

# Polymeric Materials for Corrosion Control: An Overview

Ray A. Dickie<sup>1</sup> and F. Louis Floyd<sup>2</sup>

<sup>1</sup>Ford Motor Company, Dearborn, MI 48121

<sup>2</sup>Glidden Coatings and Resins Division, SCM Corporation, 16651 Sprague Road,  
Strongsville, OH 44136

Polymeric materials are widely used to control the corrosion of metals, both to maintain appearance and to prevent loss of structural integrity. In this chapter, the fundamentals of metallic corrosion are briefly reviewed. Methods of studying corrosion, and of evaluating the performance of polymeric materials used in corrosion protection, are outlined. Factors that influence the corrosion protective performance of polymeric materials are discussed, and some of the research needs and important unsolved problems are highlighted.

The economic costs and environmental impact of metallic corrosion are well known, and need not be discussed in depth here. It has been estimated (1) that the total cost of corrosion in the United States may be as much as 4% of the gross national product, and that about 15% of the total cost might be avoidable through the economic use of available technology. Most studies of corrosion and its effects understandably concentrate on the cosmetic and structural effects of metallic corrosion; most of the papers in the present volume fall into this category. It should be noted, however, that metallic corrosion and the products of metallic corrosion can deleteriously affect the properties of non-metallic materials, particularly at joints between metals and non-metals. There are also environmental degradation phenomena that can affect non-metallic materials such as plastics, composites and glass directly; some of these phenomena resemble metallic corrosion processes in the effects observed on appearance and structural integrity. Several papers in this volume deal with corrosion effects on adhesive joints and non-metallic materials.

The present chapter begins with a brief overview of metallic corrosion and mechanisms of corrosion control. Methods of evaluating polymer performance and electrochemical characterization techniques are discussed. Barrier and adhesion aspects of corrosion control are reviewed, and some critical issues needing further study are outlined.

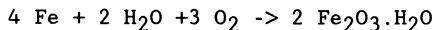
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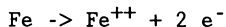
### Metallic Corrosion

Metallic corrosion has been the subject of many textbooks and scholarly compendia (e.g., 2-4), and a number of introductory treatments dealing with corrosion and corrosion protection are also available (e.g., 5-7). In this context, the term "corrosion" refers to the chemical degradation of a metal by its environment. The reactions are most often heterogeneous redox reactions and occur at the metal-environment interface. The anodic reaction is typically the oxidation of the metal; the cathodic reaction is reduction of a non-metal, typically oxygen. If the product of the metal oxidation forms a tight and adherent film, the corrosion process may be self-limiting. If the products of the corrosion reaction are soluble in the corrosive medium, or are permeable to it, then metallic corrosion can proceed. Corrosion is often represented in terms of a simple electrochemical model. The anodic and cathodic half reactions of the corrosion cell may occur at adjacent or widely separated sites on the metal surface; the electrical circuit is completed by electronic conduction within the corroding metal and ionic conduction within the aqueous electrolyte. In natural corrosion, it is common for the sites of the anodic and cathodic corrosion reactions to become more or less widely separated. In such cases, the anodic sites tend to become acidic and the cathodic sites tend to become basic. These changes in pH can be large, and can have serious implications for the performance of polymeric materials.

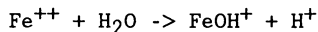
The corrosion of iron is one of the most widespread and technologically important examples of metallic corrosion. In the presence of water and oxygen, the corrosion of iron proceeds to form a complicated mixture of hydrated iron oxides and related species; a complete description is beyond the scope of the present discussion, and the interested reader is referred to the previously cited general references on corrosion as well as to the well known descriptions of electrochemical equilibria in aqueous solution given by Pourbaix (8, 9). Iron is a base metal, subject to corrosion in aqueous solutions. In the presence of oxidizing species, iron surfaces can be passivated by the formation of an oxide layer; if the oxide layer formed is imperfect, rapid corrosion may occur. In simplest form, the reaction of iron to form iron oxide can be written as:



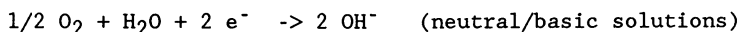
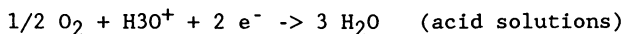
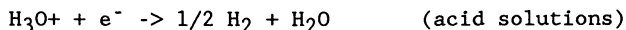
The first step in the corrosion process is the dissolution of iron to form ferrous ion:



In general, the pH decreases at sites of anodic dissolution due to hydrolysis reactions such as:



The cathodic reactions commonly observed are the evolution of hydrogen and the reduction of oxygen; hydrogen evolution is kinetically favored under acidic conditions, while oxygen reduction is kinetically favored under neutral and basic conditions.



The pH at cathodic sites tends to increase due to the production of hydroxide ion and/or consumption of hydrogen ion.

It is interesting to contrast the behavior of iron with that of aluminum. Aluminum is a very base metal; yet aqueous solutions in the neutral pH range that are quite aggressive toward iron often have little effect on aluminum. In the presence of acid solutions, aluminum dissolves with the formation of  $\text{Al}^{+3}$  ions, while under alkaline conditions, it dissolves as aluminate ions,  $\text{AlO}_2^-$ . Over the mid-range of pH from about 4 to 9, a passivating film of aluminum oxide tends to form. The structure and composition of the oxide depend on the conditions under which it is formed, and the corrosion performance of aluminum tends to be dominated by the performance of the oxide layer. Certain solution species, notably chloride, can disrupt the oxide layer and cause localized pitting. Control and modification of the aluminum surface oxide layer has been extensively studied, and is of particular importance in the protection of aluminum substrates.

#### Mechanisms of Corrosion Control

Corrosion can be controlled by isolation of the metal from the corrosive environment; by suppression of the anodic dissolution of metal; and by suppression of the corresponding cathodic reaction. Isolation of corrosion prone metals from corrosive environments is probably the most general mechanism of the corrosion protection afforded by paint films, sealers, and similar polymer-based materials. Effective isolation requires that polymeric materials have good barrier properties and remain adherent in the presence of water and the products of metallic corrosion. Barrier properties and adhesion aspects of corrosion control are discussed in detail in subsequent sections.

The anodic dissolution of metal can be suppressed by lowering the potential so that oxidation of the metal is thermodynamically impossible; this is the principle of cathodic protection of steel. Cathodic protection relies on either an external source of electric current or coupling of the metal to be protected with a more active metal (e.g., steel is protected by coupling to zinc). With the exception of some zinc-containing organic coatings applied to steel, cathodic protection is not a major mechanism of protection by polymeric materials. The mechanism of action of zinc containing coatings has been the subject of some disagreement. Part of the effectiveness of zinc pigmented coatings may be due to the formation of zinc corrosion products after an initial period of true cathodic protection. The action of the zinc compounds formed has been variously ascribed to a blocking of the pores of the film and to passivation of the surface. The evaluation (using impedance methods, see also Ref.

10) and modification of zinc pigmented coatings are discussed in this volume by Szauer and Miszczyk. The chemistry of zinc-rich and modified zinc-rich coatings were also discussed by Fawcett in the symposium on which this book is based. The paper was not made available for inclusion in this volume, but the preprint version is available (11).

Suppression of the anodic reaction can be achieved by the use of oxidizing inhibitors; essentially, the inhibitor is called upon to form (and maintain) an impervious and passivating oxide film on the surface of the metal. If the oxide film formed is imperfect, however, it is possible for rapid localized corrosion to take place. In the case of aluminum, inhibitors can be used to stabilize the oxide film against hydration, as discussed in this volume by Matienzo et al. Organic coatings designed for corrosion protection of ferrous metals often incorporate metal chromates as oxidizing inhibitors. The use of inhibitors in coatings, and the requirements for an ideal inhibitor, have been discussed by Leidheiser (12). As discussed by Funke both in this volume and elsewhere (13), the usefulness of active corrosion inhibiting pigments is open to question: the binders used for paints containing corrosion inhibiting pigments must be somewhat water permeable for the pigments to work, at least partially vitiating the barrier effect of the coating.

Adsorption inhibitors act by forming a film on the metal surface. The action of traditional oil-based red lead paint formulations presumably involves the formation of soaps and the precipitation of complex ferric salts that reinforce the oxide film. There has been substantial interest in recent years in development of replacements for lead-based and chromate-based inhibitor systems. Adsorption inhibitors based on polymers have been of particular interest. In this volume, Johnson et al. and Eng and Ishida discuss inhibitors for copper; 2-undecylimidazole is shown to be effective in acid media, where it suppresses the oxygen reduction reaction almost completely. Polyvinylimidazoles are shown to be effective oxidation inhibitors for copper at elevated temperatures. Also in this volume, Chen discusses the use of N-(hydroxyalkyl)acrylamide copolymers in conjunction with phosphate-orthophosphate inhibitor systems for cooling systems.

In many industrial coating applications, inorganic conversion coatings are used as surface pretreatments for metals. Such treatments typically result in the formation of an insoluble metal chromate or phosphate on the metal surface. The effectiveness of zinc phosphate conversion coatings has been related to their role in suppressing the cathodic reduction of oxygen (14). Bender et al. (15) have reviewed the literature extensively. The performance of inorganic conversion coating systems is dependent on bath composition and deposition conditions, on the initial condition of the substrate, and on the final rinse or post-treatment used. In this volume, Lindert and Maurer discuss a novel film-forming organic post-treatment for inorganic phosphate conversion coatings. Agarwala discusses a modified chromate conversion coating for aluminum.

### Methods of Evaluating Polymer Performance

Performance Tests. The underlying goal of corrosion testing is generally the prediction of service performance, whether directly for a device or system, or indirectly in the design or formulation of a

new material or process. The ultimate test is performance in the intended application; a close second is exposure of test panels to the normal service environment. Testing based on natural exposure is, of course, time consuming, and a large number of laboratory test methods have been developed to assess aspects of polymer properties and corrosion protection system performance. Performance tests generally involve exposure of a system, component, or test piece to a simulated or accelerated corrosion environment; evaluation of results is typically based on an assessment of the type and extent of corrosion failure. Property tests generally involve the measurement of a single, isolable, material property, or of a change in material property with exposure to an aggressive environment. Evaluation of results is typically in terms of a correlation with performance tests or field performance data.

The fundamental problems of accelerated performance testing are the selection of appropriate test conditions, and the determination and validation of acceleration factors. Ideally test conditions should be selected to accelerate all the relevant chemical reactions and physical processes equally. The determination of acceleration factors typically requires, and hence poses the same problems as, performance tests under natural exposure conditions.

Organic coatings are commonly evaluated using salt water immersion, salt fog or spray, modified salt exposure tests (e.g., salt fog with added  $\text{SO}_2$ ), and various cyclic exposure tests. Humidity exposure and water immersion, and, for many applications, physical resistance tests (adhesion, impact resistance, etc.) are widely used preliminary tests. Standard methods for most of these tests are given in compilations of standard tests such as the Annual Book of ASTM Standards (16). Test methods have been extensively reviewed (e.g., 17-23).

Despite their long and common use, none of the popular laboratory corrosion tests are entirely satisfactory. The use of standard laboratory tests to establish comparative rankings of the corrosion performance of different materials is especially susceptible to error. In one recent study, for example, the results of exterior exposure and standard laboratory tests were used to compare corrosion inhibitive primers (24); it was found that standard salt fog tests showed substantial differences in paint performance that were not observed under field exposure conditions. Cyclic exposure tests have been proposed that incorporate periods of exposure to humidity, salt water immersion, temperature cycling, and dirt (25, 26); such tests are substantially more complicated than conventional laboratory tests, but in some cases give better agreement with corrosion performance in service. Cyclic exposure tests have also been applied to precoated steels, both with and without paint coatings (27). The mechanism of failure in cyclic exposure testing has been the subject of some discussion. Standish (28) argues that the cyclic test allows corrosion products like those observed in service to form under the coating; such corrosion products are typically not observed in salt spray. Jones (29) has also discussed the formation of a bulky oxide layer. Elsewhere in this volume, Dickie discusses surface analytical results on the cyclic immersion failure of organic coatings on phosphated steel substrates; delamination of the coating is found to be associated with dissolution of the conversion coating. This result is consistent with observations of van Ooij (30) on locus and mechanism of coating delamination on phosphated steel.

Electrochemical Characterization Techniques. Since corrosion is an electrochemical process, it is not surprising that a considerable amount of work has been reported over the years on electrical and electrochemical techniques for the study of the corrosion process. Leidheiser (31) and Szauer (32, 33) have provided good reviews of the principal techniques. Walter has recently provided a review of DC electrochemical tests for painted metals (34). Both AC and DC methods have been employed to study a variety of issues related to corrosion and corrosion protection. DC techniques are especially useful for studying substrate processes, while AC impedance techniques are most useful for studying processes relating to coated substrates and the performance of coatings.

DC techniques include measurement of DC resistance, determination of polarization behavior, and measurement of polarization resistance. Coating resistance has been correlated with corrosion performance by a number of workers. As summarized by Leidheiser (31), the results of several independent investigations suggest that coating resistance below about  $10^6 \text{ ohm/cm}^2$  is associated with the formation of visible under-film corrosion. Parallel DC resistance measurements on thin film metal substrates have been used to study the deterioration of coated metals; the technique successfully detected the effects of water after migration to the coating/metal interface (35).

Polarization methods involve changing the potential (or current) of a corroding system in both the anodic and cathodic directions while monitoring current (or potential). By manipulating the resulting information, an understanding of the corrosion process can be obtained. For example, Beese (36) has used the linear polarization technique to develop information related to corrosion in beer and beverage cans that are coated with an organic enamel. Such information was ultimately employed to develop improved coatings for the container. Groseclose et al. (37) employed an anodic polarization technique to quantify the quality and variability of both cold rolled and hot rolled steels. This information was used to accurately predict the relative salt spray performance of the subsequently coated steels, and evaluate the effect of abrasive polishing and sandblasting of the substrate. The polarization resistance method widely used for studying metal corrosion has also been applied to painted metals. In principle, the polarization resistance is inversely proportional to the corrosion rate of the metal. For coated metals, the method is complicated by the correction for ohmic potential drop, diffusion limitations, and changes in film properties under the applied potential (32).

AC techniques are highly varied, but tend to converge upon the use of impedance spectroscopy. In recent publications, Hubrecht et al. (38), Mansfield and Kendig (39), and Kendig et al. (40) have reviewed the application of impedance spectroscopy to coating systems. By examining the AC impedance of the coated system as a function of frequency, useful information is obtained regarding both the barrier properties of the coating and the corrosion susceptibility of the substrate. Under proper conditions, information can be extracted relating to the interfacial layer as well. Information can also be extracted relative to the presence of water and ions in paint films as shown by Lindqvist (41). A good example of the latter has been given by Padgett and Moreland (42). In most cases, barrier properties of coatings are ultimately found to be highly important to the prevention

of corrosion of the substrate. In this particular case, it was also shown that the presence of a barrier film seems to augment the formation of a strongly passive layer at the interface between the coating and the substrate. An interesting application of electrochemical techniques involves the characterization of zinc rich paints. Fernandez-Prini and Kapista (43) and Lindqvist et al. (44) describe both DC and AC techniques for characterizing zinc rich coatings in such a way that subsequent salt spray testing is rationalized.

The present volume contains a number of papers relating to the issue of electrochemical testing. Morcillo et al. compare the results of AC impedance measurements with accelerated and outdoor exposure test results. Vijayan reports the use of AC impedance testing to study the effects of various components of the phosphating pretreatment process, paint thickness, and test variables on subsequent salt spray results. Moreland and Padget update their work on AC impedance as it pertains to the study of the passive layer which forms between a barrier coating and a steel substrate. Butler and Bartoszek-Loza describe their use of DC open circuit potentials to correlate with salt spray data as a function of post-bake temperature of UV cured coatings. Eden and co-workers describe their studies involving electrochemical noise measurements to study corrosion as it progresses. The authors' position is that the coating breakdown/failure on a steel substrate is accompanied by a change in the electrochemical noise signal, which gives a rapid indication of the state of the coating. Lomas et al. describe their novel work with harmonic analysis, combined with AC impedance testing in an attempt to detect corrosion of thickly coated substrates.

### Barrier Aspects of Corrosion Control

The relative importance of the barrier function of organic coatings in corrosion protection has been debated for years. It is clear that, if a metallic substrate could be completely isolated from its environment, no corrosion would occur. The degree to which a protection system bars oxygen, water, and ions from the substrate would seem likely to be a measure of the effectiveness of the system in preventing corrosion.

Historically, a number of different theories regarding the role of the barrier function in corrosion protection have emerged. Studies by Mayne and his co-workers (45-49), Bacon et al. (50), and Cherry (51) indicated that neither the permeability of water nor the permeability of oxygen could be the rate determining factor in corrosion control by organic coatings, since neither was sufficiently low to provide effective isolation of the metallic substrate. Protection was attributed to the high electrical resistance and low ionic permeability of coatings that afforded good protection. To varying extents, Guruviah (52), Bauman (53), and Kresse (54) disagreed with the earlier workers regarding the limits of oxygen and water permeability in films. Haagen and Funke (55, 56) agreed with Guruviah and Bauman that oxygen permeability was the controlling factor; they observed that water permeability was the determining factor for the loss of adhesion, but not for corrosion.

More recently, workers in the field have recognized the probable need for a multiple parameter model to understand the corrosion protection process. Funke (57) proposed a model based on water

permeability, oxygen permeability, and adhesion under high humidity conditions. The model was used to rationalize the rank order of salt spray results of seven different electrocoating systems. No mathematical treatment of the data was offered. Floyd et al. (58, 59) introduced a mathematical analysis of a wide range of properties in comparison with salt spray results. A barrier mechanism for corrosion control was postulated. This technique was also applied to Funke's earlier data, with a similar result. The model was further elaborated to take into account the existence of an electrochemical component in the model as a back-up to the primary barrier component. Floyd et al. further observed that no adequate characterization of this electrochemical interaction between paint and substrate existed.

The permeability of polymer systems is influenced by the properties of the polymer, by the presence of pigments or fillers, and by the interaction between polymer and fillers. Hulden and Hansen (60) have recently reviewed water permeation in coatings. Regularity of structure, crystallinity, and low segmental mobility are stated to give low permeability. Cross-link density has also been cited as resulting in reduced permeability, but results presented in this volume by Muizebelt and Heuvelsland suggest that cross-link density may be irrelevant in this respect. As Funke notes elsewhere in this volume, some of the factors that contribute to low permeability may interfere with adhesion; in particular, polar functional groups appear to be essential to achieving good adhesion, but are likely to increase permeability and contribute to water sensitivity.

Pigmentation can have a profound effect on permeability. The use of barrier pigments has been suggested as an alternative to the use of active inhibitive pigments, many of which are objectionable on environmental grounds (13). Flake shaped pigments are particularly effective, but pigment geometry is not the only important factor. If water can accumulate at the pigment-binder interface, as evidently happens in the case of mica, water absorption tends to increase with pigment volume concentration and, although permeability is still reduced by incorporation of the pigment, the effect is much smaller than with, for example, comparable loadings of aluminum flake (13). The influence of inert pigments on permeability and corrosion protective properties has been reviewed briefly by Hulden and Hansen (60), and has been discussed in a number of papers by Kresse (e.g., 61, 62). The mechanism of action of inert barrier pigments is commonly stated to be to increase the diffusion pathway to the substrate; it is also possible that pigments may tend to block or prevent the formation of pathways for direct ionic conduction to the substrate.

### Interfacial and Adhesion Aspects of Corrosion Control

Basic Mechanisms of Adhesion: Acid-Base Interactions. The understanding of polymer adhesion has been greatly advanced in recent years by the recognition of the central role of acid-base interactions. The concept of an acid was broadened by G. N. Lewis to include those atoms, molecules, or ions in which at least one atom has a vacant orbital into which a pair of electrons can be accepted. Similarly, a base is regarded as an entity which possesses a pair of electrons which are not already involved in a covalent bond. The products of acid-base interactions have been called coordination compounds, adducts, acid-base complexes, and other such names. The concept that



acids and bases vary in their ability to interact with one another was introduced by Pearson in 1968 (63, 64). He introduced the concept of polarizability of the acid or base unit, describing it on a hard-soft scale. Hard acids are those of high electronegativity and low polarizability. Soft acids, in contrast, are large in size, have high polarizability, and low electronegativity. For the purposes of this book, it is important to remember that hard acids react most readily and form the strongest complexes with hard bases, while soft acids react most readily and form the strongest complexes with soft bases.

Drago and co-workers introduced an empirical correlation to calculate the enthalpy of adduct formation of Lewis acids and bases (65). In 1971, he and his co-workers expanded the concept to a computer-fitted set of parameters that accurately correlated over 200 enthalpies of adduct formation (66). These parameters were then used to predict over 1200 enthalpies of interaction. The parameters E and C are loosely interpreted to relate to the degree of electrostatic and covalent nature of the interaction between the acids and bases. This model was used to generalize the observations involved in the Pearson hard-soft acid-base model and render it more quantitatively accurate.

In 1975, Sorensen (67) used the acid-base interaction concept to rationalize color strength, gloss, and flocculation properties of coating systems having binders of differing acid-base characteristics. Anomalies that appear when using solubility parameter concepts were successfully explained by the acid-base concept. Drago et al. (68) were starting to address the issue of corrections to the solubility parameter concept using this technique at about the same time. A good review of the subject was written in 1978 by Jensen (69). The application of acid-base interactions to the phenomenon of adhesion was discussed by Jensen at an ACS meeting in 1981 (70). Fowkes and co-workers had already been discussing the competitive absorption of polymers onto pigment surfaces in the context of acid-base interactions by this time (e. g., 71).

Manson (72) expanded the concept to the solid state by observing that the strength of composite materials also depended upon the acid-base interaction between continuous and dispersed phases. More directly, Vanderhoff et al. (73) addressed the issue of adhesion of polymeric materials to corroded steel. They synthesized eight corrosion products of iron, and used the interaction scheme developed by Fowkes and Manson first to characterize the iron corrosion products as Lewis acids or bases and then to select polymer vehicles for practical coating systems. Such results were employed to enhance the adhesion of epoxy systems to substrates which were predominantly iron oxide in nature. A good overview of these issues was presented by Fowkes in 1983 (74).

Fowkes and co-workers also clearly demonstrated that the physical interaction of polymers with neighboring molecules was determined by only two kinds of interactions: London dispersion forces and Lewis acid-base interactions (75). Calculations based on this concept were shown to correct many of the problems inherent in the solubility approach. They were also able to use the concept to study the distribution of molar heats of absorption of various polymers onto ferric oxides, and thereby more accurately described the requirements for adequate adhesion to steel substrates (76). In the symposium on which this book is based, Fowkes summarized work showing that the polar interactions between polymers and metal surfaces that are

important to adhesion are entirely of Lewis acid-base character. Calorimetric and infra-red spectroscopic methods for determining the E and C constants for polymers and metal oxides were presented. The full manuscript was not made available for publication in this volume, and the reader is therefor invited to consult the preprint manuscript (77).

Role of Adhesion in Corrosion Protection. Many of the theories regarding the mechanism of corrosion failure suggest that the loss of adhesion precedes the onset of corrosion, and is therefore of critical importance in understanding the process; Parker and Gerhart (78) considered adhesion to be crucial to corrosion performance. For organic coatings, the strength of the adhesive bond between coating and substrate does not appear to be the critical issue; what does appear to be important is that during and after environmental exposure the coating should be able to withstand the forces applied to it in its intended application. The adhesion of virtually all coatings is adversely affected by exposure to water or humid environments. Walker (79) found that the adhesive strength of a wide variety of coatings dropped from 20 to 40 MPa to 5 to 15 MPa in a direct pull-off test after exposure to humid environments. The initial (dry) bond strength was not a good predictor of performance. Haagen and Funke (56) observed that good protection was obtained if wet adhesion was good, even if the paint was highly water permeable. The importance of adhesion to corrosion protection is further discussed in this volume and elsewhere (80) by Funke.

Mechanisms of adhesion loss under various exposure conditions have been extensively studied. A survey is given elsewhere in this volume by Leidheiser, and specific examples of adhesion loss are discussed in detail by Thornton et al., Maeda et al., and Troyk et al., among others. Acoustic emission has been used to study coating adhesion and the effects of water immersion on coatings on water (see, e. g., 81-83). In this volume, Callow and Scantlebury discuss the possibility of using acoustic emission as a monitoring tool to investigate corrosion-induced debonding.

Modern surface analytical methods have led to much more detailed understanding of the interfacial chemistry of adhesion loss processes. Surface analytical studies of interfacial chemistry are reviewed in this volume by Dickie; in this paper, as in a recent paper by Castle and Watts (84), it is concluded that no single chemical mechanism adequately accounts for all of the observed behavior. In the simplest cases, loss of adhesion appears to involve displacement by water. Displacement of coatings by corrosion generated hydroxide, chemical degradation of the organic coating, and chemical attack on the underlying substrate surface or conversion coating have also been observed. Further examples of interfacial studies are given in this volume by Maeda et al., and a discussion of the reactions in conversion coatings during corrosion has been given by van Ooij (30).

A related but little studied area of adhesion and corrosion protection involves the chemical effects of metal substrates on coatings and other polymeric materials and conversely of polymeric materials on metals. In the curing of certain air-oxidizing coatings on steel, for example, reduction of ferric to ferrous species in the surface metal oxide, substantial thinning of the oxide, and oxidation of the coating material have been reported to occur in the interfacial

region. These phenomena have been studied by infra-red and X-ray photoelectron spectroscopic techniques, and are discussed in this volume by Nguyen and Byrd and by Dickie. The stored components used to make polyurethane foams are subject to long term chemical degradation; the degradation products have been associated with the corrosion of storage containers. Wischmann discusses the problem, and suggests formulation changes for improved performance.

Adhesives and sealers can be an important part of a total corrosion protection system. Structural bonding procedures and adhesives for aluminum, polymer composites, and titanium are well established in the aerospace industry. Structural bonding of steel is gaining increasing prominence in the appliance and automotive industries. The durability of adhesive bonds has been discussed by a number of authors (see, e.g., 85). The effects of aggressive environments on adhesive bonds are of particular concern. Minford (86) has presented a comparative evaluation of aluminum joints in salt water exposure; Smith (87) has discussed steel-epoxy bond endurance under hydrothermal stress; Drain et al. (88) and Dodiuk et al. (89) have presented results on the effects of water on performance of various adhesive/substrate combinations. In this volume, the durability of adhesive bonds in the presence of water and in corrosive environments is discussed by Matienzo et al., Gosselin, and Holubka et al. The effects of aggressive environments on adhesively bonded steel structures have a number of features in common with their effects on coated steel, but the mechanical requirements placed on adhesive bonds add an additional level of complication.

### Effects of Polymer Composition on Corrosion Control

Polymer composition poses not one but many critical issues for the development of materials for corrosion control. As outlined in previous sections of this chapter, the elements of molecular design for good adhesion, good barrier properties, and effective use of pigments in organic coatings are often in conflict. There does not appear to be a unifying theoretical basis on which these conflicting factors can be resolved, and an empirical balancing of properties remains an essential part of new product development for corrosion control. It is not surprising that the details of composition critical to performance often remain proprietary or appear only in the patent literature.

In addition to the customary desire for improved material performance, the development of new materials has, in recent years, been shaped by the demand for non-polluting or ecologically neutral materials. Restrictions on solvent emissions from industrial and maintenance paints, and limitations on lead-based and chromate corrosion-inhibitive pigments has had a major impact on corrosion protective material technology. In the field of organic coatings, there has been major emphasis on water-borne and so-called high solids coatings. Hill and Wicks (90) have discussed design criteria for high solids coatings; a recent book on reactive oligomers discusses a number of polymer systems of interest in high solids coatings (91). A variety of water-soluble and water-dispersible resins have been described in the literature (e.g., 90-96); the Technical Committee of the New England Society for Coatings Technology has published a series of articles on the design of waterborne coatings for the corrosion

protection of steel (97-99). The development and commercial implementation of anodic and, subsequently, of cathodic electrodeposition coatings binders for electrodeposition have made possible major improvements in the corrosion protection of appliances and motor vehicles. The chemistry of binders for electrodeposition has been reviewed by Schenk et al. (100) and by Kordomenos and Nordstrom (101); the cathodic electrodeposition process has been discussed by Wismer et al. (102).

In the present volume, several papers deal with unique materials or applications: Schreiber describes work on plasma-deposited films from organo-silicone and inorganic (SiN) starting materials. Moreland and Padgett discuss studies of a chlorine-containing vinyl acrylic copolymer that is applied as an acidic aqueous formulation and that promotes *in situ* formation of a protective film. White and Leidheiser discuss coating resins for the protection of steel exposed to sulfuric acid; Hojo et al., the behavior of epoxy and polyester resins in alkaline solution. Dreyfus et al. present results on coatings designed to protect glass in alkaline environments. Ibbitson et al. discuss structure-property relationships in tin-based anti-fouling paints.

The protection of microelectronics from the effects of humidity and corrosive environments presents especially demanding requirements on protective coatings and encapsulants. Silicone polymers, epoxies, and imide resins are among the materials that have been used for the encapsulation of microelectronics. The physiological environment to which implanted medical electronic devices are exposed poses an especially challenging protection problem. In this volume, Troyk et al. outline the demands placed on such systems in medical applications, and discuss the properties of a variety of silicone-based encapsulants.

### Critical Issues

A topical symposium provides a forum for the review and updating of work in a given field, and provides an opportunity to identify critical issues. The editors of this volume would like to suggest that the following issues are among those needing additional study:

Systems. Corrosion is usually studied in an isolated fashion in the laboratory, but in practice is clearly the result of interacting systems in the environment. Studies need to be conducted on the way in which the component parts of corroding systems interact under actual environmental conditions, and on the way in which the components of the environment interact with the total corroding system. This would suggest not only design work for corrosion protection systems, but also additional work on the sensing and monitoring of corrosion in real hostile environments.

Methods. To observe that corrosion testing in the laboratory frequently fails to predict what happens in real-world environments is to admit that the mechanisms controlling corrosion in such environments are not understood, even at this late date of study. Mechanism-based test methods for monitoring corrosion are needed that will provide reliable and rapid prediction of service life for corrosion-susceptible systems. It is expected that statistical analysis will play a

large role in any such effort, since the failure modes observed often vary widely within a statistical distribution. Such a recognition has led to the development of statistical methods for the description of mechanical failure of materials, and it is suggested that a similar effort would bear fruit in the analysis of corrosion phenomena.

Paints. Epoxies and cathodic electrocoats represent major advances in the field of corrosion control by organic coatings. The performance of these coatings represents a plateau which has not been departed from in over a decade. A great deal of attention has been devoted to interfacial processes in corrosion over the last several years, yet control of these processes remains an elusive goal. It is conceivable that, if means can be found to control interfacial failure processes, a new generation of coatings can be developed that will establish a considerably higher plateau of performance. Conversion coatings and surface treatments may play a vital role in this development.

Plastics. Part of the trend to substitute plastic and composite substrates for metals can be attributed to a desire to avoid the process of metallic corrosion and subsequent failure. Relatively little attention has been called to the possible failure modes of plastics under environments considered corrosive to metals. More extensive work should be conducted on the durability and life expectancy of plastic and composite materials under end-use environments. A further consideration is the potential for polymer degradation by the products of metal corrosion in hybrid structures comprising metal and polymer components. Since it is expected that coatings will continue to be used to protect plastic and composite substrates, ancillary programs need to be conducted on the mechanisms by which coatings can protect such substrates.

Adhesives. In many applications, there are substantial functional and economic reasons to prefer adhesive bonding over mechanical fastening of metals, of plastics, and of mixed-substrate joints. The role of corrosion in the failure of adhesive bonds is therefore becoming an increasingly crucial one. The performance demands placed on adhesive bonds by the combination of mechanical loading and aggressive environments are particularly severe, and it is clear that studies involving combined mode testing need to be greatly expanded. It is anticipated that information developed in the study of adhesives and the study of coatings should inter-relate in a sufficiently strong fashion that both fields will benefit from such studies.

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