

Environmental and Electrochemical Test Methods for the Evaluation Of Protective Organic Coatings

B.S. Skerry, A. Alavi, and K.I. Lindgren
The Sherwin-Williams Company*

Three accelerated test chamber methods and two electrochemical test methods have been used to evaluate anticorrosion properties of organic coatings. Standard salt spray (ASTM B 117) procedures were modified to include the effects of wet/dry cycling, various electrolyte species (NH_4^+ , Na^+ , SO_4^{2-} , and Cl^-), and UV radiation. Different modes of deterioration were observed depending on the test conditions used. Degradation and corrosion were studied by scanning electron microscopy (SEM)/x-ray analysis (EDX) methods. Brief comparisons are made with data from exterior exposures at marine and industrial test sites. In separate experiments, electrochemical data were obtained for protective coatings under fully immersed conditions (0.6 M NaCl) by using ac impedance and electrochemical noise monitoring techniques. Impedance data are open to mechanistic interpretation, whereas the voltage and current noise signatures give clear indications as to the state of the coating.

INTRODUCTION

Organic coatings are commonly used to protect metallic engineering structures from degradation caused by natural or artificial environments. A recent estimate suggests that in 1986, the total value of shipments of paint and allied products in the U.S. amounted to some \$10 billion.¹ It has been suggested that half of the value assessed in this way is for coatings used for corrosion protection.²

Despite the large market for organic coatings, there are no laboratory test methods available which can be used

unambiguously to predict the long-term protective capabilities of a new corrosion protective coating. Particularly for coatings intended for atmospheric service, heavy reliance is often placed on essentially subjective results obtained from routine test methods, such as continuous salt spray. The most widely used test in the U.S. for this purpose is the procedure described by ASTM Method B 117-85.³

The justification for the use of such a method is that if a coating system resists the aggressive conditions of the salt spray, then it will also resist subsequent service environments. However, the non-justified assumption being made is that the mechanisms of corrosion and degradation pertaining to the service environments will be the same as those in the specific conditions of the continuous salt spray test.

In fact, it has been recognized for many years that when ranking the performance levels of organic coating systems, there is little if any correlation between results from standard salt spray tests and practical experience.⁴⁻⁶ Consequently, the need to develop more useful accelerated laboratory test methods for the evaluation of protective organic coatings is an important current issue for the coatings industry.

Describing meaningful accelerated testing procedures for coatings intended for atmospheric service is not a trivial task considering the complexities of the natural environment. Factors which affect corrosion and degradation of coated metallic substrates will certainly include the relative availability of oxygen, moisture, sunlight energy, and ambient temperatures, as well as the chemical content of the atmosphere (e.g., O_3 , SO_2 , NO_x) and also of alighting rainwater (e.g., H^+ , Na^+ , Ca^{2+} , NH_4^+ , Cl^- , SO_4^{2-} , NO_2^-).

Presented at the 65th Annual Meeting of the Federation of Societies for Coatings Technology, in Dallas, TX, on October 5, 1987.
*10909 S. Cottage Grove Ave., Chicago, IL 60628.

Table 1—Coatings Systems Studied by Laboratory Accelerated Test Methods

Primer	Topcoat	Substrate	Approx. Total Dry Film Thickness (μm)
Alkyd (active pigments: zinc chromate/ zinc oxide)	Alkyd	Mild steel (SAE 1010; 0.5-1.0 μm pro- file, washed by d.i. water/MEK)	70
Epoxy-polyamide (active pigment: zinc phosphate)	Epoxy-polyamide	Blast steel (cold rolled; 37-50 μm profile, washed by d.i. water/MEK)	135

Although it is not the purpose of the present work to model the complexities of the natural environment, three clear factors of importance in corrosion/degradation studies which are not modelled by the standard (ASTM B 117-85) salt spray test have been studied. They are: wet/dry cycling, a suitable choice of electrolyte, and the effects of incident UV radiation.

Furthermore, since metallic corrosion is an electrochemical phenomenon, it is believed that electrochemical test methods will provide a source of quantitative performance data for coatings evaluation work. For example, ac impedance methods have been investigated extensively for this purpose and considerable progress has been reported.⁷⁻¹⁰ For this reason, ac impedance has been used in the present work to obtain information regarding the performance capabilities of anticorrosion primers. A relatively new approach utilizing electrochemical noise monitoring has also been studied. The methods and the rationale for the electrochemical noise work have been described in more detail elsewhere.¹¹ For completeness, brief details of these techniques are also given in this paper.

EXPERIMENTAL

Environmental Test Procedures

LABORATORY ACCELERATED TEST METHODS: Three laboratory accelerated test methods have been studied by exposing coated mild steel (6" \times 3") test panels to the environments described in this section. Test panels were prepared under standardized conditions using numerous coating systems (primers with and without topcoats) on a variety of substrates. In this paper, results are given for the coating/substrate combinations described in Table 1.

Scanning electron microscopy (SEM) combined with energy dispersive x-ray analysis (EDX) methods were used to examine corrosion and degradation processes on exposed test samples. These studies were conducted using a Cambridge Scientific Instruments Stereoscan 250 fitted with a Tracor Northern TN 2000 x-ray analysis spectrometer [142 eV full width, half maximum peak resolution based on the Fe(K α) peak.]

The three accelerated test methods studied are described in the following sections. For each test condition, the total exposure time used was a maximum of 2000 hr.

Standard Salt Spray Test (ASTM B 117-85³)—In this procedure, coated panels were exposed inside a standard test chamber, supported at a 15-30^o angle from the vertical, and were sprayed indirectly with an atomized 5 wt% salt spray based solely on NaCl. The test was operated at 35 \pm 1.5^oC with a steady state relative humidity of approximately 95-98%

Wet/Dry Cycle Corrosion Test—Variations on the standard salt spray test method have been in existence for many years. Some of these are described in ASTM G 85-85.¹² Elsewhere in the literature, Harrison, Tickle, and Barraclough⁴⁻¹³ concluded that salt spray tests based on continuous NaCl spray alone are particularly unreliable for accelerating atmospheric corrosion in industrial atmospheres. These workers suggested that the observed unreliability was because of the absence of ammonium and sulphate species in the test method and also because the effects of wet/dry cycling which occur in nature are not reproduced in continuous salt spray conditions. They clearly demonstrated the presence of both sulphate and ammonium species both in the atmosphere as well as on naturally weathered steel.

Accordingly, Harrison¹⁴ used a salt spray solution comprising 3.25 wt% (NH₄)₂SO₄ with 0.25 wt% NaCl, and observed improved correlations with 14-year exterior exposures in industrial environments. These ideas were further developed by Timmins¹⁵ who recommended using wet/dry cycling (3 hr salt spray alternating with 1 hr drying using ambient air) and also the use of a diluted version of Harrison's electrolyte, comprising 0.40 wt% (NH₄)₂SO₄ with 0.05 wt% NaCl.

The wet/dry cycle test used in the present work is similar to that described by Timmins.¹⁵ The method used was a wet/dry cycle conducted in a test chamber approximately 0.32 m³ in volume. Timmins' electrolyte was used, having an approximate pH of 5.2. Salt mist was produced by a venturi nozzle atomizer at a rate of 600 mL hr⁻¹. All coated panels received a similar quantity of electrolyte when located around the periphery of the chamber. During the wet cycle, the chamber was allowed to cool under ambient conditions.

In this work, dry and wet cycles were programmed for 1 hr each in order to accelerate further the effects of wetting and drying compared with Timmins' method. During the dry cycle, the test chamber was resistively heated to 35 \pm 2^oC. Thus, the coated panel surfaces appeared visibly dry at the end of each drying cycle. The relative humidity inside the test chamber was reduced to approximately 45% at the end of each dry cycle as measured by a wet/dry bulb hygrometer.

A further point to note is that with the electrolyte concentrations used in this test (substantially lower than in conventional salt spray) the corrosion inhibitive pigments may function more as they would in a natural environment; an issue already raised in the literature by Funke.¹⁶

Wet/Dry/UV-Condensation Test—UV degradation and condensation factors were incorporated into the wet/dry cycle corrosion test method previously described by making use of a standard UV-condensation test apparatus operating to ASTM G 53-84 specifications.¹⁷ In this work, the conditions used were: 4 hr radiation (UV-B 313 bulbs) at 60°C, followed by 4 hr condensation (deionized water) at 50°C. This test procedure was intended to simulate deterioration caused by water as dew and also the concomitant effects of natural UV radiation.

In this third test method, test panels were exposed to the wet/dry cycle corrosion test method for 200 hr, then cycled through the UV-condensation test chamber for 200 hr on a rotating basis until a total of 2000 hr had elapsed.

OUTDOOR EXPOSURE TESTS: In the present work, some initial comparisons have been made with results obtained from outdoor exposures. Two experiments were conducted in order to study the morphology of corrosion products produced in natural environments, and also the chemical composition of corrosion products formed in scribe lines of painted panels exposed at industrial and marine test sites.

In the first of these experiments, uncoated mild steel panels (SAE 1010:C 0.08-0.13%, Mn 0.3-0.6%, P (max) 0.04%, S(max) 0.05%) having a surface finish roughness of approximately 0.5-1.0 μm were exposed for four weeks to an industrial atmosphere (Chicago, IL). Corrosion product morphology was studied by SEM. The results obtained were then compared with the corrosion products formed on similar mild steel panels after 48 hr exposure to: (a) salt spray and (b) wet/dry cycle corrosion test conditions.

In the second experiment, the corrosion products from the scribe lines of two coated panels after exterior exposures for six months in natural environments were studied by EDX. Corrosion products were analyzed from the coated panels described in *Table 2*.

Electrochemical Test Methods

Two electrochemical test methods have been used in the present work. They are, firstly, ac impedance, and secondly, an analysis of the voltage and current noise transients which occur under intact paints when under freely corroding test conditions. The experimental test procedures used have been described in detail elsewhere.¹¹

For both techniques, the test electrodes used were coated mild steel (SAE 1010) test panels of surface area either 24 cm² or 40 cm². Plexiglass cells were attached to these panels which were filled with 0.6 M NaCl as the electrolyte. Ambient aeration was used during testing.

AC IMPEDANCE: All ac impedance measurements were conducted using a Solartron 1250 frequency response analyzer (FRA) operated under microcomputer control (HP 85). The FRA was connected to the electrochemical cell via a Thompson 251 potentiostat. For studies of relatively low impedance systems, a standard potentiostatic three electrode configuration was used with the coated (working) electrode held at the measured free corrosion potential. For relatively high impedance systems, a two

Table 2—Coated Panels Exposed Outdoors for Subsequent Scribe Line Corrosion Product Analysis

Primer	Topcoat	Substrate	Approx. Total Dry Film Thickness (μm)	Exposure Environment
Latex (active pigment: barium metaborate)	None	Mild steel (SAE 1010; 0.5-1.0 μm profile, washed by d.i. water/MEK)	100	Marine (Florida)
Epoxy-polyamide (active pigment: zinc phosphate)	Polyurethane	Mild steel (SAE 1010; 0.5-1.0 μm profile, washed by d.i. water/MEK)	85	Industrial (Chicago)

electrode configuration was used with the FRA operating in its amplitude compression mode. Applied signals were in the range 20-50 mV over a nominal frequency range of 10 kHz-10 mHz. Representative complex plane data are given for the primer coatings noted in *Table 3*.

ELECTROCHEMICAL NOISE ANALYSIS: For the electrochemical noise monitoring experiments, electrochemical cells previously described were prepared and assembled in a three electrode arrangement wherein two of the electrodes were coated steel substrates prepared so as to be nominally identical. These two coupled electrodes were connected electrolytically by an agar salt bridge and allowed to corrode freely during a period of approximately 2000 hr. The third electrode in the assembly, in each case, was an Ag/AgCl reference.

Periodically during testing, a low noise zero-resistance ammeter (ZRA) was connected between each coupled electrode pair. Two sensitive digital voltmeters (DVM's) measured, simultaneously, each cell current flow (via the ZRA) and each coupled pair electrode potential. The experiment was conducted under microcomputer control (HP 85) using eight separated channels multiplexed with a commercially available IEEE programmable switch.

Data were collected as time records of coupling currents and potentials for each pair of coated electrodes. By applying an Ohm's Law analogy as discussed previously,¹¹ derived values of an approximate "polarization resistance" parameter (R_p) for each coated electrode pair were obtained from the simple ratio of the standard deviation of the potential noise signal to the standard devi-

Table 3—Primer Coatings Studied by Ac Impedance

Primer	Substrate	Approx. Dry Film Thickness (μm)
Vinyl chloride (barrier type)	Mild steel (SAE 1010; 0.5-1.0 μm surface profile, washed by d.i. water/MEK)	60
Alkyd (active pigment: zinc chromate)	Mild steel (SAE 1010; 0.5-1.0 μm surface profile, washed by d.i. water/MEK)	30

Table 4—Coatings Studied by Electrochemical Noise Analysis

Coating	Substrate	Approx. Dry Film Thickness (μm)
Polyurethane (barrier type)	Mild steel (SAE 1010; 0.5-1.0 μm surface profile, washed by d.i. water/MEK)	30
Epoxy-polyamide (active pigment: strontium chromate)	Mild steel (SAE 1010; 0.5-1.0 μm surface profile, washed by d.i. water/MEK)	40
Alkyd (barrier type)	Mild steel (SAE 1010; 0.5-1.0 μm surface profile, washed by d.i. water/MEK)	40
Alkyd (active pigment: zinc chromate)	Mild steel (SAE 1010; 0.5-1.0 μm surface profile, washed by d.i. water/MEK)	30

ation of the current noise signal, i.e., $R_p \sim \sigma V/\sigma_i$. It should be noted that this derived resistance parameter encompasses effects due to the coating as well as to charge transfer and diffusion processes. For coated electrodes, these effects cannot be separated out. Representative data are presented here for four coating systems as described in Table 4.

RESULTS AND DISCUSSION

Environmental Test Program

LABORATORY ACCELERATED TEST METHODS:

Visual Observations—Figure 1 illustrates the deterioration observed on the alkyd coating system after 2000 hr testing in the three accelerated test environments. It is clearly apparent that the modes of degradation and types of failure thus produced depend fundamentally on the test conditions to which the coatings have been subjected.

In this example, the alkyd primer/topcoat system exhibited severe degradation as a result of exposure to the standard salt spray environment after only 1000 hr testing as shown in Figure 1(a). However, the degradation observed is quite unlike that observed in practice for alkyd paint systems. The same paint exposed to the wet/dry cycle corrosion test exhibited relatively little degradation even after 2000 hr testing, as can be seen in Figure 1(b).

In contrast, Figure 1(c) illustrates how the additional presence of UV-condensation factors in the wet/dry cycle corrosion test fundamentally altered the nature of the corrosion/degradation processes which can occur. The results produced by this combination of test factors appear, qualitatively at least, to be more closely representative of the corrosion and degradation observed for such alkyd paints in natural atmospheric service environments.

A second example, shown as Figure 2, is for an epoxy-polyamide primer/topcoat system applied over blast steel. This coating shows analogous trends. Neither the salt spray test result [Figure 2(a)] nor the wet/dry cycle corrosion test [Figure 2(b)] give particularly realistic deterioration effects. Again, in contrast, the added presence of the UV-condensation factors combined with the wet/dry cycle corrosion test conditions gave more realistic deterioration for this coating system, with some rusting in the scribe lines as well as some rust staining adjacent to the scribes being visible in Figure 2(c). Also apparent was the observation that some loss of gloss had occurred after 2000 hr exposure to the wet/dry/UV-condensation test cycle combination.

SEM/EDX Analysis of Coated Panels After Exposure to Accelerated Test Environments—In order to elucidate the effects of the additional UV-condensation factors on the overall degradation of the epoxy-polyamide paint system, SEM/EDX methods were employed. These studies revealed that the surface morphology of the coating was profoundly affected by the nature of the test atmosphere.

Figure 3(a) shows the surface of the unexposed control sample. Relatively smooth polymeric binder can be seen in this case with the added presence of some inorganic pigments underlying the surface. The effect of the wet/dry cycle corrosion atmosphere was to roughen the surface slightly, and to make more obvious the presence of the pigment particles as seen in Figure 3(b). EDX analyses confirmed that the pigment particles observed were a combination of TiO₂ and extender material.

By comparison, the additional presence of the UV-condensation factors in the wet/dry cycle corrosion test method produced very significant changes in the nature of the painted surface. Figure 3(c) illustrates that, in these circumstances, much of the surface layer of the binder

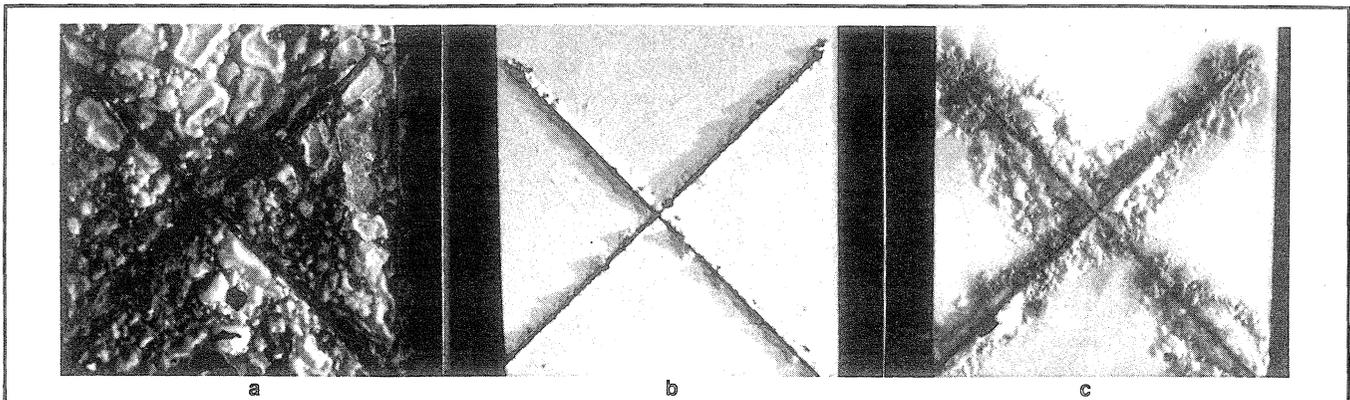


Figure 1—Visual degradation of alkyd coating system on steel after exposure to laboratory accelerated test conditions: (a) 1000 hr salt spray (ASTM B 117-85); (b) 2000 hr wet/dry cycle [(NH₄)₂SO₄/NaCl electrolyte]; and (c) 2000 hr wet/dry/UV-condensation cycle

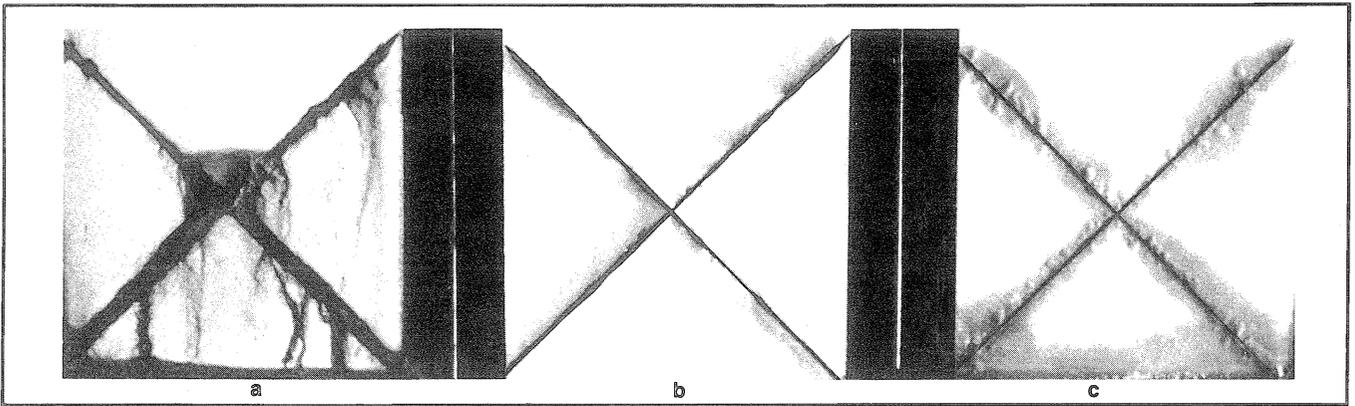


Figure 2—Visual degradation of epoxy-polyamide coating system on steel after exposure to laboratory accelerated test conditions: (a) 2000 hr salt spray (ASTM B 117-85); (b) 2000 hr wet/dry cycle [(NH₄)₂SO₄/NaCl electrolyte]; and (c) 2000 hr wet/dry/UV-condensation cycle

had been degraded, leaving merely discrete “islands” of polymer coated pigment surrounded by the inorganic pigment matrix. An obvious result is the observed reduction in gloss of the paint. The pigment matrix is presumably held together by the underlying organic binder which had not yet been degraded.

Such changes in the surface condition of a paint are likely to affect subsequent interactions with the environ-

ment to which it is exposed. The roughened inorganic pigment rich surface would be likely to be more hydrophilic than the organic binder. Hence, after degradation the coating may retain moisture longer and so will be subject to longer periods of wetness than when the binder was relatively intact.

Investigation of the surface rust staining adjacent to the scribe lines [Figure 3(d)] suggested the presence of iron

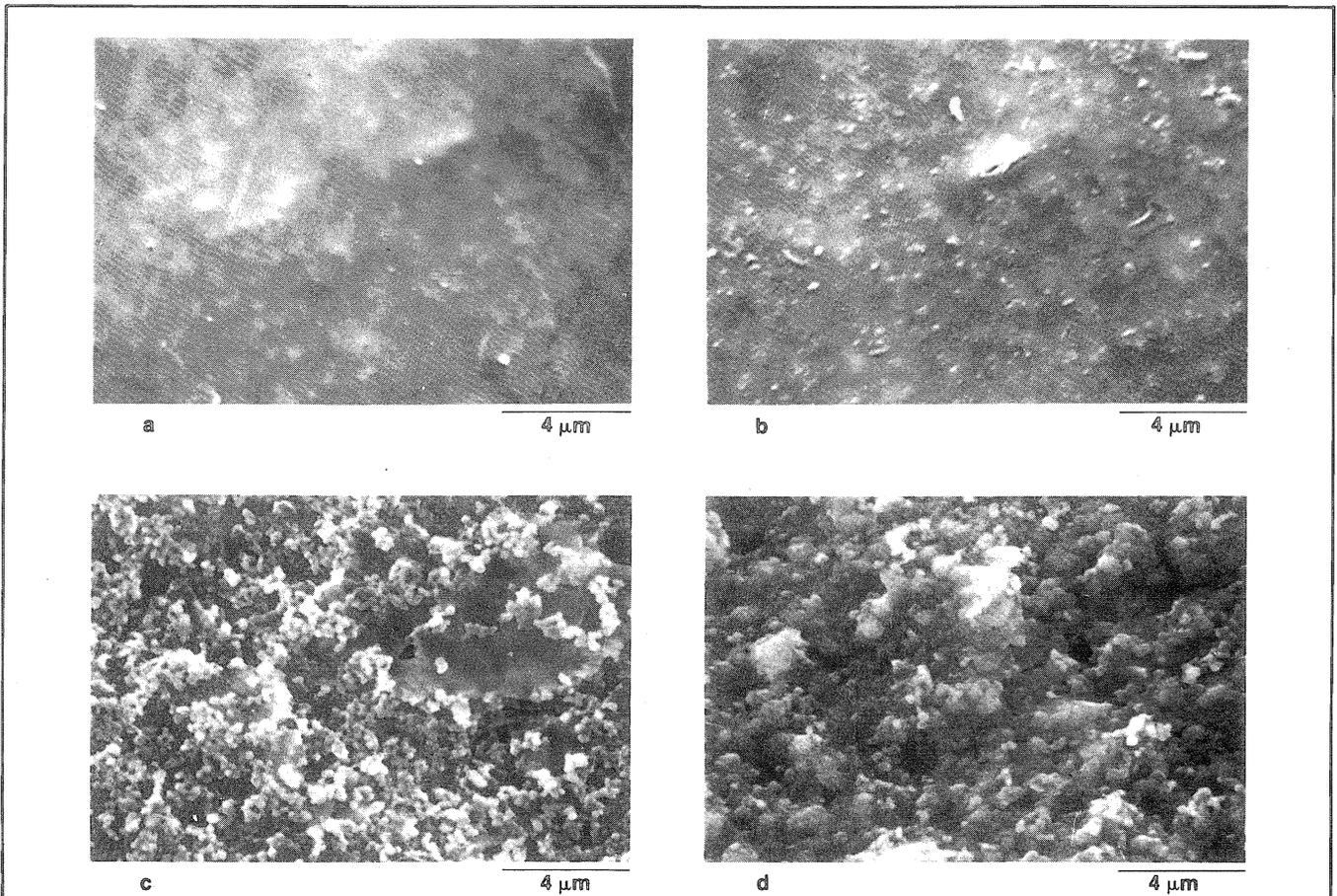


Figure 3—Scanning electron micrographs of epoxy-polyamide coating on steel illustrating surface degradation after exposure to laboratory accelerated test conditions: (a) control (i.e., no test exposure); (b) 2000 hr wet/dry cycle test—remote from scribe line; (c) 2000 hr wet/dry/UV-condensation test—remote from scribe line; and (d) 2000 hr wet/dry/UV-condensation test—adjacent to scribe line

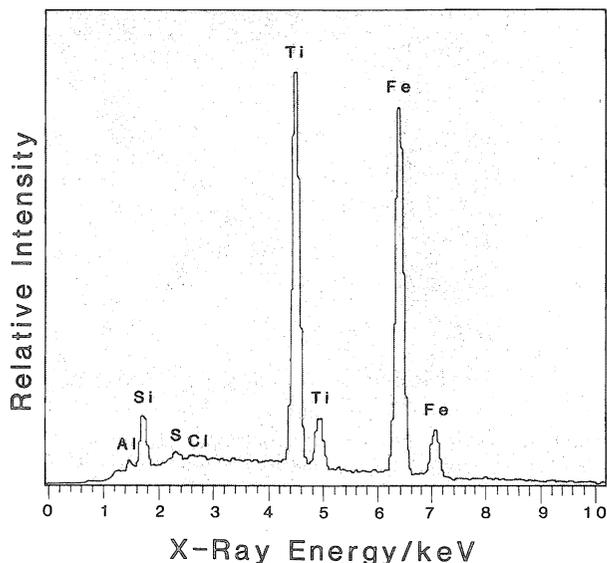


Figure 4—Energy dispersive x-ray analysis of corrosion products produced adjacent to the scribe line of a steel panel coated with epoxy-polyamide paint after 2000 hr exposure to the wet/dry/UV-condensation test procedure

corrosion products. EDX analyses of these corrosion products revealed the presence of sulphur species above background levels (Figure 4). This result implies that sulphur species may become involved in the overall corrosion process.

It should be noted that in the present work, attempts have not been made to correlate the photodegradation chemistry occurring in the accelerated test methods used with that which may occur in natural environments. In a recent study, Bauer, et al.¹⁸ noted that an incorrect distribution of light intensity as a function of wavelength is a possible cause of unnatural photodegradation chemistry in organic coatings. Furthermore, the possibility of some degree of abnormal thermal degradation arising from the relatively high test temperatures used in the UV-condensation cycles (i.e., 60/50°C) cannot be ruled out.

Nevertheless, since the visual observations from the wet/dry/UV-condensation test method as shown in Fig-

ures 1(c) and 2(c) appear to be more realistic of natural degradation processes than results from either of the other test conditions, the importance of including UV-condensation factors into a wet/dry cycle corrosion test seems clear. Such parameters, it is suggested, should not be excluded from a laboratory corrosion performance test if that test is to be meaningful.

COMPARISONS WITH OUTDOOR EXPOSURE TEST DATA:

Corrosion Product Morphology on Uncoated Steel Panels After Four Weeks Exposure to an Industrial Environment—In order to determine whether the laboratory test methods under consideration compare successfully with corrosion processes which occur in natural environments, corrosion products formed on uncoated mild steel panels after four weeks outdoor exposure to an industrial environment (Chicago) were compared with the corrosion products produced after 48 hr exposure to the standard salt spray test, and also with those formed after 48 hr in the wet/dry cycle corrosion test.

The corrosion products produced in the salt spray environment are shown in Figure 5(a). In general, these products appear amorphous in nature. In contrast, corrosion products formed in the wet/dry cycle corrosion test atmosphere appear to be more crystalline as seen in Figure 5(b). The corrosion products occurring on samples exposed outdoors for four weeks are illustrated in Figure 5(c). Comparing Figures 5(b) and 5(c) suggests that the corrosion products produced in the wet/dry cycle test environment more closely resemble those formed after four weeks of outdoor exposure. Neither of these products resemble those formed in the salt spray test environment [Figure 5(a)].

The nature of the corrosion products is likely to influence physical delamination of the coating adjacent to damage regions. Standish¹⁹ has shown that the solid corrosion products which are produced in natural environments as well as in laboratory wet/dry cycle tests can cause mechanical damage to the coating. Solid corrosion products, it may be noted, were not produced in the constant high humidity conditions of the standard salt-spray test, wherein the corrosion products remained colloidal and gelatinous in nature.

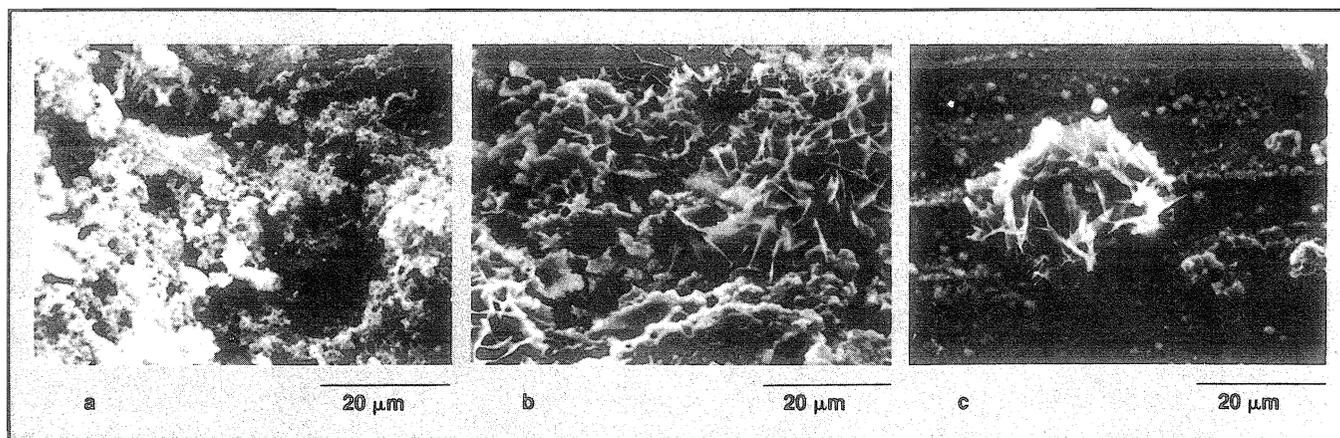


Figure 5—Scanning electron micrographs of corrosion products produced on bare mild steel after exposure to various test environments: (a) 48 hr salt spray test (ASTM B 117-85); (b) 48 hr wet/dry cycle corrosion test; and (c) four weeks at an outdoor industrial test site (Chicago, IL)

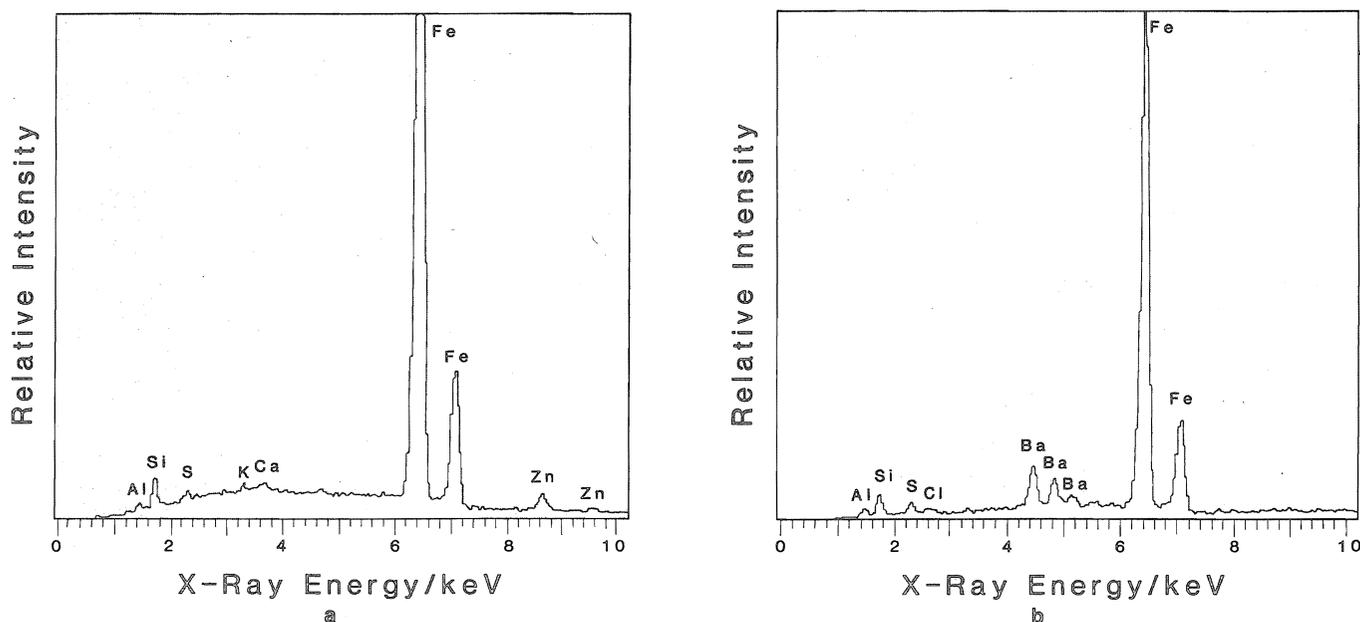


Figure 6—Energy dispersive x-ray analyses of corrosion products produced in scribe lines of coated steel panels after exterior exposures: (a) steel coated with epoxy-polyamide primer and polyurethane topcoat after six months exposure at an industrial test site (Chicago, IL); and (b) steel coated with latex primer after six months exposure at a marine test site (Florida)

It is thought likely that any mechanical stress induced damage caused to the coating by the actions of relatively voluminous, solidified corrosion products would also be exacerbated by the influence of incident UV energy. Therefore, the importance of combining UV-condensation factors with wetting and drying cycles in laboratory tests, again, should not be overlooked.

A further consideration is that wetting and drying cycles influence the likely formation and possible destruction of liquid electrolyte layers on the specimen surfaces. In contrast with the standard salt spray test, which operates at a steady-state relative humidity of 95-98%, inside the wet/dry cycle test chamber the relative humidity diminished to approximately 45% towards the end of the dry periods. This level is below the relative humidity (%) of the atmosphere over saturated solutions of the individual salts used for the electrolyte spray (i.e., ~ 75-80%^{20,21}). This would suggest that continuous surface electrolyte layers will not be maintained on the test panel surfaces throughout the duration of the wet/dry cycle test. This fact is considered significant since, at least for the case of atmospheric corrosion of pure iron, transient corrosion effects in periods either following wetting or during drying out may dominate the overall corrosion process.²²

Analysis of Corrosion Products from Painted Panels After Natural Environment Exposures—The EDX trace obtained from the corrosion products formed on the painted panel exposed for six months to the Chicago industrial atmosphere test environment are given in Figure 6(a). Relatively large Fe $K\alpha/K\beta$ peaks associated with the iron rust are visible. Zinc species emanating from the paint also were detected in the corrosion products and so may influence the overall corrosion process. Active species likely to be present in the industrial atmosphere can also participate in the corrosion process. For example, sulphur

species are visible above background levels in Figure 6(a). This result appears similar to the sulphur signal observed after 2000 hr testing in the wet/dry cycle UV-condensation combination test environment as shown in Figure 4.

Even on the panel exposed for six months to a marine environment, the presence of sulphur species in the corrosion products could be readily detected above background levels as shown in Figure 6(b). This result, perhaps, should not be surprising considering that sea-water typically exhibits a sulphate concentration of the order of 2.7 parts per thousand.²³ However, it reinforces the suggestion that in laboratory tests, the chemical composition of the salt spray electrolyte is important if the corrosion products generated are to bear a compositional resemblance to those produced in natural environments.

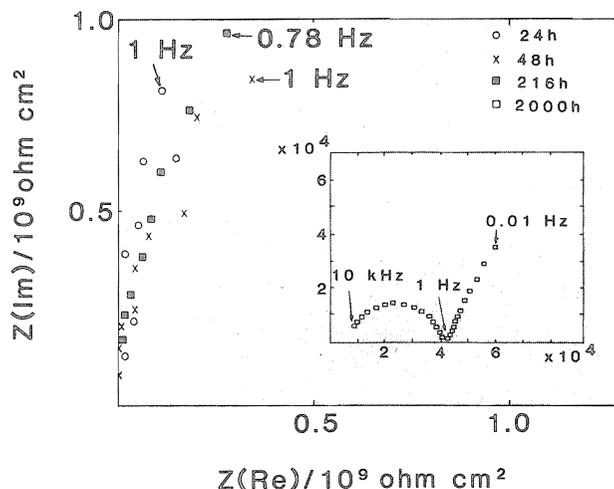


Figure 7—Complex plane impedance data for vinyl chloride coated mild steel for up to 2000 hr exposure to a 0.6 M NaCl electrolyte

Interestingly, in Figure 6(b), the sulphur $K\alpha/\beta$ peak height exceeds the chlorine $K\alpha/\beta$ peak height. It is considered likely that this result reflects the relative solubility of chloride corrosion products on iron compared with sulphates, since it is known that iron cannot bind chloride ions to form compounds that are only sparingly soluble.²⁴ Therefore, whereas corrosive chlorides could be solubilized (e.g., by rainwater), sulphates are more likely to be retained within the corrosion products to influence corrosion whenever the sample (or structure) is sufficiently damp.

Electrochemical Test Method Results

AC IMPEDANCE: Figure 7 shows the impedance response data for the vinyl chloride primer described in Table 3. For the first 216 hr of immersion in 0.6 M NaCl, an almost purely capacitive response was obtained. Since little apparent change is observed during this time, this suggests relatively little water uptake in the film and that the primer is, in effect, functioning as if it were an intact coating film. This coating was tested also after approximately 2000 hr immersion and the response pattern at that time was quite different, as seen in the inset to Figure 7.

At least for the first 216 hr of the test, an approximate estimate of the overall impedance of the system would yield a value $> 10^9$ ohm cm^2 which supports the suggestion that the coating is acting as a reasonably intact barrier during this period. This estimated value is in accordance with comparable data published by Strivens and Taylor⁹ who described this phase of degradation as being the "initial or passive" period. During this time, the impedance response obtained is due to the coating alone with little or no additional effects caused by Faradaic (corrosion) processes.

After 2000 hr immersion, two frequency dependent components of impedance can be observed. The higher frequency component (> 1 Hz) is probably due to the coating, whereas at the lower frequencies, the straight line close to 45° gives an indication that the corrosion process is rate controlled by diffusion effects. An esti-

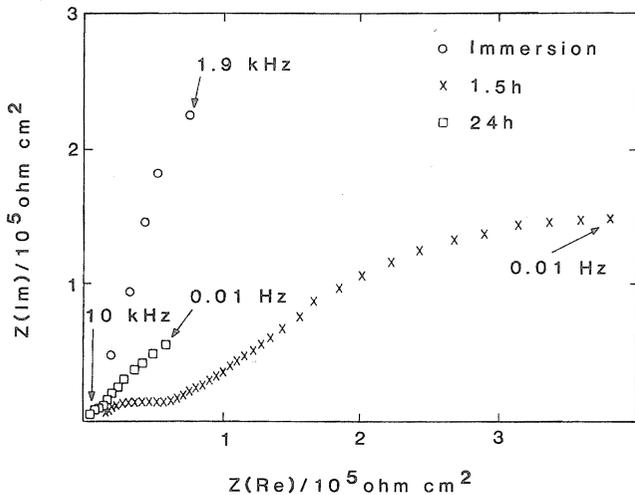


Figure 8—Complex plane impedance data for alkyd coated mild steel for up to 24 hr exposure to a 0.6 M NaCl electrolyte

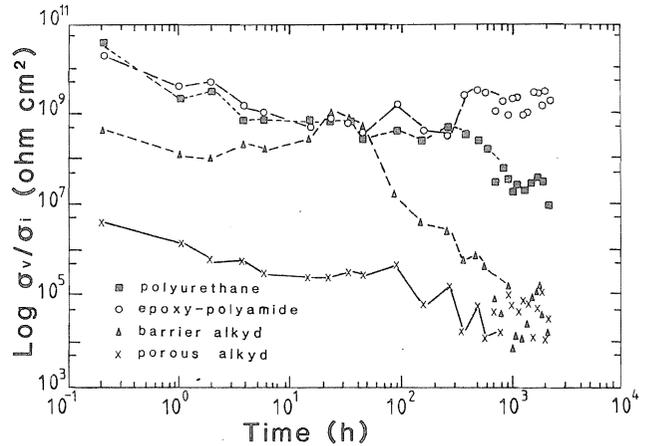


Figure 9—Polarization resistance data for coated mild steel electrode systems derived from voltage and current transients during exposure to a 0.6 M NaCl electrolyte

mate for the system impedance at this time indicates that it had decreased considerably to a value of the order of 6×10^4 ohms cm^2 . The frequency separation of the response components also indicates that the coating had degraded after 2000 hr immersion. At this time, many blisters (1-4 mm diameter) were apparent over the 24 cm^2 electrode surface, two of which were showing clear signs of rust through the paint.

By comparison with the vinyl chloride example, Figure 8 shows the impedance responses obtained in the first 24 hr after immersion of the alkyd primer described in Table 3. In this case, on immersion, a clear semi-circle was obtained. (Only the high frequency portion is shown in Figure 8.) This result indicates that this primer exhibited inherent porosity. The overall impedance on immersion for this coating was estimated at approximately 1.5×10^7 ohms cm^2 . More importantly, from Figure 8, it can be seen that a frequency dependent separation of the impedance response occurs after only 1.5 hr. Furthermore, major defects in this coating may be inferred after 24 hr testing from the fact that an assessment of the overall impedance had already diminished to a value of the order of $< 1 \times 10^5$ ohms cm^2 , which is a significant reduction compared with the value obtained on immersion.

These results indicate the potential sensitivity of ac impedance methods when monitoring the degradation characteristics of corrosion protective primer coatings. Moreover, ac impedance data can provide information about the corrosion protection processes which are open to mechanistic interpretation.

ELECTROCHEMICAL NOISE ANALYSIS: The low frequency impedance data derived from the potential and current noise standard deviation time records are shown in Figure 9. As noted earlier, the R_p values obtained were computed from the $\sigma V/\sigma i$ ratio for each of the four coating systems listed in Table 4.

From the data shown, several trends are apparent. Firstly, all the coatings studied here display a tendency towards decreasing R_p values during the 2000 hr immersion test period. This would be the expected result as indeed the coatings are progressively degrading. Howev-

er, clear distinctions can be made between the supposedly better coatings and the expectedly poorer coatings.

For example, the anticipated good performance characteristics of the epoxy-polyamide primer were reflected in the fact that the derived R_p value remained relatively high for the duration of the immersion test at approximately 1×10^9 ohms cm^2 . At the conclusion of the test, the epoxy-polyamide primer appeared to be in excellent condition with no blistering or rusting visible on the electrode surfaces.

Although the polyurethane barrier coating exhibited similar R_p trends to the epoxy-polyamide coating for the first 300 hr of the test, thereafter, some reduction in this parameter was apparent, decreasing to a value of the order of 10^7 ohms cm^2 after about 2000 hr immersion. Associated with this trend was the formation of small paint blisters over the surfaces of the electrodes.

At the other performance extreme, the derived R_p values for the porous alkyd coating progressively diminished from about 5×10^6 ohms cm^2 at the start of the test to a value of the order of 5×10^4 ohms cm^2 by the end of the test. This is a clear indication that this primer would be expected to exhibit poorer corrosion protective properties than the epoxy-polyamide primer discussed above.

A particularly interesting result was obtained from the barrier alkyd coating. As can be seen in *Figure 9*, for the first 40 hr of immersion, the derived R_p value remained

relatively high (between 10^8 and 10^9 ohms cm^2). However, thereafter, a relatively rapid decline in R_p was observed which correlated well with visual observations of the initiation of blistering and rusting under the coating. This suggests that the barrier property of this particular coating became ineffective after approximately 40 hr immersion.

SUMMARY

This paper describes some recent developments in attempting to resolve the long-standing problem of evaluating the corrosion resistance properties of protective organic coatings in a meaningful way in the laboratory. Specifically, the use of three environmental salt spray methods and two electrochemical techniques are discussed.

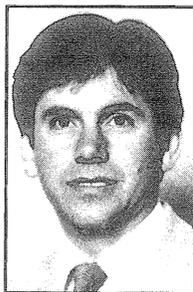
The environmental test factors studied were: wet/dry cycling, an appropriate choice of electrolyte, and the effects of UV incident radiation. The results obtained from coated steel panels indicated that the specific conditions of the test effected fundamental changes to the degradation and corrosion processes which occur. Qualitatively, at least, more realistic degradation and corrosion were produced in the test method which incorporated wet/dry cycling, a low concentration electrolyte based on ammonium sulphate with sodium chloride, and also UV-condensation test cycles.

Brief comparisons with outdoor exposure data suggested that the corrosion products formed on uncoated steel in natural environments more closely matched those produced in the wet/dry cycle corrosion test rather than those formed in the standard salt spray test. Further, the composition of the salt spray electrolyte would appear to be an important consideration if the corrosion products generated in laboratory tests are to bear a compositional resemblance to those produced in natural environments.

It is not the purpose of the present work to suggest that the test practices investigated here be considered as universal options to the standard (ASTM B 117) salt-spray test. Indeed, due to the complexities of natural environments as well as of coating systems themselves, it may be unreasonable to suppose that the use of any single test method would be feasible; a point discussed some years ago by Funke.¹⁶ Nevertheless, it is concluded that much progress in salt spray chamber tests can be made with the objective of establishing more appropriate test practices than are in current, common use.

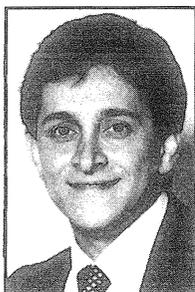
The use of salt spray tests, however, produce data which remain qualitative in nature. For quantitative performance data, recently emerging electrochemical test methods deserve attention, particularly ac impedance and electrochemical noise monitoring techniques.

Ac impedance is a sensitive method by which to assess protective organic coatings for their corrosion resistance properties. Moreover, the data obtained are open to mechanistic interpretation. Electrochemical noise monitoring, by comparison, is a powerful method by which to assess coating degradation/breakdown processes without having to perturb the system to collect the data. Both methods provide quantitative coating performance data.



BRIAN S. SKERRY graduated with a Ph.D. Degree in Corrosion Science in 1980 from the University of Manchester Institute of Science and Technology, England. After post-doctoral appointments at Manchester and Monash University, Melbourne, Australia, he joined the Sherwin-Williams Company in 1984 where he is presently Group Leader—Corrosion. Current interests include the incorporation of new electrochemical techniques into coatings evaluation programs.

ABBIE ALAVI joined the Sherwin-Williams Corrosion Group as an Electrochemist in 1987 after a post-doctoral appointment at Lehigh University, Bethlehem, PA. He obtained a Ph.D. Degree in Corrosion Science in 1983 from the University of Manchester Institute of Science and Technology, England.



KATHRYN I. LINDGREN holds a B.A. Degree in Biology from Augustana College. Since joining Sherwin-Williams in 1981, she has been involved in formulating and paint chemistry technology.

The environmental and electrochemical test methods described in this paper are complementary and provide essentially different information as to the effectiveness of corrosion protective coatings. A judicious combination of these two approaches can be used to characterize in some considerable detail the projected ability of a coating to provide corrosion control.

ACKNOWLEDGMENT

The authors would like to express their gratitude to the management of the Sherwin-Williams Company for permission to publish this work. They would also like to acknowledge the assistance of D.T. Smith and J.E. Pierre with the SEM/EDX studies.

References

- (1) Bureau of the Census, U.S. Dept. of Commerce, "Paint and Allied Products," p. 2, Current Industrial Report MA28F(86)-1, Washington, D.C., Oct. 1987.
- (2) Uhlig, H.H. and Revie, R.W., "Corrosion and Corrosion Control," 3rd Ed., John Wiley & Sons, Inc., New York, 1985, p. 251.
- (3) Annual Book of ASTM Standards, Vol. 06.01.
- (4) Harrison, J.B. and Tickle, T.C.K., *J. Oil & Colour Chemists' Assoc.*, 45, 571 (1962).
- (5) Funke, W., *J. Oil & Colour Chemists' Assoc.*, 62, 63 (1979).
- (6) Appleman, B.R. and Campbell, P.G., "Salt Spray Testing for Short-Term Evaluation of Coatings, Part I: Reaction of Coatings in Salt Spray," *JOURNAL OF COATINGS TECHNOLOGY*, 54, No. 686, 17 (1982).
- (7) Scantlebury, J.D. and Ho, K.N., *J. Oil & Colour Chemists' Assoc.*, 62, 89 (1979).
- (8) Walter, G.W., *J. Electroanal. Chem.*, 118, 259 (1981).
- (9) Strivens, T.A. and Taylor, C.C., *Materials Chemistry*, 7, 199 (1982).
- (10) Kendig, M.W., Mansfeld, F., and Tsai, *Corrosion Sci.*, 23, 317 (1983).
- (11) Skerry, B.S. and Eden, D.A., *Progr. Org. Coat.*, 15, 269 (1987).
- (12) Annual Book of ASTM Standards, Vol. 03.02.
- (13) Barraclough, J. and Harrison, J.B., *J. Oil & Colour Chemists' Assoc.*, 48, 341 (1965).
- (14) Harrison, J.B., *J. Oil & Colour Chemists' Assoc.*, 62, 18 (1979).
- (15) Timmins, F.D., *J. Oil & Colour Chemists' Assoc.*, 62, 131 (1979).
- (16) Funke, W., *J. Oil & Colour Chemists' Assoc.*, 67, 71 (1984).
- (17) Annual Book of ASTM Standards, Vol. 08.03.
- (18) Bauer, D.R., Paputa-Peck, M.C., and Carter, R.O. III, "Evaluation of Accelerated Weathering Tests for a Polyester-Urethane Coating Using Photoacoustic Infrared Spectroscopy," *JOURNAL OF COATINGS TECHNOLOGY*, 59, No. 755, 103 (1987).
- (19) Standish, J.V., *Ind. Eng. Chem. Prod. Res. Develop.*, 24, 357 (1985).
- (20) Weast, R.C. (Ed.), "Handbook of Chemistry and Physics," 59th ed., Chemical Rubber Co., Cleveland, OH, 1978, Table E-46.
- (21) Barton, K., "Protection Against Atmospheric Corrosion," John Wiley & Sons, Inc., New York, 1976, p. 23.
- (22) Stratmann, M., Bohnenkamp, K., and Engell, H.J., *Werkstoffe Korrosion*, 34, 604 (1983).
- (23) Shrier, L.L. (Ed.), "Corrosion," 2nd Edn, Newnes-Butterworths, London, 1976, p. 2:52.
- (24) Ref. (21), p. 43.

Reprinted with permission of Journal of Coatings Technology.