The Performance of Thermoset Polymers in Mineral and Organic Acid Service

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Most severe corrosion problems encountered in chemical processing, paper mills, food plants, and tank cars involve mineral acids and their derivatives. Typically, in these industries, corrosion of steel depends upon the concentration of acids. In some cases, corrosion increases and in others it decreases with increasing acid concentration. When aeration or oxidizing agents are also present, corrosive conditions are usually extreme.

In addition to the mineral acids, most other acid-environments are corrosive to a greater or lesser degree. Mild corrosives such as organic acids, alkalis, and high purity water can cause severe corrosion under certain conditions. Chemical-resistant coatings or linings used in these cases provide long-term protection of steel and prevent costly damage of an industrial structure.

This article explains the corrosive agents found in most industrial processing facilities, summarizes how thermoset linings protect steel against these agents, reviews resin types and reinforcements for linings, and explains laboratory tests used to evaluate linings for acid service. Sample performance test data are included.

Corrosive Conditions

Mineral Acids

In terms of corrosive conditions, sulfuric, nitric, and hydrochloric acids are the 3 most important inorganic acids. Sulfuric acid is produced more than any other chemical. It is used extensively in many processes—directly or indirectly in nearly all industry—in the production of hydrochloric acid, other chemicals, and their derivatives. It is used in petroleum refining and in the manufacture of explosives, synthetic detergents, fertilizers, dyes, drugs, pigments, textiles, storage batteries, and rubbers.

Sulfuric acid is made by the contact process or lead-chamber process, with the former accounting for about 70 percent of total production. Sulfur, or sulfur compounds such as copper sulfide ore, are burned to form SO₂, which is converted to SO₃ in the
Most concentrations of nitric acid rapidly attack ordinary cast iron, nickel cast irons, magnesium, steel, and low alloy steel. Occasionally, cast iron and steel are used in very strong acid at room temperature when danger of dilution is not present. Metals, stainless steels, and other alloys are generally suitable for various temperatures and concentrations. Hydrochloric acid is the most difficult of the common acids to handle from the standpoint of corrosion and construction materials, because it is very corrosive to most of the common metals and alloys.3,4

Organic Acids
Acetic acid, which is frequently used in the food and beverage industry, is the most commonly produced organic acid. Other organic acids show similar corrosion behavior and, in the absence of data, one must assume that they all are corrosive. Organic acids are weaker than inorganic acids because they are only slightly ionized. Aluminum is not suitable for formic acid, one of the strongest and most corrosive organic acids. Maleic and lactic acids are more aggressive than acetic acid with regard to intergranular attack on stainless steel. The fatty acids such as stearic acid are less corrosive, but a stainless steel is required at high temperatures. Naphthenic acid presents a corrosion problem in petroleum refining, mainly because of the high temperatures involved. Citric and tartaric acid are found in food products.3,4

Corrosion Control with Thermoset Coatings
Mechanisms of Protection
Corrosion control with thermoset coatings involves the design of a barrier between
The lower the lining's permeability, the better its adhesion.

The passage of electrons or electricity. The lower the permeability of a coating, the better its adhesion.

Water can diffuse through the polymer coating and collect at the interface. This adds to the delamination force and hydrolyzes existing metal-polymer bonds. The accumulation of water reduces bonding strength and releases metal ions to the interface/polymer to help catalyze other degradation (such as photo oxidation).

The permeability of a coating film is measured by the moisture vapor transmission rate, that is, the passage of water molecules through the intramolecular spaces and filler/binder interfaces in the coating. The lower the moisture vapor transmission, the more effective the polymer is as a vehicle for protective coatings. In general, even though thin, non-reinforced coatings can resist many chemical environments, they should not be used for severe service because they have higher permeation rates. As a result, they may fail in service by blistering, leading to early system failures because of corrosion of the substrate.

The second mechanism by which thermoset coatings prevent corrosion is chemical resistance. The choice for the system reinforcement/resin is usually determined by a number of factors. The corrosion resistance is the most critical but not the only determining factor. Because linings are expected to be serviceable for many years, laboratory testing is of the utmost importance in determining the limitations of a formulation.

Thermoset Resin Formulations

The resins used in heavy corrosion control are various formulations of 3 common categories: polyester, vinyl ester, and epoxy. These are treated in detail in the current JPCL series, Generic Coating Types.7,8 Table 1 shows the typical properties of these base resins.

Polyester linings offer good overall chemical resistance to oxidizing, acidic, and
Solvent environments. Polyester resins used in corrosion control linings and coatings are produced by the condensation polymerization of unsaturated dibasic organic acids with polyols. Variation in chemical resistance is obtained by the choice of organic acid and polyol used to make the resin. This unsaturated polyester resin is dissolved in a cross-linking monomer to lower its viscosity to aid in application. The polyester resins that provide the higher chemical resistance are those synthesized from bisphenol A and fumaric acid or maleic acid. The most common cross-linking monomer is styrene. The curing process uses a free radical addition reaction to polymerize the resin. Organic peroxides provide the source of the free radicals required for curing.

Vinyl ester resins used in corrosion control linings also contain an ester linkage and can be cross-linked with unsaturated monomers by free radical reaction. Vinyl ester prepolymer is formed by reaction of epoxy novolac resin with acrylic or methacrylic acid. They typically withstand exposure to strong acids, salts, and oxidizing materials with limited alkaline resistance. They excel in resistance to strong oxidizing conditions such as sodium hypochlorite manufacturing and storage tanks, where most other materials fail. Formulations are tailored using combinations of promoters and various peroxides to achieve maximum performance and handling characteristics. Polyester and vinyl ester undergo high shrinkage during cure. Though strong, they are brittle if not reinforced.

Conventional epoxy (bisphenol A) coatings cure by internal linkage by reaction with amines. These coatings have excellent resistance to alkalis, salts, weak non-oxidizing acids and some solvents. They have poor resistance to organic acids, concentrated inorganic acids, oxidizers, and strong solvents. They possess excellent adhesion to a variety of substrates and exhibit minimal shrinkage. Failure typically occurs when the lining is exposed to chemicals beyond its resistance properties or to thermal cycling, which causes disbondment.

Bisphenol F epoxy (also known as epoxy novolac) coatings are similar to conventional epoxies but with improved solvent resistance. They can handle strong acids (up to 98 percent sulfuric acid) and concentrated alkalis better than conventional epoxies.

### Table 1
** Typical Properties of Various Thermosetting Polymers Used in Linings**

<table>
<thead>
<tr>
<th></th>
<th>Chemical Resistance</th>
<th>Physical Characteristics</th>
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<tbody>
<tr>
<td></td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>Polyester</td>
<td>Weak acids</td>
<td>Strong solvents</td>
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<tr>
<td></td>
<td>Bleach</td>
<td>Strong acids</td>
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<tr>
<td></td>
<td>Alcohol</td>
<td>High strengths</td>
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<tr>
<td>Vinyl ester</td>
<td>Broad range of acids and alkalis</td>
<td>Strong alkalis</td>
</tr>
<tr>
<td></td>
<td>Bleach</td>
<td>High shrinkage</td>
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<tr>
<td></td>
<td>Oxidizers</td>
<td></td>
</tr>
<tr>
<td>Epoxy</td>
<td>Alkalis</td>
<td>Strong acids</td>
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<td>Epoxy</td>
<td>Alkalis</td>
<td>Oxidizers</td>
</tr>
<tr>
<td></td>
<td>Concentrated</td>
<td>Low shrinkage</td>
</tr>
<tr>
<td></td>
<td>Sulfuric acid</td>
<td>High heat resistance</td>
</tr>
<tr>
<td></td>
<td>Many solvents</td>
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Polyester and vinyl ester resins have been used as lining materials for many years and have good resistance to many chemicals. With all conditions remaining equal, vinyl ester coatings have the broadest overall chemical resistance and have been used successfully in chemical, paper, sewage, food processing, and atomic power plants.
Testing for Chemical Resistance
The laboratory procedure commonly used to determine chemical resistance is ASTM D 543, Practices for Evaluating the Resistance of Plastics to Chemical Reagents. In this test, castings are immersed in a selected chemical, and the changes in weight are measured. Typically, a gain in weight is interpreted as swelling of the polymer matrix, whereas a loss in weight indicates chemical attack. The analysis of the change in weight over time and the observation of the samples after the test are both critical. They help assess the likely long-term performance of the coating in service.

An example is an epoxy resin formulation exposed to methanol that showed a weight gain as follows:
- 5.9 percent at 3 days;
- 8.5 percent at 7 days;
- 10.3 percent at 14 days; and
- 8.2 percent at 28 days.

While the overall gain in weight may not be seen as a failure, the drop in weight gain between 14 and 28 days did show that the material underwent some chemical attack beyond 28 days.

The changes in weight of various resin formulations when exposed to concentrated sulfuric acid, nitric acid, and acetone, are shown in Figs. 1 to 4. The figures show that the overall chemical resistance of the vinyl ester resin formulations is superior to that of the epoxy novolac. In fact, the epoxy novolac has begun to lose weight at 14 days of immersion in acetone. Epoxy novolac is, however, the only resin to survive concentrated sulfuric acid, but its performance in concentrated sulfuric acid is limited to 49 °C (120 °F).

Testing for Degree of Cure
The chemical resistance of a thermoset resin system is related not only to its chemistry, but also to its degree or extent of cure and its functionality. In other words, how much of the functionality or how many of the reactive sites have participated in the formation of the hardened polymer. Most often, it is the temperature at which a lining cures that ultimately defines the amount of cure. During the curing process, three-dimensional networks are formed that determine the cross-link density. The higher the density, the more difficult it is for the aggressive chemicals to penetrate and swell the polymer resins. However, when the resin begins to cure, the mobility of reactive sites decreases, making it less likely for them to react with each other. High temperatures may be required to increase the cross-link density. A commonality of all thermosetting systems is the liberation of heat (exothermic reaction) accompanying cure.
The degree of cure can be determined using a thermal analysis technique such as Differential Scanning Calorimetry (DSC). In this laboratory procedure, heat is applied to a “cured” polymer sample in a cell at a constant rate that promotes residual functionality to react. DSC is preferred to other thermal methods because it is a heat flow measurement technique and yields a quantitative measure of both heat and rate of reaction.

The heat of reaction of the resin can be seen as an exotherm and is determined by comparison to an empty cell that is being heated simultaneously. For a “cured” polymer, the area under the exotherm peak represents the heat generated during the reaction of residual functionality. The smaller the area (indicating that most of the reaction has occurred), the more completely cured the polymer. If an uncured specimen is placed in the cell, a total heat of reaction can be generated. This total is then compared to the residual heat of reaction of the already cured sample, and a percentage of total cure can then be calculated.

The DSC exothermic peaks obtained for a bisphenol F epoxy with triethylene tetra amine as a cross-linker is shown in Fig. 5a. The total heat generated during the curing reaction (DHR) is represented by the total area under the curve. The residual heat of reaction for the same resin initially cured for 7 days at 21 C (70 F) is shown in Fig. 5b. The extent of reaction or the percent of cure (a) can be calculated as:

$$a = \frac{(DHR - DH_{t,\text{resid}})}{DHR}$$

With DHR equals 543.7 J/g and DH_{t,\text{resid}} equals 126.2 J/g obtained from Fig. 5, the percent cure is calculated to be 77 percent. Typically, the residual exotherm of a polyester lining of similar functionality, also cured for 7 days, is found to be much lower than that of the epoxy novolac (Fig. 5c). The polyester resin is more fully cured than epoxy novolac, and therefore, all conditions being equal, will display greater resistance to chemicals.

To take advantage of the functionality of a novolac epoxy, it is often necessary, though not always practical, to post cure the resin at elevated temperatures up to 60 C (140 F). Thermal analysis with DSC allows the determination of an appropriate temperature and time for post curing by measuring residual exotherms at various cure schedules.
Reinforcement for Thermoset Resins

Thermoset coatings suitable for heavy-duty corrosion control are typically used in combination with a reinforcement that reduces permeation rates and provides protection against physical abrasion and coating damage.\textsuperscript{10,11} The reinforcement material is selected based upon its handling characteristics and its compatibility with the resin selected. The 3 most common types of rein-

Fig. 5 - DSC exothermic peaks obtained for an uncured bisphenol epoxy resin immediately after reaction with triethylene tetramine as a cross-linker (a), and for the same resin initially cured for 7 days at 21 C (70 F) (b), and for polyester cured for 7 days at 21 C (70 F) (c). DSC scans were performed at 10 C/min (50 F/min).
forced linings are flake-filled linings, fiber-glass mat-reinforced linings, and woven fabric-reinforced linings (Fig. 6). These linings can be constructed from polyester, vinyl ester, and epoxy resins.

Flake-filled linings are generally highly filled with glass or mica flakes (Fig. 6a). These linings are either sprayed or trowel-applied in 2 coats to a thickness of 0.8 to 3.8 mm (31 to 150 mils), depending on the
type of service required. The operational temperature limit for immersion services is between 54 C and 93 C (130 F and 200 F), depending on the type of resin, and the type and size of the flake reinforcement. The flakes reduce the permeation characteristics by increasing the tortuosity of the path that an ion or molecule has to follow to migrate through the composite system. They are the most effective in providing a barrier to permeation within the lining.

Fiberglass mat-reinforced linings typically consist of a trowel-applied, mineral-filled base-coat, 1 or 2 layers of chopped strand mat, a layer of chemical grade surface veil, and 1 or 2 resin finish coats (Fig. 6b). Limitations for immersion service are in the maximum range of 71 C to 82 C (160 F to 180 F), depending on the resin type incorporated into the composite. Both woven fabric linings and fiberglass mat-reinforced linings are useful in protecting against thermal cycling, thermal shocks, and impact.

The woven fabric lining typically consists of 3 main layers: a trowel-applied, mineral-filled base-coat; a resin-saturated woven fabric layer; and a trowel-applied topcoat (Fig. 6c). These linings have been successfully used for years to protect steel vessels under constant immersion conditions up to 77 C (170 F).

Testing for Moisture Vapor Permeation in Reinforced Linings

The moisture vapor permeation of a coating is an important factor in its performance. It can be determined according to ASTM D 1653, Standard Test Method for Water Vapor Transmission of Organic Coating Films. A film of coating, either individual components or lining (made of multiple components as shown in Figure 6), is fastened over the mouth of a cup containing a desiccant (such as CaCl₂) and placed in a chamber set to 38 C (100 F) and 90 percent relative humidity. Since the relative humidity inside the cup is effectively 0 percent, a pressure gradient exists, providing a driving force for moisture vapor to permeate the lining. Daily weight gains are recorded until a steady state is reached. The slope of the weight change versus time can then be used to calculate the permeance. For low permeability linings, “dummy” specimens without desiccant are tested simultaneously.

### Table 2
**Water Vapor Permeation for Various Resin Systems**

<table>
<thead>
<tr>
<th>Resin</th>
<th>Lining type</th>
<th>Thickness (mils)</th>
<th>Permeability:&lt;sup&gt;a&lt;/sup&gt; g·Pa⁻¹·s⁻¹·m⁻¹</th>
<th>Permeance:&lt;sup&gt;b&lt;/sup&gt; g·Pa⁻¹·s⁻¹·m²</th>
<th>Max T&lt;sup&gt;o&lt;/sup&gt; service C (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Novolac</td>
<td>Flake glass</td>
<td>1.8 (70)</td>
<td>1.6 x 10⁻¹³</td>
<td>9.15 x 10⁻¹¹</td>
<td>93 (200)</td>
</tr>
<tr>
<td>Vinyl ester</td>
<td>Trowel and roll; 2 coats</td>
<td>1.8 (70)</td>
<td>3.2 x 10⁻¹³</td>
<td>1.8 x 10⁻¹⁰</td>
<td>93 (200)</td>
</tr>
<tr>
<td>Polyester</td>
<td>Woven fabric</td>
<td>3.8 (150)</td>
<td>2.4 x 10⁻¹²</td>
<td>6.4 x 10⁻¹⁰</td>
<td>71 (160)</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Trowel and roll; 2 coats</td>
<td>3.3 (129)</td>
<td>2.46 x 10⁻¹²</td>
<td>7.7 x 10⁻¹⁰</td>
<td>71 (160)</td>
</tr>
</tbody>
</table>

<sup>a</sup>Permeability is the moisture transmission rate of the lining at the stated thickness. It is given in g·Pa⁻¹·s⁻¹·m⁻¹ (perm in).

<sup>b</sup>Permeance is the moisture transmission rate of the lining. It is given in g·Pa⁻¹·s⁻¹·m². One perm is equal to 1 grain of H₂O/hr/sq ft per 1 in. difference in Hg vapor pressure across the membrane.
so that moisture absorbed by the sealant material and any changes in barometric pressure can be subtracted.

Table 2 shows vapor permeation data for various lining systems prepared with thermoset resins. Since linings are designed to act as barriers by physically isolating the substrate from moisture, low permeation linings are the preferred choice of specifiers, scientists, and technologists. These types of linings are rarely prone to blistering when exposed to wet elevated temperature environments.

Because permeation is a major issue common to all linings, laboratory testing should also conform to the Atlas test, ASTM C 868, Standard Test Method for Chemical Resistance of Protective Linings, which simulates temperature gradient across the liner. The lining is applied to the substrate of choice (steel or concrete). Three quarters of the test cell is filled with water or another solution to form both the vapor phase and the liquid phase. The cell is also equipped with ports for a heater, thermocouple, and condenser. This setup allows evaluation of the lining at elevated temperatures, which are common in processing plants and outdoor chemical storage. In a steel vessel, elevated product temperature creates a thermodynamic gradient between the outside ambient air and internal elevated temperature environment. This process is commonly known as the cold wall effect, important to the performance of the lining. This situation provides a driving force for moisture into the lining system, which can delaminate the lining. Fig. 7 shows an Atlas test cell setup.

The Atlas test is a convenient way of obtaining coating performance data at elevated temperatures and simultaneously tests a coating’s resistance in both liquid and vapor phases. This test is helpful in determining a coating’s resistance to the stresses that occur when a temperature differential exists across the coating film. Exposure should be a minimum of 3 months, and observations should include general degradation, loss of adhesion, loss of material and softening, and discoloration.

Several modifications have been made to the standard Atlas cell test. In one, a jacket is held in place on the external surface of the panels used in the cell. This jacket has fluid running through it, and the fluid temperature is controlled to produce a thermal gradient. The importance of this modification is illustrated by the marked decrease in coating performance as the thermal gradient increases. Another modification is the use of pressure in the cells. This has been achieved by designing a metal cell with large flanges used to hold test panels in place. The pressurized cell
better simulates the environment in pressure vessels and also affords the possibility of introducing various gases into the cell to account for the service conditions in which the coating or lining is used.12,13

**Final Considerations:**

**Field Practices**

It has been the authors’ experience that linings fail in actual exposure conditions primarily because of poor application practices. The performance of a coating varies enormously with the quality of the application. Some of the most important application conditions are the surface preparation method and surface cleanliness, the application method and coating thickness, the application temperature and humidity, and the cure temperature and time. The surface of the substrate to be coated may be severely pitted or may have significant salt contamination. Contamination on a steel surface can cause quick and total failure of a lining system. Contamination can occur before or during surface preparation. Blasting is typically required, but it does not always remove all the chloride.

In a tank relining situation, the substrate should be free of any of the previous material that was stored in the tank. During the lining application, it is important to ensure the full saturation of the mat layers, to avoid wicking of the chemical into the lining and a reduction in the permeation resistance. Failure to detect pinholes can be disastrous because they accelerate corrosion of steel and promote delamination. Fig. 8a shows a relining of steel tank after the previous coating has failed under exposure to concentrated sulfuric acid above the maximum recommended service temperature. The failed lining was removed, and the steel was blasted. Fig. 8b shows the pitted steel, the result of chemical corrosion made possible by the chemical destruction of the lining. **JPCL**

**References**