thickness of water at a coating/substrate interface has been developed. The technique is based on a two-layer model, which was derived rigorously from internal reflection theory. The model takes into account: (i) water at the coating/substrate interface; (ii) water taken up by the coating within the probing depth of the evanescent wave; (iii) change of the penetration depth as water displaces the coating from the substrate. Experimentally, the method requires the application of an organic coating, transparent or opaque, of sufficient thickness on an internal reflection element (IRE), which is used as the substrate. A water chamber is attached to the coated specimen. After adding water to the chamber, Fourier transform infrared-multiple internal reflection (FTIR-MIR) spectra are taken automatically at specified time intervals without disturbing the specimen or the instrument. Water uptake in the coating and FTIR-MIR spectra of water on the coating-free substrates are obtained and used for the analysis. Several examples of clear and pigmented organic coatings on iron-evaporated and iron-free IREs were presented to demonstrate the capability of this technique for measuring in situ water at the organic coating/substrate interface. The technique also provides a means for determining the rate of water transport through a coating applied to the substrate. Quantitative information on water at the coating/substrate interface and the transport of water through organic coatings on a substrate is essential for the development of models for predicting the service lives of coating systems. Finally, the technique should be equally applicable to studies of organic and inorganic compounds at the coating/substrate interface and their transport rates through coatings adhered to a substrate.

#### References

- [1] H. Leidheiser, Jr., W. Wang and L. Igetoft, *Prog. Org. Coat.*, 11 (1983) 19.
- [2] W. Funke, *Ind. Eng. Chem. Prod. Res. Dev.*, 24 (1985) 343.
- [3] R.A. Dickie, in R.A. Dickie and F.L. Floyd (eds.), *Polymeric Materials for Corrosion Control*, ACS Symposium Series 322, American Chemical Society, Washington, DC, 1986, p. 136.
- [4] J.F. Watt, *J. Adhes.*, 31 (1989) 73.
- [5] T. Nguyen, J.B. Hubbard and G.B. McFadden, *J. Coat. Technol.*, 63 (794) (1991) 43.
- [6] J.M. Martin, M.E. McKnight, T. Nguyen and E. Embree, *J. Coat. Technol.*, 61 (722) (1989) 39.
- [7] P. Walker, *Off. Dig.*, 12 (1965) 1561; *J. Paint Technol.*, 31 (1967) 22.
- [8] W. Funke, *J. Oil Colour Chem. Assoc.*, 68 (1985) 229.
- [9] H. Leidheiser, Jr. and W. Funke, *J. Oil Colour Chem. Assoc.*, 5 (1987) 121.
- [10] K.L. Mittal (ed.), *Adhesion Aspects of Polymeric Coatings, Part III: Bond Durability*, Plenum, New York, 1983.
- [11] A.J. Kinloch (ed.), *Durability of Structural Adhesives*, Applied Science, New York 1983.
- [12] M.A. Taylor and N.P. Khosla, *Transp. Res. Record*, 911 (1983) 150.
- [13] L.H. Little, *Infrared Spectra of Adsorbed Species*, Academic Press, New York, 1966.
- [14] A.V. Kiselev and V.I. Lygin, *Infrared Spectra of Surface Compounds*, Wiley, New York, 1975.
- [15] P.A. Thiel and T.E. Madey, *Surf. Sci. Rep.*, 7 (1987) 211.
- [16] K. Ashley and S. Pons, *Chem. Rev.*, 88 (1988) 673.
- [17] R. Miles, *Surf. Interface Anal.*, 5 (1983) 43.
- [18] J.N. Israelachvili, *J. Colloid Interface Sci.*, 110 (1986) 263.
- [19] R.G. Horn, D.T. Smith and W. Haller, *Chem. Phys. Lett.*, 162 (1989) 404.
- [20] W. Funke and H. Haagen, *Ind. Eng. Chem. Prod. Res. Dev.*, 17 (1978) 50.
- [21] T. Nguyen, W.E. Byrd and C. Lin, *J. Adhes. Sci. Technol.*, 5 (1991) 697.
- [22] T. Nguyen, D. Bentz and W.E. Byrd, *J. Coat. Technol.*, 66 (834) (1994) 39.
- [23] T. Nguyen, W.E. Byrd, C. Lin and D. Bentz, *Adv. Composite Mater.*, 19 (1991) 1051.
- [24] T. Nguyen, D. Bentz and W.E. Byrd, *J. Coat. Technol.*, 67 (844) (1995) 37.
- [25] T. Nguyen, E. Byrd and D. Bentz, *Int. Rep. No. NISTIR 4783*, National Institute of Standards and Technology, Gaithersburg, MD, Mar. 1992.
- [26] T. Nguyen, W.E. Byrd and D. Bentz, *J. Adhes.*, 48 (1995) 169.
- [27] T. Nguyen, W.E. Byrd, D. Alsheh, W. McDonough and J. Seiler, *Proc., Materials Research Society Meet., Apr. 1995*, Vol. 385, Materials Research Society, Pittsburgh, PA.
- [28] T. Nguyen, W.E. Byrd, D. Alsheh and D. Bentz, *Proc., Adhesion Society Meet., Orlando, FL, Feb. 1995*, p. 252.
- [29] N.J. Harrick, *J. Opt. Soc. Am.*, 55 (1965) 851.
- [30] N.J. Harrick, *Internal Reflection Spectroscopy*, Harrick Science, Ossining, NY, 1979.
- [31] F.M. Mirabella, *Appl. Spectrosc. Rev.*, 21 (1985) 95.
- [32] F.M. Mirabella, *Spectroscopy*, 5 (1990) 20.
- [33] R. Iwamoto and K. Ohta, *Appl. Spectrosc.*, 38 (1984) 359.
- [34] K. Ohta and R. Iwamoto, *Appl. Spectrosc.*, 39 (1985) 418.
- [35] R.J. Jakobsen, in J.R. Ferraro and L.J. Basile (eds.), *Fourier Transform Infrared Spectroscopy—Applications to Chemical Systems*, Vol. 2, Academic Press, New York, 1979, p. 165.
- [36] V.M. Zolotarev, V.I. Lygin and B.N. Tarasevich, *Russ. Chem. Rev.*, 50 (1981) 14.
- [37] T. Nguyen, *Prog. Org. Coat.*, 13 (1985) 1.
- [38] H. Ishida, *Rubber Chem. Technol.*, 60 (1987) 498.

- [39] J. Yardwood, *Spectroscopy*, 5 (1990) 35.
- [40] Y. Ozaki, Y. Fujimoto, S. Terashita and N. Katayama, *Spectroscopy*, 8 (1993) 36.
- [41] J.C. Bolger, in K.L. Mittal (ed.), *Adhesion Aspects of Polymeric Coatings*, Plenum, New York, 1983, p. 3.
- [42] T. Nguyen, W.E. Byrd and D. Bentz, *Proc. American Chemical Society*, Vol. 66, PMSE Division, American Chemical Society, Washington, DC, 1992, p. 414.
- [43] H. Leidheiser, Jr., *Corrosion*, 39 (1983) 189.
- [44] G. Muller, D.K. Abraham and M. Schaldach, *Appl. Opt.*, 20 (1981) 1182.
- [45] T. Ohwaki, *Ph.D. Thesis*, Case Western Reserve University, 1993.
- [46] J. Crank and G.S. Park, in J. Crank and G.S. Park (eds.), *Diffusion in Polymers*, Academic Press, New York, 1968, p. 4.
- [47] C.L. Schutte, *Mater. Sci. Eng.*, R13 (1994) 265.
- [48] G.W. Walter, *Corrosion Sci.*, 32 (1991) 1085.
- [49] F.P. Bowden and W.R. Throssell, *Proc. R. Soc., London*, 209 (1951) 297.
- [50] W. Funke, *Prog. Org. Coat.*, 9 (1981) 29.
- [51] D.R. Lefebvre, K.M. Takahashi, A.J. Muller and V.R. Raju, *J. Adhes. Sci. Technol.*, 5 (1991) 201.
- [52] W. Funke, *J. Oil Colour Chem. Assoc.*, 68 (1985) 229.
- [53] A.J. Kinloch, in A.J. Kinloch (ed.) *Durability of Structural Adhesives*, Applied Science, New York, 1983, p. 24.
- [54] S. Wu, *Polymer Interface and Adhesion*, Marcel Dekker, New York, 1982, p. 589.
- [55] J. Comyn, in A.J. Kinloch (ed.), *Durability of Structural Adhesives*, Applied Science, New York, 1983, p. 85.
- [56] T. Nguyen and W.E. Byrd, *Proc. XVIII Fatigue Congr., Venice, Italy, 1986*, Vol. 3, p. 331.
- [57] D.L. Allara, *Polym. Sci. Technol.*, 12B (1980) 751.
- [58] H. Leidheiser, Jr., *J. Adhes. Sci. Technol.*, 1 (1987) 79.
- [59] J.C. Bolger and A.S. Michaels, in P. Weiss and D. Deever (eds.), *Interface Conversion for Polymer Coatings*, Elsevier, New York, 1969, p. 3.
- [60] E.M. Kinsella and J.E.O. Mayne, *Br. Polym. J.*, 1 (1969) 173.
- [61] J.E.O. Mayne and J.D. Scantlebury, *Br. Polym. J.*, 2 (1970) 240.
- [62] A. Lekatou, Y. Qian, S.E. Faidi, S.B. Lyon, N. Islam and R.C. Newman, *Proc. Materials Research Soc. Symp.*, 1993, Vol. 304, Materials Research Society, Pittsburgh, PA, p. 27.
- [63] R.E. Cuthrell, *J. Appl. Polym. Sci.*, 12 (1968) 1263.
- [64] W.D. Bascom, *J. Adhes.*, 2 (1970) 168.
- [65] W. Funke, U. Zorll and B.G.K. Murphy, *J. Paint Technol.*, 41 (1969) 210.
- [66] H. Corti, R. Fernandez-Prini and D. Gomez, *Prog. Org. Coat.*, 10 (1982) 5.
- [67] I. Linossier, F. Gaillard and M. Romand, *Proc., Adhesion Society Meet., Orlando, FL, Feb. 1995*, p. 86.