A Brief History on Corrosion

Corrosion in industrial processes has always threatened pipes, ducting, process equipment, scrubbers and storage tanks, creating high maintenance costs and significant production interruptions.

In the 1950’s, chemically resistant FRP (Fiber Reinforced Plastic) resins were first developed to meet the needs of the chemical process industries. Pioneering fabricators initially utilized polyester resins synthesized from chlorendic anhydride and fumaric acid (Figure 1) to build corrosion-resistant equipment. FRP made with chlorendic polyesters was found to be particularly resistant to corrosive wet chlorine gas as well as strong oxidizing acids such as nitric, sulfuric, and chromic acid. In fact, chlorendic polyester resins are still widely used by chlorine manufacturers today. Unfortunately, most polyester resins including chlorendic polyester resins are not suitable for caustic environments.

Figure 1. Hetron™ 197 chlorendic polyester resin.

Bisphenol A fumarate based resins were next introduced into the competitive mix of materials. The chemical structure for bisphenol A fumarate polyester resin is shown in Figure 2. Unlike most products at the time, they offered good caustic resistance. Their corrosion resistance in chlorine service was no improvement, and they were (and remain) inferior performers in strong inorganic acid service - e.g. chromic and nitric - where chlorendic polyester resins remain without peer. In the pulp and paper industry, FRP soon replaced the wood and tile materials employed at the time for chlorine dioxide storage and pulp bleaching.

Figure 2. Bisphenol A fumarate resin
Both chlorendic and bisphenol A fumarate resins provided big improvements in corrosion performance over earlier polyester chemistries. Unfortunately, these resins lacked toughness. FRP made from these resins tended to crack, not only during use, but also during fabrication and transport. This was the main cause of failure with these resins in aggressive environments. New technology was needed to make tougher, crack-resistant FRP without reducing its chemical resistance. Even with the rigidity of the chlorendic polyester resin and bisphenol A fumarate resins there are still a few environments where they remain the material of choice. Chlorendic polyester resins are still the material of choice such for applications such as nitric acid and chromic acid. Bisphenol A fumarate is still used for high temperature sodium hydroxide service.

In the late 1960’s, bisphenol A epoxy vinyl ester resins answered this challenge. FRP made with bisphenol A epoxy vinyl esters demonstrated significantly greater toughness than earlier polyester technology. The bisphenol A epoxy vinyl ester resin structure is shown in Figure 3. These tougher composites were considerably more resistant to mechanical and thermal stress. As a result, FRP made from bisphenol A epoxy vinyl esters could be used in a much wider variety of chemical environments. These first epoxy vinyl ester resins remain on the market today and are sold under the trade names Derakane and Hetron resins. Since their introduction, they have become the gold standard against which all other corrosion-resistant resins are judged.

![Figure 3. Bisphenol A epoxy vinyl ester resin.](image)

Derakane 411 epoxy vinyl ester resin in particular has proven itself to be invaluable in a wide variety of applications. Some of the more aggressive applications like hot wet chlorine, chlorine dioxide and strong oxidizing acids, however, still needed improved chemical resistance. The industry also demanded a resin that could deliver corrosion performance at higher temperatures than what Derakane 411 resin delivered. Derakane 470 epoxy novolac vinyl ester resin (Figure 4) emerged in the 1970’s to address the need for higher temperature performance and greater corrosion resistance to strong oxidizing acids and hot, wet chlorine gas.
Performance

Tanks, pipes, ducting, scrubbers, etc. made with Derakane resins resulted in industrial equipment with numerous advantages over those fabricated with conventional metals or polyester resins, including:

Excellent corrosion resistance in a variety of chemical environments, including acids, alkalis, bleaching agents (chlorine) and organic solvents – at various temperatures (contact Ashland Technical Service for specific recommendations).

- High impact resistance, excellent toughness.
- Strong resistance to thermal fatigue.
- High mechanical strength combined with low weight.
- Excellent thermal and electrical insulation.

Mechanical Strength

The corrosion industry rapidly adopted Derakane resins over their polyester predecessors due to the superior toughness and thus greater resistance to cracking and crazing that they deliver. Unsaturated polyester resins such as bisphenol A fumarate or chlorendic cure by a cross-linking reaction at the numerous ester sites which run throughout the resin backbone. This inherent curing mechanism greatly increases the rigidity of the cured laminate. Conversely, epoxy vinyl ester resins cure by terminal crosslinks, thus leaving the vast majority of its structure free to stretch and bend under tension, thereby absorbing significantly more mechanical stress and thermal shock.

FRP equipment must resist both chemical and mechanical stresses, such as thermal shock, pressure and vacuum. Fiberglass reinforcement in the laminate provides mechanical strength, while the cured resin acts as a chemical barrier. The tensile strength of an FRP laminate is primarily dependent on the fiberglass reinforcement. The toughness of the laminate is based on the resin. One way to measure resistance to cracking is the tensile elongation of the clear casting. Epoxy vinyl ester resins have a higher tensile elongation compared to unsaturated polyester resins. Thus, laminates with Derakane 411-350 resins have a considerably higher deformation capacity before cracking.
Chemical Resistance

Chemical attack on both unsaturated polyester resins and epoxy vinyl ester resins generally occurs through the hydrolysis of ester groups and / or breakage of the carbon-carbon double bonds by oxidation or halogenation. In polyesters such as bisphenol A fumarate and isophthalic, ester groups occur along the entire molecular chain, making these chains considerably more susceptible to attack by hydrolysis.

Derakane resins, however, are designed with the double bonds and ester groups located at the ends of each molecular chain. The reduced number of double bonds and ester groups in the resin results in greater chemical resistance. The ester groups are further shielded from chemical attack by the unique structure of the resin backbone which contains a methyl group next to the ester linkage to protect it still further. Derakane resins also contain secondary hydroxyl groups on the backbone which react with the hydroxyl groups on the surface of the fiberglass reinforcement, resulting in excellent wettability and adhesion to glass fibers. In the final analysis, Derakane resins produce significantly more corrosion resistant laminates. It’s really no surprise that this resin technology has emerged as the preferred solution over previous polyester alternatives.

Applications

Derakane resins are used in the production of coatings and linings, tanks, pipes, pumps, ducts, chimneys, filters, hoods, scrubbers, and other equipment used in the transport, processing and storage of highly corrosive chemicals or which require high resistance to chemical, thermal and mechanical degradation. Derakane resins combat corrosion and are present in a variety of applications:

- Pulp and Paper
- Chlor-Alkali
- Petrochemical Processing
- Fertilizer
- Chemical Processing
- Ethanol and Sugar
- Food
- Mineral Processing

Unique Derakane Resin Specific for the Application

There are different types of Derakane resins depending on conditions, applications and need for your company. Among them, we can cite:

<table>
<thead>
<tr>
<th>Derakane Momentum™ 411-350 resins</th>
<th>Provides ample resistance to chemical corrosion, including oxidizers, alkali’s and several acids. It also features high mechanical strength, and outstanding toughness.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Derakane 441-400 resins</td>
<td>Provides chemical and thermal resistance intermediate between Derakane 411 and Derakane 470. Outstanding performance in the Pulp &amp; Paper applications.</td>
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<tr>
<td>Derakane 455-400 resins</td>
<td>Derived from Novolac epoxy, it has good resistance to solvents and improved toughness with a minor reduction in thermal properties compared to Derakane 470 resin.</td>
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<tr>
<td>Derakane Momentum 470-300 resins</td>
<td>Derived from novolac epoxy, this resin combines corrosion resistance with superior high temperature performance. It also delivers outstanding resistance to oxidation and mixtures of chemicals, including solvents.</td>
</tr>
<tr>
<td>Derakane 510 e 515 fire retardancy resins</td>
<td>Derakane 510A, 510C, 510N and 515-400 resins combine corrosion resistance and excellent flame retardance, accomplishing ASTM E84 Class I or II depending on grade (without antimony trioxide) or class I, with antimony trioxide.</td>
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For specific resin recommendations you should consult the Chemical resistance guide or contact the Ashland corrosion technical service team.

Technical Assistance

Derakane has all the technical assistance of Ashland worldwide, including:
• Analysis of chemical environments
• Specification advice
• Resin Recommendations based upon C-581 Corrosion Testing and Case Histories
• Knowledge developed during the more than 50 years of success.

For more information, please contact:

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