Ion transport through protective polymeric coatings exposed to an aqueous phase

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This paper describes the status of work in our laboratory to develop an improved understanding of the chemical and physical aspects of ion transport through polymeric coatings which are exposed to an aqueous phase.

Introduction

Protective polymeric coatings for metal and electrical component surfaces are designed primarily to serve as barriers for environmental constituents such as water, oxygen and other atmospheric gases, and ions. Water permeation is undesirable because liquid-phase development at the metal/polymer interface may lead to water disbondment [1] or to corrosion. Oxygen permeation is undesirable because oxygen is a component of the cathodic half of the corrosion reaction which may occur in the aqueous phase under the coating. Ion permeation is undesirable because ions are the charge carriers in polymeric coatings, and processes such as corrosion or short-circuiting are dependent on charge transport.

Many biological processes are dependent on ion transport through membranes, and many afflictions of humans are caused by perturbations in the normal ion-transport processes. In this paper, however, we limit our discussions to the transport of ions through neat resin or formulated coatings that range in thickness from 3 to 7500 μm.

Our interest in ion transport through polymeric coatings developed as a result of studies of the phenomenon of cathodic delamination [2]. This term is applied to the consequences of the application of a cathodic potential to a metal having a perforated coating while the system is immersed in an electrolyte. The phenomenon is important because of the use of cathodic protection to reduce corrosion of coated pipelines, ships, and chemical processing vessels. Our studies led us to the conclusion that the rate of delamination of the coating in the presence of the applied cathodic potential was determined by the rate of ionic migration through the coating. This conclusion met initial resistance from two generations of graduate students, but most of them came to accept it as they pursued research on the phenomenon of cathodic delamination. Our interest then turned to understanding the process by which ions move through a coating and the chemical nature of an ion when present within a coating matrix. The ion-transport process with which we are concerned is that which occurs when the polymeric coating is in contact with an aqueous phase containing an ion concentration of 0.001M or greater. The ion-transport process may occur in the absence or presence of an externally applied potential. Three aspects of ion transport are discussed in this paper: a) methods used in our laboratory to measure ion transport; b) the morphology of polymeric coatings as related to ion transport; and c) the chemical nature of an ion in a coating.

The presence and behavior of ionic groups in polymers have been extensively studied; a symposium on this subject is a good reference [3]. Polymeric coatings differ from ionic polymers in that they generally contain relatively few ionic groups, are used in thin-film form, are applied to a solid substrate, contain pigments, fillers, and other components, are often applied as a solution or a dispersion, and are formed on the solid surface by many different techniques. These unique characteristics of a coating, as opposed to a neat polymer, place added emphasis on the morphology of the coating and the effect of this morphology on ion transport.

Measuring ion transport through a coating

Four techniques have been used in our studies: dc measurements, electrochemical impedance spectroscopy, under-the-coating sensing, and radiotracer measurements. Some of the results obtained using each of these techniques are described.

dc measurements

The classic work of Bacon, Smith, and Rugg [4] and more recent studies [5] have shown that high resistances ($>10^9$ $\Omega \cdot \text{cm}^2$) of the coating are associated with good corrosion protection, and low resistances ($<10^7$ $\Omega \cdot \text{cm}^2$) are associated with poor corrosion protection. [This representation ($\Omega \cdot \text{cm}^2$) of the coating resistance is given in terms of the resistance of a cm^2 section of the coating. The thickness of the coating is not taken into account in this value.] This generalization appears to hold true when coatings are exposed to 0.5M NaCl solutions, but does not appear to hold true in dilute alkali chloride solutions [6]. The reasons for this latter inconsistency will become apparent in the discussions which follow.

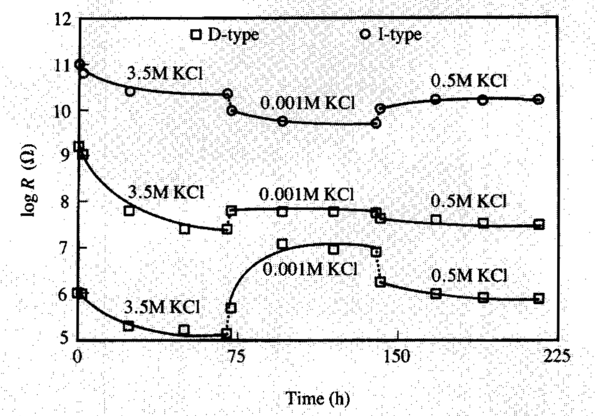

Figure 1

The effect of changing the solution concentration on the resistance of a 25-μm-thick polybutadiene film. From [8], reproduced with permission of The Electrochemical Society.

Mayne and Mills [7] were the first to point out that coatings exhibit two types of electrical behavior when immersed in ionic solutions. In the first case, to which the term "I-type" has been applied, the coating (or the free film) has a high resistance, and the resistance of the coating is inversely proportional to the resistance of the electrolyte with which it is in contact. In the second case, to which the term "D-type" has been applied, the resistance of the coating is low and is directly proportional to the resistance of the electrolyte with which it is in contact. An example of this type of behavior for a 25-μm-thick polybutadiene coating is shown in **Figure 1** [8]. It is interesting that different sections of the same coating may be I-type or D-type. In the original work of Mayne and Mills, 11 of the 25 1-cm^2 sections had dc resistances of 10^8 $\Omega \cdot \text{cm}^2$ or less (D-type) and 14 had dc resistances of 10^{11} $\Omega \cdot \text{cm}^2$ or greater (I-type).

Coatings exhibit "I" behavior when there are no continuous aqueous pathways through the coating. Water ingress or egress is then controlled largely by the relative thermodynamic activities of water within the polymer and within the electrolyte. In the case of coatings exhibiting "D" behavior, aqueous pathways through the coating exist, and the aqueous phase within these pathways equilibrates with the bulk electrolyte.

The above work, as well as additional work done by Mills in our laboratory [9], shows that the ion-transport process in coatings is not homogeneous, that there are regions where ion transport occurs with a high resistance, and that there are other regions where ion transport occurs with a relatively low resistance.

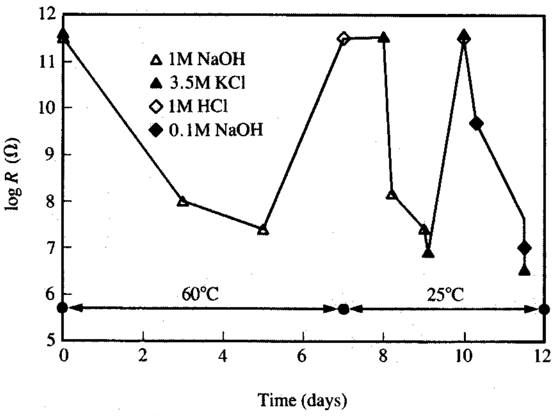

Figure 2

The change in resistance of an I-type polybutadiene film, 35 μm in thickness, when exposed to different ionic solutions. From [8], reproduced with permission of The Electrochemical Society.

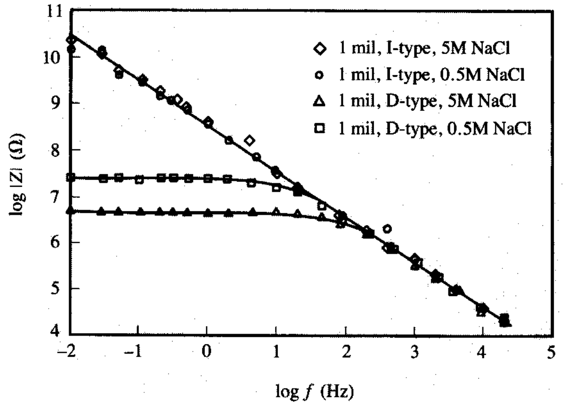

Figure 3

Bode plots for I- and D-type polybutadiene coatings on steel exposed to two different concentrations of NaCl. From [8], reproduced with permission of The Electrochemical Society.

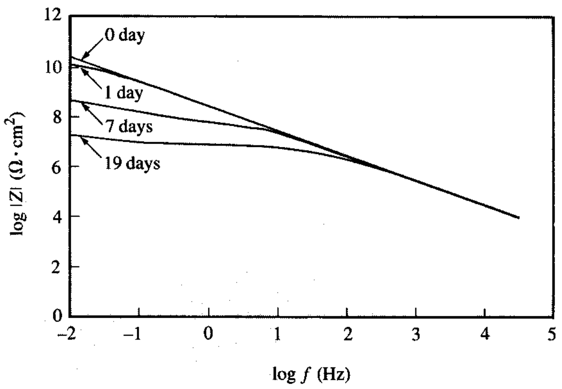

Figure 4

Changes in impedance spectra for different times of exposure to an aggressive electrolyte.

The resistances of the majority of thin-film coatings decrease with time of exposure to alkali metal solutions, as shown by the data in **Figure 2,** where the resistance of a polybutadiene coating is seen to decrease from a value in excess of 10^{11} Ω·cm^2 to approximately 10^7 Ω·cm^2 when the coating is immersed in 1M NaOH at 60°C for five days. The sensitivity of the resistance to the electrolyte in contact with the coating is also shown in the same figure, where we note that the resistance decreased in any solution containing Na^+ or K^+ ions but could be brought back to its original value upon immersion in a solution containing H^+ ions. It is apparent from these measurements that the coating is permeable to ions and that the type of ions present in the electrolyte controls the ability of the coating to transport charge. The increased charge-transport capability of some coatings in the presence of alkali metal ions is an interesting phenomenon.

Electrochemical impedance spectroscopy

In the absence of active corrosion at the metal/coating interface, the coating may be characterized simplistically as a resistor and a capacitor in parallel. This circuit is, in turn, in series with a resistor representing the resistance of the solution. Typical impedance spectra for sections of the polybutadiene coating whose behavior was outlined in Figure 1 are given in **Figure 3** in a Bode plot representation. The I-type section of the film exhibits a simple capacitance-like behavior with a −1 slope over the range of frequency examined, whereas the D-type sections show a plateau region at low frequencies; the plateau is characteristic of a resistor. The impedance value at 10^{-3} Hz is approximately the same as the value of the dc resistance.

Changes in the impedance spectra with time of exposure to an electrolyte have been very useful in characterizing the protective properties of the coating [10–12]. An example of the changes in the spectrum with time is given in the Bode plot shown in **Figure 4.** The plateau at the low frequency is the sum of the resistance of the coating and the resistance of the electrolyte. The latter value is very small in comparison to the resistance of the coating, and thus the changes are a consequence of the change in resistance of the coating. Such measurements show that as corrosion proceeds, the low-frequency impedance decreases in value, indicative of the fact that ion passage through the coating is facilitated in concert with the deterioration of the protective properties of the coating.

The impedance spectrum of some coatings is especially sensitive to temperature. An example is given in **Figure 5** for an epoxy coating whose impedance spectra were determined in 0.5M NaCl as a function of temperature. Note that the room-temperature impedance at low frequency was of the order of $10^9\ \Omega\cdot\text{cm}^2$, and it progressively decreased in value with increasing temperature until it reached approximately $10^5\ \Omega\cdot\text{cm}^2$ at 80°C. An interesting feature of these experiments is the fact that the low-frequency impedance returned to its original value when the system was cooled to room temperature at the conclusion of the experiment. In contrast, some high-impedance coatings exhibit little change in impedance when exposed to distilled water over a temperature range of 25–80°C.

Under-the-coating sensing

Vedage [13] has utilized a sensor beneath a coating to determine the rate at which ions pass through a coating. She inserted an insulated iridized-titanium electrode through small holes drilled in a steel substrate, applied the coating, and measured the pH electrochemically against a standard electrode immersed in the same solution to which the coating was exposed. This procedure provided two kinds of information. There was no electrical response until sufficient conductivity developed in the vicinity of the pH electrode. The onset of conductivity determined the time required for water to pass through the coating and to establish a conducting matrix. Changes in the potential were used to determine the changes of the pH of the conducting phase in the vicinity of the electrode. Measurements were made with four coatings during immersion in 0.1M H_2SO_4 at 60°C: a polyester, an epoxy, a fluoropolymer, and a vinyl ester. The pH which the electrode sensed as a function of time is given for three of the four coatings in **Figure 6.** Note that the polyester coating exhibited a low pH beneath the coating after one-day immersion, whereas the vinyl ester coating required approximately 45 days before the pH under the coating achieved a low value.

Vedage also used the blistering rate of an epoxy polyamideamine coating to determine the rate of diffusion of hydrogen ions through the coating. She determined the time to first blister as a function of coating thickness and calculated a diffusion coefficient from a plot of time to first blister vs. the square root of the thickness of the coating. Values of the calculated diffusion coefficient when the coated steel was immersed in various electrolytes at 60°C are given in **Table 1.**

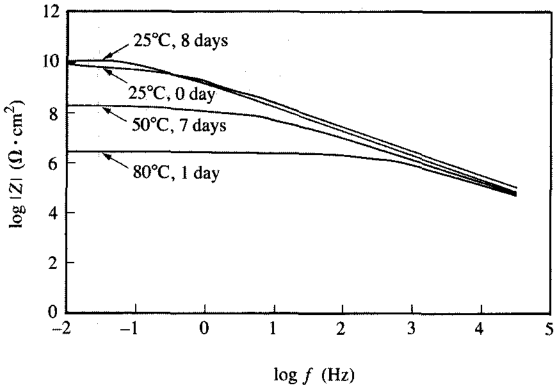

Figure 5

The impedance spectrum of an epoxy coating on steel immersed in 0.5M NaCl under different experimental conditions.

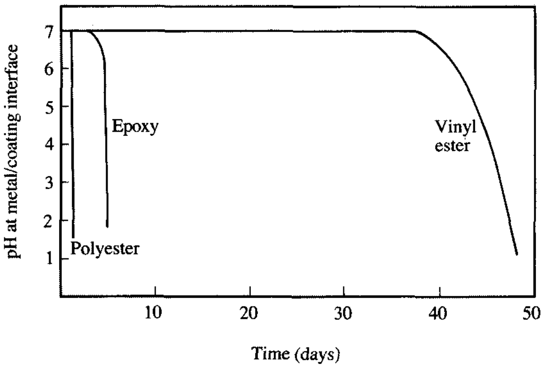

Figure 6

The pH beneath a coating as a function of time of exposure to 0.1M H_2SO_4 at 60°C [13].

Table 1 Calculated diffusion coefficients for hydrogen ions diffusing through an epoxy polyamideamine coating on steel.

Electrolyte	*Calculated diffusion coefficient* (cm^2s^{-1})
0.5M H_2SO_4	6.5×10^{-9}
0.1M H_2SO_4	2.1×10^{-9}
0.1M H_2SO_4 + 0.5M Na_2SO_4	5.6×10^{-10}

Table 2 Rate of blistering of a 0.6-mm-thick epoxy polyamideamine coating when immersed in 0.1M H_2SO_4 containing other sulfates.

Electrolyte	*Approximate time to blister* (h)
0.1M H_2SO_4	60
0.1M H_2SO_4 + 0.5M Li_2SO_4	150
0.1M H_2SO_4 + 0.5M Na_2SO_4	300
0.1M H_2SO_4 + 0.5M K_2SO_4	425
0.1M H_2SO_4 + 0.5M $SnSO_4$	75
0.1M H_2SO_4 + 0.5M $MgSO_4$	150

Table 3 Effect of an applied potential on the migration coefficient of two cations in three organic coatings.

Coating system	*Applied potential*	*Migration coefficient* (cm^2/h)	
		Na^+	*Cs^+*
Alkyd top coat	None	4.6×10^{-8}	8.9×10^{-8}
	−0.2 V	3.5×10^{-7}	5.7×10^{-7}
Alkyd top coat plus primer	None	3.2×10^{-9}	2.0×10^{-9}
	−0.2 V	4.7×10^{-8}	3.2×10^{-8}
Polybutadiene	None	1.8×10^{-9}	1.7×10^{-9}
	−0.2 V	3.7×10^{-8}	2.0×10^{-8}

It is clear from the table that the diffusion coefficient of the hydrogen ion based on blistering data was less in the presence of Na_2SO_4 than in pure H_2SO_4 of the same molarity. A study was then made of the rate of blistering as a function of the addition of other sulfates to the sulfuric acid solution. Foreign ions had a major effect on the rate of blistering, as can be noted from the data in **Table 2.**

These data suggest that the second ion competes for diffusion sites within the coating and reduces the rate at which the hydrogen ion can diffuse through the coating. This competition for sites also appears to depend on the size of the hydrated ion, with the larger ions such as $Li(H_2O)_x^+$ having only a small effect relative to the smaller $K(H_2O)_y^+$ ion. The relative behavior of these ions in affecting the blistering is circumstantial evidence that the ions diffusing through the coating are hydrated.

Radiotracer measurements

Many studies have been made of the migration of species through a coating using radiotracer techniques (see for example the citations in [14]). Our remarks will be limited to our own studies, which focused on the effect of an applied potential. Parks [14] measured the migration of radiotracer sodium and cesium ions through three different types of coatings on steel under both open-circuit conditions and an applied cathodic potential. As can be seen in **Table 3,** the migration coefficient was approximately ten times greater under those conditions where a small cathodic potential was applied than under open-circuit conditions. (The term "migration coefficient" rather than "diffusion coefficient" is used because the application of a potential results in a migration that is not based solely on diffusion.) The cathodic potential of −0.8 V vs. SCE represents a driving force of approximately −0.2 V.

Morphology of organic coatings

The morphological features that are our concern in the present context are those that affect ion transport. The foregoing electrical measurements suggest that ion transport takes place through polymeric coatings by two different mechanisms. In those cases where the impedance at low frequencies is very high and where capacitive behavior is observed to frequencies of 10^{-3} Hz or less, it is likely that charge transport by cations occurs through the polymer matrix by a random-walk process. The transport process involves the migration of cations through the matrix into dynamic free volumes caused by thermal motion of polymer segments. The transport involves the matrix as a whole, with no continuous pathways of easy migration. Circumstantial evidence in support of this mechanism comes from the work of Turoscy and Granata [6], who observed that polybutadiene coatings on steel immersed in dilute chloride solutions corroded uniformly over the entire substrate even though the impedance remained as high as $10^9\ \Omega \cdot cm^2$. Under normal circumstances in 0.5M NaCl the corrosion process is highly localized [15] and the impedance is in the 10^6-$\Omega \cdot cm^2$ range. It appears that high concentrations of Na^+ degrade the barrier properties of polybutadiene. This degradation may come about through an effect of the Na^+ ions on carboxyl groups that are present in the uncured polymer and/or are formed during the oxidative curing process. Infrared spectra of polybutadiene after different amounts of curing [16] are given in **Figure 7.**

The low-impedance coatings, as stated above, generally lose their protective properties in a highly localized manner. This low value of the impedance and the nature of the corrosion process lead us to believe that ion transport under these conditions occurs largely by way of continuous pathways through the polymer coating. The dimensions of these pathways and their geometry within the coating are unknown, although it is suspected that they have diameters before immersion in the electrolyte of the order of 1–10 nm. Once the corrosion process starts, local changes in the pH or in the ion concentration within the pathway lead to degradation of the coating and an increase in the diameter of the pathway or an improvement in the continuity of the pathway.

Coatings that retain solvent may also affect the pathways by introducing stresses in the coating. Such effects appear to be very important in the case of retained solvents, such as

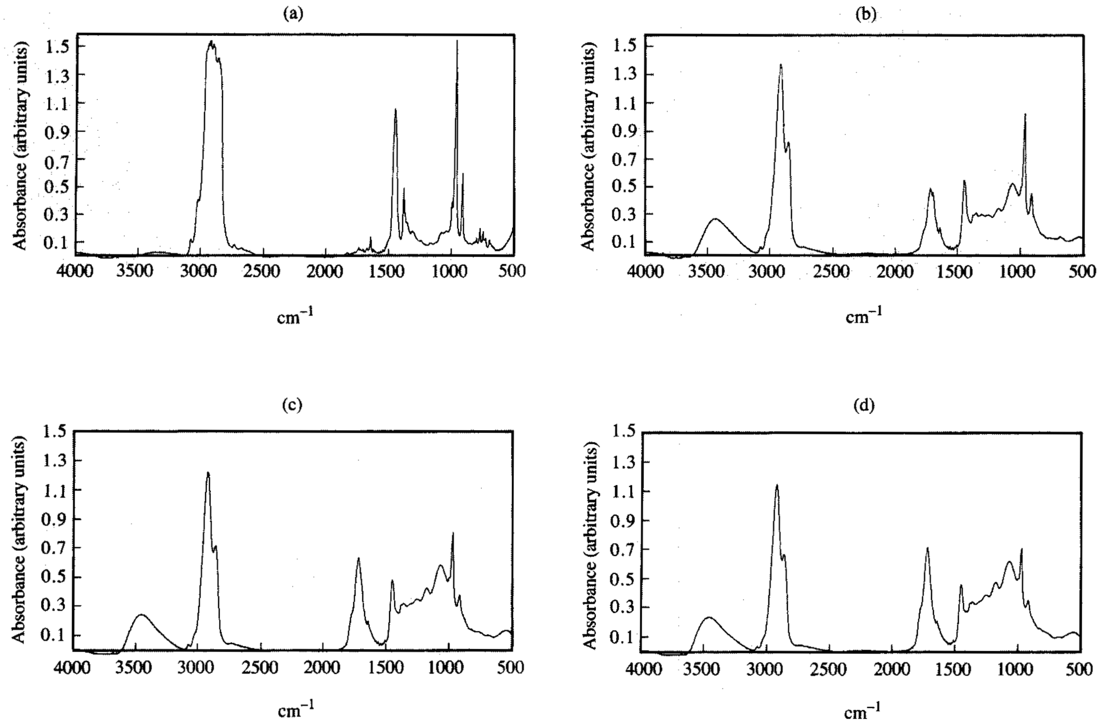

Figure 7

Infrared spectra of a polybutadiene resin coating after different amounts of curing in air at 200°C [16]: (a) before curing; (b) after 10 min of curing; (c) after 20 min of curing; (d) after 30 min of curing.

the glycol ethers, that are hydrophilic in nature and that develop local stresses when osmotic forces, caused by thermodynamic activity gradients, result in the enlargement of minute aggregates of the retained solvent.

Thus, in summary, the electrical measurements are best interpreted in terms of two charge-transport paths, one through the matrix and the other through continuous pathways of small dimension. These two mechanisms suggest that a sodium ion, for example, should be present in the coating in two different environments, one in which its neighbors are part of the polymer matrix and the other in which it exhibits the properties of an ion in aqueous solution. A natural method for testing these conclusions is nuclear magnetic resonance (NMR) spectroscopy, since this technique is quite sensitive to very small differences in the energy state of atoms as determined by the near-neighbor environment. One of the early experiments done to test its applicability to this problem is now described.[1]

Sodium ions were introduced into polybutadiene coatings on steel by the application of a cathodic potential. The subsequent delamination that occurred permitted the removal of the coating from the metal, thorough washing in water, and insertion of sufficient coating into the spectrometer cavity to develop a satisfactory NMR spectrum. A representative spectrum is shown in **Figure 8,** in which it can be seen that there exists a sharp peak superimposed on a broad background absorption peak. Our preliminary interpretation of this experiment is that the sharp peak represents the sodium ion in an aqueous phase within the easy charge-transport pathways, and the broad peak represents the sodium ion present in the polymer matrix in a very large number of slightly different chemical environments. This interpretation is supported by the observation that the sharp peak disappears when such a coating is dried, as shown by the spectrum in **Figure 9.** The spectrum of the type shown in Figure 8 was regenerated when the dried sample was exposed to water.

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[1] J. Roberts, R. Turoscy, and H. Leidheiser, Jr., work in progress.

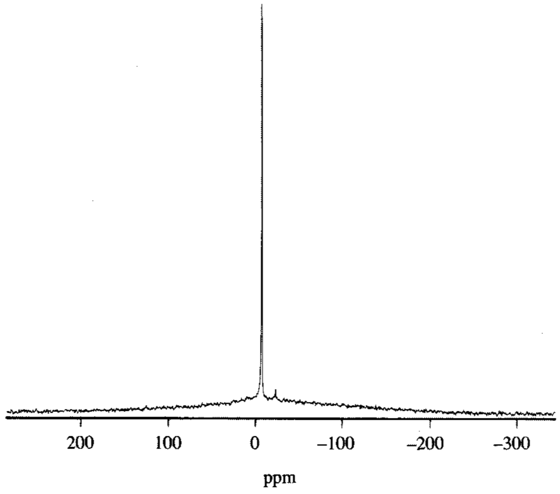

Figure 8

NMR spectrum of Na^+ ions introduced into a polybutadiene coating on steel by the application of a cathodic potential while coating is exposed to 0.5M NaCl. (J. Roberts, R. Turoscy, and H. Leidheiser, Jr., work in progress. Data are given with reference to solid NaCl.)

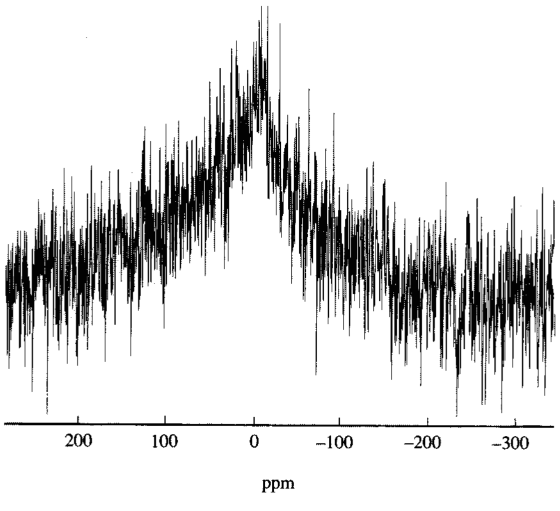

Figure 9

NMR spectrum of Na^+ introduced into a polybutadiene coating on steel by the application of a cathodic potential while coating is exposed to 0.5M NaBr. Coating was dried before the spectrum was determined. (J. Roberts, R. Turoscy, and H. Leidheiser, Jr., work in progress. Data are given with reference to solid NaCl.)

Table 4 Positron annihilation behavior in five coatings.

Type of coating	*Positrons annihilated in large voids* (%)
Powder epoxy	11.2
Vinyl ester (solvent)	17.4
Epoxy 2 (solvent)	20.7
Epoxy 3 (solvent)	15.2
Epoxy 4 (solvent)	16.7

An important aspect of the morphology of coatings is the effect of pigments and fillers. It is well known that some pigments and fillers develop strong interactions with the polymer matrix while others do not. The ability of aqueous pathways to form adjacent to the pigments and fillers is determined to an important extent by the type of interaction between the pigment or filler and the polymer matrix. Our research in this subject area is limited at the present time.

A second approach to an understanding of the morphology of coatings utilizes positron annihilation. When positrons are implanted in polymeric coatings, their lifetimes fall in three different ranges, a short lifetime of the order of 200 ps, an intermediate lifetime of the order of 500 ps, and a long lifetime of the order of 2500 ps. The physical processes that are responsible for the two shorter lifetimes in polymeric materials are not firmly established, but the long lifetime is associated with the formation of orthopositronium within voids in the polymer matrix. The size of these voids has not been determined, but we are conjecturing that their dimensions are 1 nm or more. Recently, the positron annihilation spectra have been determined for four epoxy coatings and a vinyl ester coating. The percentages of annihilated positrons with the long lifetime are summarized in **Table 4.** It can be seen that the solvent-based coatings cured at room temperature had values for the long-lifetime intensity in the range of 15–21%, whereas the corresponding value for the powder coating which was cured at 200°C was 11%. Since the chemical natures of the epoxy coatings are all very similar, we concluded that the low value in the case of the material cured at 200°C is a consequence of the absence of solvent and the formation of a coating that has a minimum number of voids. Solvent-based coatings presumably leave residual voids during the drying process when the coating begins to become firm and is still losing solvent.

The presence of solvent in aggregated form within the coating is suggested by the fact that hydrophilic solvents remaining in the coating cause blisters to form when the coating is exposed to pure water at elevated temperature. Activity gradients between water and solvent in the polymer matrix and between the solvent/water mixture in a liquid phase within the matrix cause the liquid phase to increase in volume locally within the coating and the coating to blister as a consequence.

Impedance measurements of coatings cured at different temperatures also provide useful information. **Table 5** provides data on the impedance of six different coating systems, three cured at elevated temperature and three cured at room temperature. The coatings cured at the elevated temperature exhibited impedances at low frequency in the range of 10^{11} to 10^{12} $\Omega\cdot cm^2$, whereas the coating cured at room temperature had impedances of 10^6 to 10^8 $\Omega\cdot cm^2$. Our interpretation of these representative data is that the high-temperature curing removed the pathways which are the origin of the charge pathways responsible for the low impedance values.

There is substantial evidence that at room temperature the exterior portion of the coating cures at a faster rate than does its interior; in particular, the rate is slowest at the metal interface. This cured "surface skin" reduces the rate of solvent evaporation and probably plays an important role in determining the eventual morphology of the coating. The long-term entrapment of solvent is important in determining the physical characteristics of the coating upon aging.

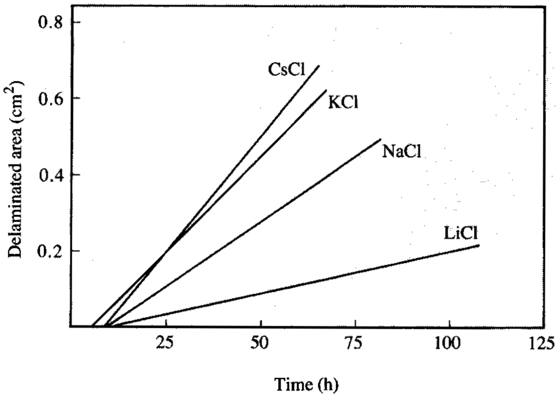

Figure 10

The relative rates of the cathodic delamination of polybutadiene from steel when polarized at –0.8 V vs. SCE in different 0.5M alkali halide solutions.

Chemical nature of an ion in a coating

As stated previously, it has been shown that the rate of cathodic delamination of coatings on steel is determined by the rate of transport of the cation through the coating. It has also been shown in published [2, 17] as well as unpublished work that the cathodic delamination in alkali chloride solutions increases in the order Li^+, Na^+, K^+, Cs^+. An example is shown in **Figure 10.** This order has been observed in all coating systems studied, including polybutadiene, epoxy, alkyd, and acrylic coatings. A similar order has been observed in cathodic blistering studies of an epoxy primer coating on steel [18]. This order parallels the size of the ion, including its hydration sheath. The size of the hydrated ion is reflected in the transference number of the cation and the diffusion coefficient, which both increase in the order Li^+, Na^+, K^+, Cs^+. This correlation strongly suggests that the nature of the cation in these polymer matrices is the hydrated species. The ions thus do not lose their hydration sheath when they leave the electrolyte and enter the polymer matrix. Since the water molecules surrounding the cation are held there by electrostatic forces, it is likely that this sheath is readily deformed as the ion takes its random walk through the polymer.

Another approach to understanding the nature of an ion in a polymer matrix is based on emission Mössbauer spectroscopy. Mössbauer-active ions such as ^{57}Co and ^{129m}Sn were introduced into alkyd, epoxy, and polybutadiene coatings, and the gamma-ray spectrum of the ion in the matrix was determined [19, 20]. In the case of Co^{+2} it was possible to implant the ion into only the alkyd coating, whereas it was possible to implant the Sn^{+4} ion into all three coatings. On the basis of the emission spectrum, the cobalt ion was interpreted to be associated with carboxylate ions within the coating. The tin ion, on the other hand, existed in the coating as an isolated ion in a symmetrical chemical environment and with an ionicity greater than that of the tin atom in tin dioxide.

Table 5 Impedance at low frequency of coatings on steel after exposure to 0.5M NaCl for one day.

Type of coating	*Curing temperature* (°C)	*Thickness* (μm)	*Log impedance at 10^{-3} Hz* ($\Omega\cdot cm^2$)
Baked polyester	200	30	11
Epoxy powder	180	100	12
Polybutadiene (some sections)	200	25	11
Acrylic urethane	RT	60	8
Epoxy solvent	RT	210	8
Alkyd	RT	100	6

Studies have been initiated seeking to determine whether ^{13}C NMR spectroscopy can be used to obtain a better understanding of Na^+ ions present in a coating. Preliminary experiments have shown differences in the spectrum before and after the introduction of sodium into a coating. It is not known at the time of writing whether these changes are a consequence of the introduction of the Na^+ ion or arise from another source.

Summary

The studies discussed here further support the conclusion that cation transport through protective polymeric coatings exposed to an aqueous electrolyte occurs largely by means of aqueous pathways. The major fraction of cations in a coating exist within these pathways.

Acknowledgment

It has been our privilege to cooperate with Donald P. Seraphim and his colleagues in the IBM System Products Division at Endicott, New York, on technical issues related to photoresists and corrosion-protective coatings. It is an honor to be part of the group acknowledging his contributions. Appreciation is expressed to the Office of Naval Research, which provided support for much of the research described herein. Special appreciation is expressed to the following colleagues for the privilege of citing unpublished data: J. Roberts, R. Turoscy, A. Vértes, and P. Deck.

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Received October 1, 1987; accepted for publication January 14, 1988

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