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1999: Coatings Permeability Research with EIS. Electrochemical Impedance Spectroscopy is a useful tool in assessing the permeability of a coating. This research reports on EIS measurements for a number of different coatings.

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY MEASUREMENTS OF BARRIER COATINGS

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SUMMARY

Polymer based coatings use barrier technology to protect substrates from corrosive chemicals and environments, particularly when in immersion service. Barrier technology uses materials such as flake reinforcements and provides an almost impermeable barrier between the chemicals and the substrate. Water transport in the coating, which may carry oxygen and aggressive ions from the environment to the metal/coating interface, is a critical parameter in assessing the ability of a coating to protect a steel substrate from corrosion. ASTM E96 is the most widely used procedure for measuring the water vapour permeability of a coating system.

In this work, EIS (electrochemical impedance spectroscopy) has been used to investigate the water absorption/transportation for a number of coatings including high performance barrier coatings used in immersion service. EIS spectra showed the pore resistance of the coatings, and the data was used to calculate the water absorption of the coatings as a function of testing time. A good correlation was established between water vapour permeability and EIS measurements for the coatings studied. It is concluded that EIS data will be useful in predicting lifetime expectancy of coatings used in immersion service.

Vinyl ester flakeglass coatings showed no detectable water absorption over the 12 days of the test. This unique behaviour has not been seen in reported literature before. Thus the EIS testing data is in line with the outstanding performance of vinyl ester flakeglass systems in immersion service in actual installations.

The results in this investigation demonstrate that EIS techniques can provide quick, reliable, and reproducible measurements for water transport evaluation in coatings. This work shows that EIS techniques are also applicable to thick barrier type coatings as well as the thinner coatings studied by other researchers.

Keywords: EIS, electrochemical impedance spectroscopy, barrier coatings, vinyl ester flakeglass coatings, water absorption, corrosion.

1. INTRODUCTION

Polymer based coatings use barrier technology to protect substrates from corrosive chemicals and environments, particularly when in immersion service. Due the harsh environments this type of coatings is subject to, low permeability is critical for the barrier coatings to protect steel substrates from corrosion in immersion service [1]. The permeability of the coating determines

the rate of transport of water, oxygen and other small molecules to the steel surface where they participate in the slow corrosion process. The rate of transport in turn is a function of the immersion temperature [1]. Hence, water permeability evaluation is particularly important in practical coating applications and in new coating developments.

Water absorption can be measured by classical gravimetric [2] and capacitance [3] methods. The traditional gravimetric methods, such as ASTM E-96 standard, are time taking and incorporate measurement errors and reproducibility difficulties, while capacitance techniques provide quick, accurate, and reproducible measurements [4] of water uptake during immersion tests. However, the application of capacitance techniques for permeability assessment of barrier type polymer coatings can be rarely seen in the published literature.

Washburn et al [1] measured the water vapour permeability of several polymer materials using the ASTM E-96 standard, which subjects the coatings to a fixed difference in water vapour pressure from one side to the other. It was found that non-permeable fillers were effective in retarding the moisture intrusion. Platelet type fillers were found to be most effective, with the overlapping flakes providing maximum effectiveness in restricting permeation of water and other small molecules through the coating.

Electrochemical impedance spectroscopy (EIS) is a powerful tool for studying coating degradation and corrosion of polymer coated metallic materials [5]. Through appropriate modelling, EIS can provide some critical information on moisture intrusion, coating degradation, development of coating defects, coating delamination, and under film corrosion mechanisms [5, 6]. This paper reports results of an investigation of the water permeation of various coating systems including barrier coatings using EIS techniques. The effects of coating thickness and filler contents in the coatings were also studied. In comparison with data obtained by ASTM E-96 standard tests, the applicability of EIS technique for coating permeability assessment is discussed.

2. EXPERIMENTAL

Coating samples were prepared on 150 × 150 mm steel panels of 4 mm thick. The steel surfaces were prepared by abrasive blasting with steel grit to achieve a minimum surface profile of 75 μm, and the coatings were applied according to their standard data sheets. The coatings were applied and allowed to cure at ambient temperature in the range 15°C to 20°C. Coatings tested are listed in Table 1.

The EIS measuring system employed in this investigation consisted of a PARC EG&G 273 potentiostat and a Solartron SI 1255 frequency response analyser. The impedance spectra were obtained using PARC M398 EIS software. A section of a plastic tube (100 × 100 mm) was glued on each coated sample to form an electrochemical cell with the steel substrate as the working electrode, a Ag/AgCl electrode as the reference electrode, and a platinum mesh as the counter electrode. Each cell was filled with 300 ml of 0.6 M NaCl solution prepared with analytical reagent and distilled water. All the measurements were performed at an ambient temperature of 22 ± 2°C.

Table 1. Coatings tested.

Label	Coating Type & Description	Thickness, mm
1A	Vinyl ester trowel applied: 0% Flakeglass	1.70
1B	Vinyl ester trowel applied: 15% Flakeglass	2.35
1C	Vinyl ester trowel applied: 25% Flakeglass	2.40
1D	Vinyl ester trowel applied: 35% Flakeglass	2.60
2A	Vinyl ester flakeglass trowel applied: 1 Coat	1.25
2B	Vinyl ester flakeglass trowel applied: 2 Coats	2.60
2C	Vinyl ester flakeglass trowel applied: 3 Coats	3.50
2D	Vinyl ester flakeglass trowel applied: 4 Coats	4.00
3A	Vinyl ester flakeglass trowel applied: Standard	3.00
4A	Vinyl ester flake filled brush applied	1.15
4B	Vinyl ester fibreglass laminate	2.20
4C	Vinyl ester lining: Filled basecoat plus laminate	3.00
4D	Vinyl ester lining: Filled basecoat and topcoat, reinforced	3.00
5A	Epoxy flake filled spray applied: 1 coat	0.35
5B	Epoxy flake filled spray applied: 2 coats	0.60
5C	High build epoxy plus polyurethane: spray applied	0.40
5D	High build epoxy plus polyurethane: spray applied	0.35
5E	Epoxy flake filled: brush applied	0.80
5F	Epoxy flake filled: trowel applied	3.00

3. RESULTS AND DISCUSSION

Figure 1 shows examples of the EIS spectra representing two different behaviours observed for the coating systems investigated in this work. Figure 2 shows an equivalent RC circuit applicable for most organic coatings [5]. The pore resistance, R_p , which represents the ability of a coating to protect the substrate, can be determined in the low frequency region in which the coating impedance is independent of frequency. The results show that some of the coatings (mostly in sample 5 series) have their well-defined pore resistance in the Bode diagrams, as shown by sample 5A in Figure 1. The other type of EIS behaviour, which represent most of the coatings from samples 1 to 4, is characterised by a nearly perfect - 1 slope in the Bode diagram extending to the frequency range of < 0.01 Hz, indicating the extremely high pore resistance of these coatings ($> 10^{10} \Omega$). In this case, the pore resistance of the coating cannot be precisely determined in the Bode diagrams with the frequency range of 100 kHz to 10 mHz tested in this investigation.

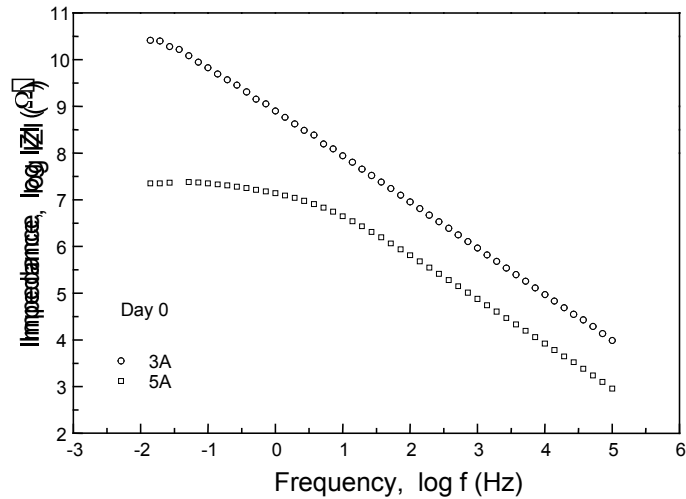


Figure 1. EIS spectra of samples 3A and 5A immediately after immersion.

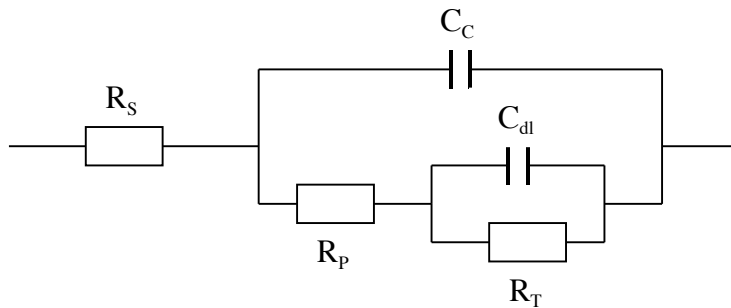


Figure 2. Equivalent RC circuit for organic coating/metal systems. R_S is the solution resistance, R_P is the pore resistance of the coating, R_T is the charge transfer resistance at metal/solution interface, C_{dl} is the double layer capacitance, and C_C is the coating resistance.

In a review on optimising the performance of fast-cure epoxies for pipe and tank linings, O'Donoghue et al [7] listed EIS as a test method for screening or pre-qualifying organic coatings. They indicated that coating impedance measured at a frequency of 0.1 Hz can be used as the key for coating screening (Figure 3).

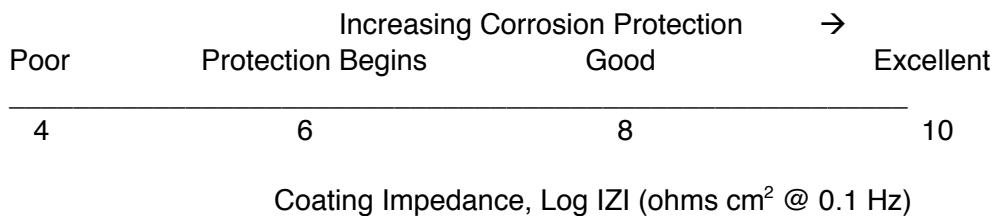


Fig 3: Corrosion protection of organic coatings [7].

Table 2 summarises the coating impedance at 0.1 Hz obtained in this investigation as a function of immersion time. The coating impedance at 0.1 Hz does not represent the exact pore

resistance for most of the coatings tested in this work, as discussed above, and so the impedance figures can only be used for comparison purposes.

Table 2. Coating impedance, IZI, at 0.1 Hz as a function of immersion time.

Sample	Coating Thickness (mm)	Impedance @ 0.1 Hz ($\Omega \text{ cm}^2$)			
		0 Day	4 Day	8 Day	12 Day
1A	1.70	4.66×10^9	4.53×10^9		4.46×10^9
1B	2.35	5.94×10^9	6.21×10^9	6.50×10^9	6.30×10^9
1C	2.40	5.38×10^9	5.60×10^9		5.42×10^9
1D	2.60	6.37×10^9	6.27×10^9		6.03×10^9
2A	1.25	3.33×10^9	3.35×10^9		3.48×10^9
2B	2.60	6.06×10^9	6.06×10^9		6.31×10^9
2C	3.50	7.24×10^9	7.43×10^9		7.07×10^9
2D	4.00	8.23×10^9	7.96×10^9		7.94×10^9
3A	3.00	6.72×10^9	6.99×10^9		7.53×10^9
4A	1.15	2.85×10^9	2.82×10^9	2.85×10^9	2.83×10^9
4B	2.20	5.83×10^9	5.50×10^9		5.91×10^9
4C	3.00	6.56×10^9	5.97×10^9		
4D	3.00	3.15×10^9	3.00×10^9		
5A	0.35	2.93×10^7	2.69×10^6		
5B	0.60	7.01×10^7	7.54×10^6	7.64×10^6	
5C	0.40	3.23×10^8	1.38×10^8	1.79×10^8	
5D	0.35	4.79×10^8	1.94×10^8		
5E	0.80	5.18×10^8	2.12×10^8		
5F	3.00	1.30×10^9	1.09×10^9		

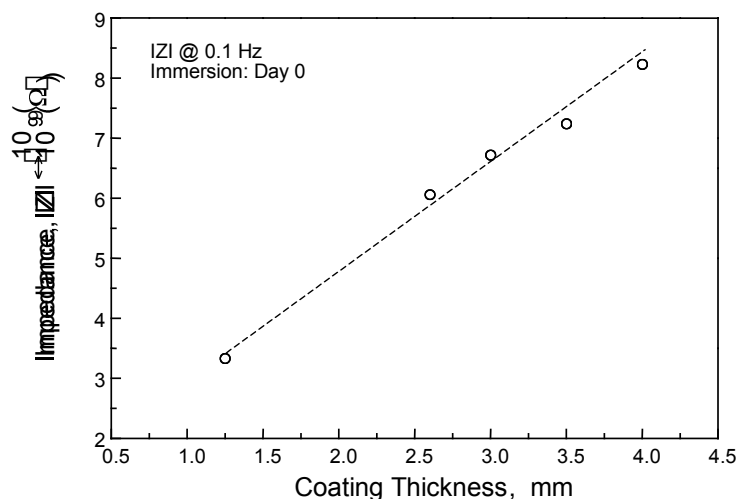


Figure 4. Relationship between IZI at 0.1 Hz and coating thickness for sample series 2 and 3 coatings.

Figure 4 plots the IZI at 0.1 Hz as a function of coating thickness for sample series 2 and 3 which are of the same coating type but at different thicknesses. The results demonstrate that the coating impedance increased with coating thickness. As can be seen in Table 2, no significant change of the coating impedance was observed in the sample series from 1 to 4 during 12 days of immersion (Figure 5). However, a very different behaviour was found for the sample series 5 coatings. As shown in Figure 6, the coating impedance at 0.1 Hz decreased by one order of magnitude after only four days of immersion. A minor decrease was observed during further immersion up to 12 days.

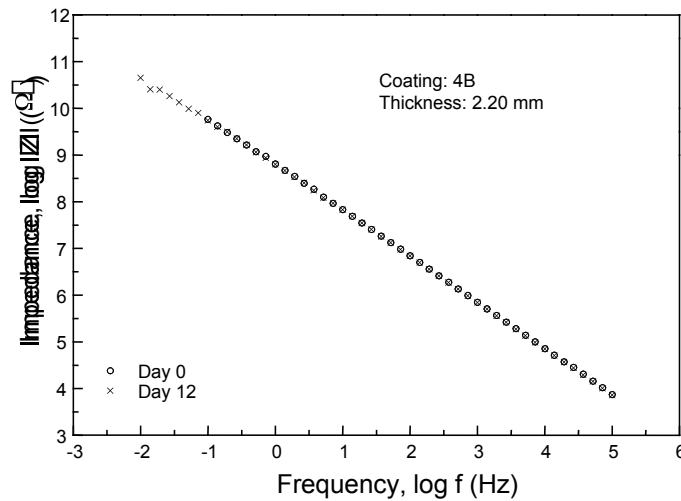


Figure 5. EIS spectra of sample 4B as a function of immersion time.

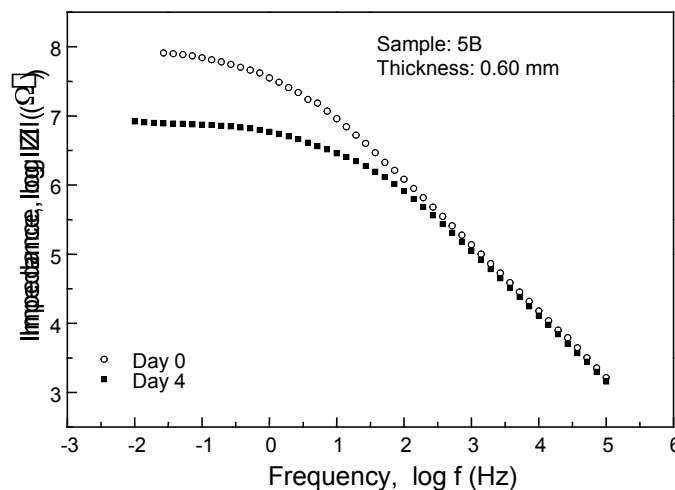


Figure 6. EIS spectra of sample 5B as a function of immersion time.

During the EIS measurements, no significant corrosion or coating degradation was observed during 12 days of testing. The decreases of coating impedance during the immersion tests is most likely due to the intrusion of moisture and ions into the micro pore structures in the

coatings, which in turn increased the pore conductance. The measurement of the water absorption or water permeability using EIS techniques is based on the determination of the changes of the coating capacitance. The coating capacitance can be calculated from the EIS data $C = 1/|Z|$ at the frequency of $1/2\omega$ Hz. The water absorption can be calculated by the formula given by Hartshorn et al [8].

$$\omega = [\log (C_t / C_0)] / [\log \epsilon_{H_2O}]$$

where ω is the volume fraction of the absorbed water, C_t is the coating capacitance at time t , C_0 is the capacitance at $t = 0$, and ϵ_{H_2O} is the dielectric constant of water. In this investigation, the coating capacitance measured immediately after immersion is taken as C_0 . The calculated ω using the capacitance values obtained in this work are summarised in Table 3. Any calculated ω less than 0.01 is taken as zero due to the limits of measurement errors. A close examination of the data in Tables 2 and 3 reveals a correlation between $|Z|$ and ω during the immersion tests, indicating that the decrease of $|Z|$ was due mainly to the water absorption in the coatings.

Table 3. Water absorption, ω , as a function of immersion time.

Sample	Coating Thickness (mm)	Water Absorption, ω		
		4 Day	8 Day	12 Day
1A	1.70	~ 0		~ 0
1B	2.35	~ 0	~ 0	~ 0
1C	2.40	~ 0		~ 0
1D	2.60	~ 0		~ 0
2A	1.25	~ 0		~ 0
2B	2.60	~ 0		~ 0
2C	3.50	~ 0		~ 0
2D	4.00	~ 0		~ 0
3A	3.00	~ 0		~ 0
4A	1.15	~ 0	~ 0	~ 0
4B	2.20	~ 0		~ 0
4C	3.00	~ 0		
4D	3.00	0.029		
5A	0.35	0.110		
5B	0.60	0.077	0.080	
5C	0.40	0.151	0.150	
5D	0.35	0.131		
5E	0.80	0.087		
5F	3.00	0.030		

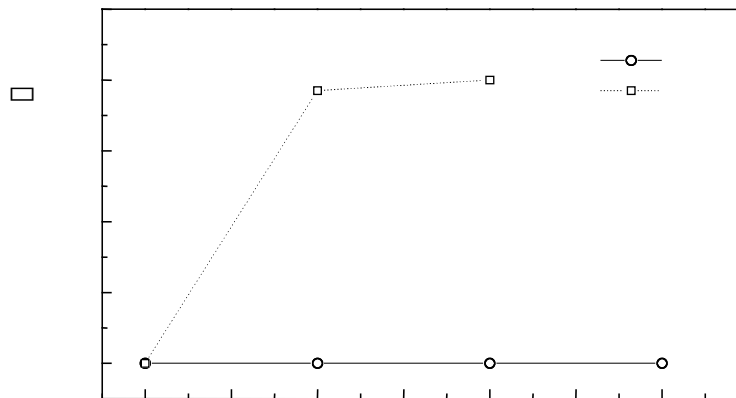


Figure 7. Comparison of water absorption as a function of immersion time for coating (4A) and coating (5B).

Figure 7 shows two different water absorption behaviours for an epoxy coating (sample 5B) and a vinyl ester flakeglass coating (sample 4A), respectively. Bellucci et al [4] studied the water transport in organic coatings ranging from 2 to 200 μm . They found that the coating capacitance increased initially upon immersion and levelled off afterwards, which was consistent to the case of sample 5B in Figure 7. The water absorption behaviours reported by Brasher et al [3] were also similar to that of sample 5B. However, most of the coatings in sample series 1 to 4 showed no detectable water absorption during 12 days of immersion. This unique water absorption behaviour of the vinyl ester flakeglass coating obtained in this work has not been seen in the reported literature.

In the determination of diffusion coefficients of water in paint films, Bellucci et al [4] attributed the early water transport to a homogeneous dissolution in the coatings studied. Touhsaent et al [9] divided the water absorption process into capillary action in the early stage and the following homogeneous dissolution stage. The exact mechanism may be related to the type of the coating systems tested. For the thin epoxy coatings (<1 mm) tested in this investigation, the rapid water absorption in the first four days of immersion could be best explained by the capillary action in the micro pore/defect structures, which was followed by a slow water dissolution in the coatings. This is supported by the fact that if homogeneous water dissolution played a major role in the early water uptake stage, water absorption should have been detected in the thicker vinyl ester flakeglass coatings such as 2A and 4A, after 8 or 12 days of immersion. Touhsaent et al [9] found that the capillary penetration depth increased with coating thickness to about 10 μm and then levelled off with a further increase in coating thickness. If this is generally the case for the coatings tested in this work, the total capillary volume fraction decreased as the coating became thicker. Therefore, the water absorption process for thick vinyl ester flakeglass coatings (> 1 mm) in this work was not dominated by capillary water absorption. The total capillary volume fraction in this type of coatings might be so small that the determination of coating capacitance changes due to capillary water absorption may be beyond the detection limit. The undetectable water absorption for the thick vinyl ester flakeglass coatings (> 1 mm) during 12 days of testing suggested that the rates of homogeneous water dissolution into the coatings were extremely slow.

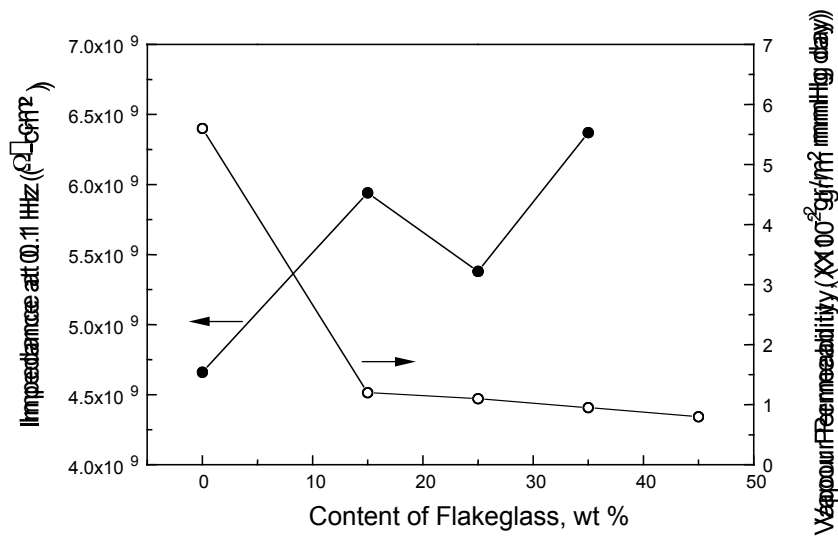


Figure 7. Comparison of IZI at 0.1 Hz and vapour permeability as a function of flakeglass content in coatings of sample series 1.

Figure 8 compares the IZI at 0.1 Hz and water vapour permeability for sample series 1. With the increase of flakeglass content, the water vapour permeability decreased [10], and at the same time, the IZI at 0.1 Hz increased. Therefore, there is a rough correlation between water vapour permeability and the impedance data, suggesting a possibility of using the IZI data to evaluate the water vapour permeability of coatings.

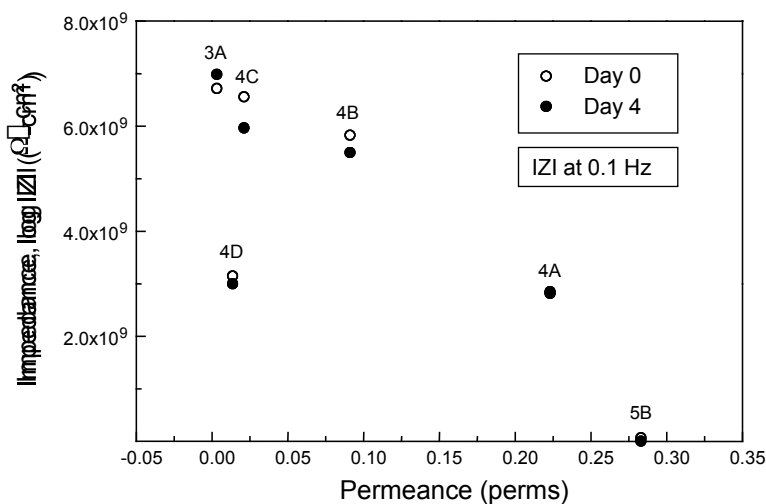


Figure 9. Correlation between IZI at 0.1 Hz and water vapour permeance.

Figure 9 plots the IZI data obtained in this work at 0.1 Hz against the water vapour permeance data reported elsewhere [1]. It is clear there is a good correlation between IZI at 0.1 Hz and water vapour permeance. As already discussed, significant water absorption was observed for the epoxy coatings less than 1 mm thick. Although the reported water vapour permeance data available [1] are limited to only some of the coatings tested in this investigation, it is likely that a

correlation exists between the water absorption obtained using EIS in this work and the water vapour permeability measured using ASTM E-96 standard.

The preliminary results have demonstrated the capability of EIS technique in evaluating the water transport properties of barrier type coatings. By an appropriate modelling of the coating system, EIS can provide information such as water absorption rate and depth of micro capillary/defect structures, water diffusion coefficient of homogeneous dissolution, which in turn can be used to calculate the water permeability in coatings. Normally the measurement error is less than 5% corresponding to a σ detection limit of less than 0.01. This provides a high degree of reproducibility of measurement as compared with the traditional gravimetric methods, such as ASTM E-96 standard. As indicated above, EIS can also reveal the mechanisms of water transport in the coatings as well as the under film corrosion mechanisms following the water absorption.

It is the author's experience that coatings of the type trowel applied vinyl ester flakeglass have an almost indefinite life in a mild aqueous solution such as salt water, and a life in a chlorine solution in the order of 15 years. The high performance of this type of coating has been reflected by EIS data measured during 12 days of immersion. EIS measurements did not reveal any significant changes during the testing period, which is indicative of extremely low water absorption and ion intrusion processes in these coatings. The results suggest that a coating with a IZI value at 0.1 Hz in excess of $6 \times 10^9 \Omega\text{-cm}^2$ represents a high performance barrier coating suitable for continuous immersion service in a mild aqueous solution. This figure provides a benchmark for comparing to other coatings. EIS techniques have been used to predict coating lifetime [4]. For the barrier coatings examined in this investigation, the assessment of coating life expectancy may require longer immersion periods and accelerated tests such as tests at elevated temperature.

4. CONCLUSIONS

This preliminary EIS investigation of the water absorption in the polymer coatings produced using barrier technology has led to the following conclusions:

- EIS spectra showed the pore resistance of different types of coatings. Vinyl ester flakeglass coatings showed an extremely high pore resistance.
- For the same coating type, the coating impedance increased with increasing coating thickness.
- The decrease in coating impedance with immersion time for some of the samples may best be explained by the water/ion absorption, leading to the increase of the conductance in the coatings.
- For the epoxy coatings of < 1 mm thick, the quick water absorption at early immersion stage could be explained by a capillary action of the pore/defect structure in the coatings.
- For the vinyl ester flakeglass coatings, there was no detected water absorption over the 12 days of the test. Thus the EIS testing data is in line with the outstanding performance of vinyl ester flakeglass systems in immersion service in actual installations.
- There is a correlation between water vapour permeability and EIS measurements for the coatings studied. Therefore EIS data appears useful in comparing different coatings for use in such applications as immersion in aqueous solutions. It is concluded that EIS data will be useful in predicting lifetime expectancy of coatings in immersion service.

- EIS techniques can provide quick, reliable, and reproducible measurements for water transport evaluation in coatings. This work shows that EIS techniques are also applicable to thick barrier type coatings as well as the thinner coatings studied by other researchers.

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ACKNOWLEDGEMENT

The authors wish to thank Technologies New Zealand for funding this project. The performance of EIS measurements by B. Lin is also acknowledged.