2019 Award Nomination

Title of Innovation:
Derakane™ Signia™ resins for FRP

Nominee(s)
Ashland LLC

Category:
(select one below)

- Coatings and Linings
- Cathodic Protection
- Materials Design
- Chemical Treatment
- Instrumentation
- Testing
- Integrity Assessment
- Other—fill in

Dates of Innovation Development:
(from Feb 2017 to March 2018)

Web site: www.ashland.com/derkane-signia

Summary Description:
Introduced in 1965 to combat corrosion in hot, wet chlorine environments, Derakane™ epoxy vinyl ester resins have become the industry standard for corrosion resistant fiber reinforced polymer (FRP) equipment. High performing derivatives have been introduced over the years to allow vinyl ester solutions for expanded chemical environments, high temperature performance and areas requiring improved toughness.

Assurance of corrosion performance is critical to users and specifiers of FRP equipment. Since the Derakane™ Signia™ polymer backbone is the same compared to previous Derakane™ products, asset owners and engineers can be assured that all previous Derakane™ corrosion
studies, historical data and field case histories remain relevant to demonstrate performance for their design requirements. Moreover, Derakane Signia offers the first identifiable resin system. Samples or cutouts of finished FRP articles can be evaluated to validate the materials supplied and delivered were the materials specified on a project.

Today many FRP fabricators are challenged with finding and retaining qualified, experienced operators to meet current demands. Anticipating these needs, Derakane™ Signia™ resins were designed to deliver improved processing characteristics driving faster laminate consolidation, lower foaming, and greatly reduced sanding for application of secondary laminations. These benefits, combined with reduced styrene emissions and less odor in finished parts, lead to the availability of better, more efficiently produced and more environmentally friendly FRP equipment.

Derakane™ Signia™ resins provide significant advantages for fabricators, designing engineers and owner / end users of corrosion-resistant FRP equipment.

in the frp shop
- low styrene emission
- improved shop efficiency
- longer shelf life

in the field
- unchanged polymer backbone
- identifiable resin system

With the introduction of Derakane™ Signia™, Ashland has leveraged new production capabilities to modernize resin features including improved environmental performance, better workability, increased workplace conditions and worker satisfaction. These features help construct higher quality and identifiable FRP piping and vessels for corrosive environments.
**Full Description:**
(Please provide complete answers to the questions below. Graphs, charts, and photos can be inserted to support the answers.)

1. **What is the innovation?** Derakane™ Signia™ is a new vinyl ester resin for manufacturing of fiber reinforced plastic (FRP) equipment (tanks, duct, pipe.) FRP is often used versus metals to extend the service life of process equipment in acidic, caustic or other harsh environments.

2. **How does the innovation work?** With Derakane™ Signia™ resins, Ashland has combined the best technological features of the Derakane™ and Hetron™ lineage with additional new learnings to introduce a leap forward in stability and usability compared to previous generations of epoxy vinyl ester resins. Liquid, thermo-mechanical, and corrosion performance data of Signia™ resins have an unchanged polymer backbone – assuring customers the vast library of Derakane™ corrosion and case history data collected over the past 50 plus years applies to Signia™ resins. These new properties are bundled in the first identifiable resin system and offer a 30% reduction in styrene emission when compared to traditional vinyl ester resins.

3. **Describe the corrosion problem or technological gap that sparked the development of the innovation? How does the innovation improve upon existing methods/technologies to address this corrosion problem or provide a new solution to bridge the technology gap?**
Introduced in 1965 to combat corrosion in hot, wet chlorine environments, Derakane™ epoxy vinyl ester resins have become the industry standard for corrosion resistant fiber reinforced polymer (FRP) equipment. High performing derivatives have been introduced over the years to allow vinyl ester solutions for expanded chemical environments, high temperature performance and areas requiring improved toughness. The last innovation in epoxy vinyl ester technology took place in 1999. Today, fabricators of FRP equipment have new challenges to meet the pressures of environmental regulation and to find and retain skilled labor. With the introduction of Derakane™ Signia™, Ashland has leveraged new production capabilities to modernize resin features including enhanced environmental performance (lower styrene emission), better workability, improved workplace conditions and worker satisfaction.

4. **Has the innovation been tested in the laboratory or in the field? If so, please describe any tests or field demonstrations and the results that support the capability and feasibility of the innovation.**

**Unchanged Polymer Backbone**
Ashland knows through direct chemical structure evaluation the Derakane™ Signia™ polymer backbone is unchanged compared to previous versions of Derakane™. The challenge is to demonstrate this to the industry without revealing proprietary information. The first step towards this is comparing thermal and mechanical properties and validating they are the same for Derakane™, Derakane™ Momentum™, and Derakane™ Signia™ bisphenol-A epoxy vinyl ester resins. Properties such as tensile and flexural strength, modulus and heat distortion temperature measure directly the characteristic of the cured polymer matrix crosslinking. Table 1 presents thermal and mechanical properties for cured clear castings of Derakane™ Signia™ 411, Derakane™ 411-350, and Derakane™ Momentum™ 411-350. Taking standard deviation into account for each of the test methods, it can be seen the thermal and mechanical properties for the three resins are the same.

<table>
<thead>
<tr>
<th>property of casting</th>
<th>derakane™ signia™ 411</th>
<th>derakane™ 411-350</th>
<th>derakane™ momentum™ 411-350</th>
<th>unit (SI)</th>
<th>method</th>
</tr>
</thead>
<tbody>
<tr>
<td>tensile strength</td>
<td>85.6</td>
<td>81.3</td>
<td>83.6</td>
<td>MPa</td>
<td>ASTM D638</td>
</tr>
<tr>
<td>tensile modulus</td>
<td>3.1</td>
<td>3.0</td>
<td>3.0</td>
<td>GPa</td>
<td>ASTM D638</td>
</tr>
<tr>
<td>tensile elongation</td>
<td>5.1</td>
<td>5.1</td>
<td>5.2</td>
<td>%</td>
<td>ASTM D638</td>
</tr>
<tr>
<td>flexural strength</td>
<td>147.9</td>
<td>138.6</td>
<td>144.8</td>
<td>MPa</td>
<td>ASTM D790</td>
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<tr>
<td>flexural modulus</td>
<td>3.3</td>
<td>3.2</td>
<td>3.3</td>
<td>GPa</td>
<td>ASTM D790</td>
</tr>
<tr>
<td>heat distortion temperature</td>
<td>105</td>
<td>105</td>
<td>105</td>
<td>°C</td>
<td>ASTM D648</td>
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</tbody>
</table>

Table 1. Typical mechanical properties of Derakane™ Signia™ 411, Derakane™ 411, and Derakane™ Momentum™ 411 clear castings. All properties were calculated on a clear casting that was cured for 24 hours at ambient conditions then post-cured.

Resin viscosity and density are largely governed by polymer chain length and the percent of monomer (styrene) present. In Table 2 the viscosity of Derakane™ Signia™, Derakane™ Momentum™, and Derakane™ 411 family resins are presented. The data shows the percent of styrene and the viscosity are the same for each of the resins. If there was a difference in polymer chain construction for these resins, more styrene would be needed for longer average chain lengths, or less styrene for shorter average chain lengths to achieve the same viscosity. Variations in polymer chain construction would create differences in mechanical properties – which is not seen in Table 1 data.

<table>
<thead>
<tr>
<th>property at 25°C (77°F)</th>
<th>derakane™ signia™ 411</th>
<th>derakane™ 411-350</th>
<th>derakane™ momentum™ 411-350</th>
<th>unit (SI)</th>
<th>method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brookfield viscosity</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>cps</td>
<td>ASTM D2196</td>
</tr>
<tr>
<td>styrene content</td>
<td>44</td>
<td>44</td>
<td>44</td>
<td>%</td>
<td>ASTM D638</td>
</tr>
<tr>
<td>density</td>
<td>1.046</td>
<td>1.046</td>
<td>1.046</td>
<td>g/ml</td>
<td>ASTM D1475</td>
</tr>
</tbody>
</table>

Table 2. Typical liquid properties of Derakane™ Signia™ 411, Derakane™ 411, and Derakane™ Momentum™ 411 resins.

To confirm corrosion performance is unchanged, two relatively aggressive chemical environments were chosen for evaluation of Derakane™ Signia™ resin versus the corrosion resistance of the classic Derakane™ 411 type bisphenol-A epoxy vinyl ester resin backbone. Hydrochloric acid and sodium hydroxide are bookends of conditions found in many industrial applications such as chemical process and mineral processing – consistent performance in these environments is critical and are key indicators of an unchanged backbone.
The graphs of C581 corrosion data in Figure 1 show the percent retention of C581 coupon modulus after exposure to 32% hydrochloric acid at 66°C (150°F) (Figure 1, left) and after exposure to 10% sodium hydroxide at 93°C (200°F) (Figure 1, right). Laminate modulus is mainly determined by the reinforcement, not the resin. The retention of modulus relates directly to degradation of glass reinforcement and the ability for the resin to protect the glass from the chemical environment\(^2\). The data demonstrates that the performance between Derakane™ Signia™ and the classic Derakane™ bisphenol-A epoxy vinyl ester polymer backbone is similar – taking variations inherent to C581 testing into account. It should be noted 10% sodium hydroxide at 93°C (200°F) is relatively aggressive and the coupon construction chosen is not what would be recommended for this service in a real-world application. This construction was chosen to better evaluate how each resin protects glass reinforcement from chemical attack.

**Low Styrene Emission**

vapor suppression effectiveness
Reduction of styrene emission has gained importance to the composites industry over the past several years with the introduction of MACT and many regulations around the globe regarding human exposure to styrene. Derakane™ Signia™ resins contain a unique vapor suppression technology that greatly reduces styrene emissions upon curing. Because the suppression technology requires air to pass over the laminate surface in order to promote formation of the vapor suppressant film, the FRP fabrication method used governs its efficacy. Once formed, this film creates a barrier to block the evaporation of volatile compounds like styrene. For laminate production by hand layup the suppression film begins to form once consolidation and rollout has stopped. In non-atomized spray-up applications, the suppression film forms once resin spray-up stops. Styrene emission occurs when the resin surface is disturbed for processing, but the suppression film quickly re-forms. In filament winding the rotating mandrel provides good air flow at the laminate surface and promotes rapid formation of the vapor suppression film.
All vapor suppression testing was performed, and results calculated according to rules promulgated by U.S. EPA regulations establishing the RPC MACT (Subpart WWWW). Test methods used are defined on page 46, Appendix A to Subpart WWWW – Test Methods Vapor Suppressant Effectiveness Test Protocol1. A Signia™ 411 test specimen is pictured in Figure 1.

The calculated Vapor Suppression Effectiveness (VSE) factor for Derakane™ Signia™ 411 and Equivalent Non-Vapor Suppressed (also known as non-LSE) Styrene Content are reported in Table 1. The actual styrene content in Derakane™ Signia™ 411 is 44%, but its vapor suppression technology allows it to perform the same as resins with far less styrene content. This is seen in the second row of Table 1 – the percent of styrene shown here is what a typical resin would contain to achieve the same emissions as the EPA calculates for manual layup, non-atomized spray-up or by filament winding. Reinforcement content also affects the rate of styrene emission.

<table>
<thead>
<tr>
<th>Resin Application Method</th>
<th>Manual</th>
<th>Non-Atomized Mechanical</th>
<th>Filament Winding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Derakane™ Signia™ 411 Resin Emissions (lbs/ton)</td>
<td>104</td>
<td>78</td>
<td>118</td>
</tr>
<tr>
<td>Equivalent Non-Vapor Suppressed Styrene Content (%)</td>
<td>37</td>
<td>35.7</td>
<td>32.4</td>
</tr>
</tbody>
</table>

Table 1: Derakane™ Signia™ 411 Resin Emissions Calculations.

lower styrene odor
In trials at various fabrication shops, workers noted far less styrene odor during fabrication. Finished, cured laminates also had considerably less styrene odor as compared to non-Signia™ resins. At the Ashland Corrosion Science Center, the amount of styrene emitted by neat castings of cured resin was measured using headspace gas chromatography (HSGC)2 with a mass spectrum detector (MSD). A typical sample within a 25 mL headspace vial is represented in Figure 2. Resin samples were tested 2 and 24 hours after cure. This interval was chosen since this time is representative of how long a fabricator would be working on an FRP part in a typical shop. Test samples were prepared by adding a drop of promoted and initiated resin with a 15-minute cure to a 25 mL headspace vial. The vial then was sealed and measured at 25 °C (75 °F) by headspace GC using a fused silica HP-624 capillary column attached to a MSD operating in single ion mode (m/z 57 and 91).
Looking at Figure 3, we see the amount of styrene emitted by Derakane™ Momentum™ 411-350 is dramatically higher than that of Derakane™ Signia™ 411. In fact, the Momentum™ resin casting overloaded the detector when measured 2 hours after cure. If the detector had been able to measure the amount of styrene emitted from the Momentum™ casting 2 hours after cure, it would have been several orders of magnitude higher than what is seen for the Signia™ sample, Figure 3, top graph. This dramatic difference in measured styrene emission after cure demonstrates why customers experienced substantially reduced styrene odor in finished laminates for Signia™ 411 compared to other epoxy vinyl ester resins during shop trials.

**Improved Processing for FRP Manufacturing**

**improved laminating**

**reduced foaming**

Reduced foaming in Signia™ resins leads to less entrapped gas bubbles and faster consolidation of reinforcement layers. In Figure 1 the foaming of Derakane™ Signia™ 411 (left) is compared to Derakane™ Momentum 411-350 (right) 1 minute 30 seconds after adding Norox®1 925H MEKP. Much less foaming is seen in the Signia™ resin. This feature leads to laminates with fewer voids.
fewer entrapped voids
In shop trials with Derakane® Signia™ 411, operators consistently noted that wet-out and air release is significantly improved compared to Derakane® Momentum 411-350 and Hetron™ 922. To demonstrate this improvement, experiments were conducted where 2 plies of 450 g/m² (1.5 oz/ft²) chopped strand glass mat were made where only 10 passes of a serrated roller was allowed to consolidate the plies and eliminate bubbles. The resin to glass content for these experiments was controlled at 65% resin to 35% glass. Figure 2 shows typical images of laminates from this experiment. Note the appearance of fewer voids in the Signia™ resin laminate (top) compared to the Momentum laminate (bottom). Cured laminate images were analyzed using an in-house image analysis tool to quantify the number of voids in each picture. Signia™ laminates were shown to have only 0.008 to 0.01 percent voids compared to 0.04 to 0.06 percent entrapped voids in the Momentum laminates.

Figure 2: Backlit images of Derakane™ Signia™ 411 (top) and Derakane™ Momentum 411 (bottom) laminates used in image analysis for void content analysis.

easy surface preparation
Reduction of steps in fabrication is one of the shortest paths to improving shop efficiency. Reducing the amount of preparation needed to apply secondary layups of FRP is a key benefit of Signia™ resins. We used two methods to confirm good secondary bonding for Signia™ 411 — qualitative analysis through fiber tear evaluation and quantitative shear strengths values through ASME RTP-1-2017 Appendix M5 bonding test standard.

secondary bonding test laminate preparation – fiber tear evaluation
Fiberglass-reinforced laminates were prepared for fiber tear evaluation using standard hand lay-up preparation methods. The laminates were prepared in the Ashland Corrosion Science Center (Dublin, Ohio) and at various customer locations. Several resin cure schedules based on MEKP, Cobalt Naphthenate, and Dimethylaniline were used. To understand the effect of reactive mass on cure and secondary bonding fiber tear, thick and thin laminates were prepared. Primary laminates were fabricated as a representative FRP substrate, aged, subjected to surface preparation by sanding/grinding or no preparation performed, and finally a secondary lamination was applied to the primary laminate.
The final laminate constructions were split at the interface between the primary and secondary layers using a wedge. The degree of fiber tear due to the failure of the secondary bond was evaluated according to an established scale.

thick laminate preparation
Primary substrate laminates were constructed using 7 plies of 450 g/m² (1.5 oz/ft²) chopped strand mat and promoted and initiated epoxy vinyl ester resin. The primary laminates were cured at ambient conditions for 24 hours. In some cases, primary laminates were post-cured for 4 hours at 82 °C (180 °F) to simulate extended aging. A secondary layup of 7 plies of 450 g/m² (1.5 oz/ft²) chopped strand mat and promoted and initiated epoxy vinyl ester resin was applied on top of the primary laminate. For ease of driving the wedge between the primary and secondary layers, a one-inch border of tape was applied to the primary laminate before application of the secondary layer (see Figure 3). The laminates were cured at ambient conditions, 17 °C to 26 °C (63 °F to 79 °F), for a minimum of 72 hours, followed by separation of the primary and secondary layers to evaluate bond peel resistance and fiber tear. A completed secondary bonding laminate is shown in Figure 3.

thin laminate preparation
Thin laminates were prepared as described above in the Thick Laminate Preparation section, but 3 plies of 450 g/m² (1.5 oz/ft²) chopped strand mat were used in place of 7 plies.

secondary bonding fiber tear
Secondary bonding by wedge or peel test is difficult to evaluate as it is largely based on subjective observations of the observer/operator. A wedge test standard was developed by Ashland Technical Service for previous secondary bonding studies. Figure 4 shows the relative level of fiber tear at 20, 60 and 100%. The top picture in Figure 5 shows the general setup of the test apparatus, with the wedge placed into the taped split initiation area of the upper laminate. In Figure 5 at the bottom are pictured examples of tested specimens. The tested specimens shown in Figure 5 gave excellent fiber tear and are representative of the typical fiber tear witnessed from specimens made in Signia® trial fabrication shops and in Ashland labs. In Figure 5 the bottom fiber tear specimen was post cured for 4 hours at 82 °C (180 °F) before application of the second layer where the fiber tear specimen above had no post-cure applied.
When constructing equipment to a manufacturing standard such as RTP-1 or an end user specific specification where sanding is mandated between secondary overlays, these protocols should be followed, and surface preparation should be performed as directed by the standard or specification.

**ASME RTP-1-2017 appendix M5 secondary bond test specimen construction and testing**

The ability to quantify secondary bonding in a way that is meaningful to fabricators of FRP equipment was identified in the ASME RTP-1-2017 Appendix M5 Secondary Bonding test standard. Following the procedures defined in Appendix M5, a FRP pipe section was produced using Derakane® Signia® 411. A 15-minute promotion and initiation schedule was used for pipe and secondary layup of the M5 test specimens. The pipe was allowed to cure for a minimum of 72 hours between 21 °C (70 °F) and 27 °C (80 °F) before the secondary lamination was applied. The application of the secondary layup can be observed on prefabricated pipe in the top picture of Figure 6. Note the pipe is pigmented blue so the pipe laminate can be distinguished from the secondary laminate for test specimen machining. Machined specimens can be seen in the bottom picture of Figure 6. ASME RTP-1-2017 Section 4-320 and Appendix M5 specify that the pipe surface should be prepared by sanding before application of the secondary bonded laminate. The goal of the testing described here is to evaluate the ability of Derakane® Signia® 411 to bond to prepared and unprepared surfaces; therefore, in some cases during these tests there was no preparation of the pipe surface by sanding.
Machining and testing of specimens was conducted by Fiberglass Engineering Mechanics (FEMech) Testing Lab, in Harrison, AR, as well as the Ashland Physical Testing Lab (APTL) in Dublin, OH. The top picture in Figure 7 shows a close-up view of the M5 test specimen after machining. The picture on the bottom in Figure 7 shows a closeup view of the M5 test specimen in the Instron™ compression fixture. Using the ASME RTP-1-2017 Appendix M5 test standard a shear strength value can be calculated to evaluate how well a secondary bond is made by a fabricator. To pass, the specimen must reach a minimum shear strength value of 13.79 MPa (2000 psi). Test samples were prepared in two RTP-1 certified shops by Appendix M5 certified fabricators. Samples made with sanded and un-sanded pipe were sent to Ashland’s Physical Testing Lab (an ISO9001 independently certified lab) and to Fiberglass Mechanics. Figure 8 presents data for RTP-1 Appendix M5 test specimens for sanded and un-sanded pipe. This data clearly shows that shear values for sanded (Prep) and non-sanded (No-Prep) pipe are similar, and in all cases, bonding exceeded the minimum M5 shear strength requirement of 13.79 MPa.
faster fabrication
The cure and processing characteristics of Derakane™ Signia™ 411 resin makes it possible to reduce the number of steps required to make thick part such as a hand laid-up flange or filament wound vessel. Signia™ is not sensitive to air inhibition which leads to excellent Barcol development and surface cure allowing fabricators to begin secondary layups sooner than with previous resin systems used. This is useful in flange attachment layups and application of repad for construction of headers, columns and tanks. Signia™ resin technology has been shown to make thick parts without warping and scorching related to heat development. In several customer trials very thick parts were made without issue related to heat development.

filament winding of thick tank sections
The vessel wall pictured in Figure 9 was produced in one continuous winding process using a common MEKP / Cobalt Naphthenate cure to a thickness of 27 mm (2 in) with a high glass content (~65%). When building vessels by filament winding the fabricator can build the corrosion barrier by hand layup and chopper gun and then take advantage of Signia™ 411’s excellent secondary bonding by not having to sand the surface before starting the winding process. It’s important to note that the best practice is to apply a layer of resin and chopped strand for a bedding layer between the cured corrosion barrier and the layers of glass filament roving. This practice is common when laying up on a sanded surface.

hand lay-up of thick laminates
When building large manway flanges it commonly takes a fabricator three to four steps to lay up the complete sequence corrosion barrier and structural layer reinforcements. It is common for there to be 26 to 36 layers of alternating 450 g/m² (1.5 oz/ft²) chopped strand mat and 680 g (24 oz) woven roving. Typically, MEKP/CHP initiator blends are required to achieve long gel times to provide the desired working time and minimize high heat build-up upon cure. With Signia™ 411, Copper Naphthenate (CuNap) has been successfully used to reduce the peak exotherm and extend the gel-to- peak exotherm with minimal effect on gel time. This gives fabricators the time needed to lay up the full reinforcement sequence for the flange, while preventing high heat development that can scorch the upper layers of resin and reinforcement. In Table 1 the effect of Copper Naphthenate can be seen in standard 100 gram cup gel time studies. It can be seen in this data that high hydrogen peroxide (H₂O₂) containing MEKP initiators like Luperox® DDM-9 have a larger reduction of peak exotherm when using Copper Naphthenate. The effect is not as large for high dimer MEKP initiators like Norox® 925H.
In a recent trial a fabricator was able to make 36” ID manway with a ¾ inch (20 mm) thick flange in one layup, significantly reducing the amount of needed to make this part. In addition to producing a good quality laminate in the flange and next of the manway the amount of drawback is critical to if the part is acceptable or not. In Figure 10 it can be seen the drawback on the flange is minimal and consistent with existing flanges made by a multi-step process. Using Derakane™ Signia™ 411 with CuNap allowed the customer to reduce fabrication time from a multi-step production process that took 2–3 days to complete from start to demolding to a 6-hour process from start to demolding.

5. How can the innovation be incorporated into existing corrosion prevention and control activities and how does it benefit the industry/industries it serves (i.e., does it provide a cost and/or time savings; improve an inspection, testing, or data collection process; help to extend the service life of assets or corrosion-control systems, etc.)? Because Derakane™ Signia™ is the first identifiable resin system, it is recommended that asset owners specify the Signia™ product when corrosion-resistant FRP is specified. Samples from the finished part are shipped to Ashland’s laboratory for validation of the resin system. Derakane™ Signia™ allows engineers and designers to know that the materials supplied on a project were the materials specified in the design.

6. Is the innovation commercially available? If yes, how long has it been utilized? If not, what is the next step in making the innovation commercially available? What are the challenges, if any, that may affect further development or use of this innovation and how could they be overcome? Derakane™ Signia™ is commercially available – more information is available at www.ashland.com/derakane-signia.

7. Are there any patents related to this work? If yes, please provide the patent title, number, and inventor.

No