Development of Polyester Resins for Oxygenated Fuels Service

ABSTRACT
AOC developed two new resins recognized by Underwriters Laboratories (UL) for the manufacture of underground gasoline storage tanks for petroleum products, alcohols and alcohol-gasoline mixtures. The tests were the corrosion testing portion of UL 1316 standard for glass fiber reinforced tanks and UL 1746 Parts 2 and 3 standard for external corrosion protection systems for steel underground storage tanks. This paper presents the UL data for flexural strength retention; flexural modulus retention and falling ball impact retention in selected tough UL test environments. Accelerated high temperature UL test results at 48°C are recorded.

INTRODUCTION
High-crosslinked isophthalic (Vipel®F764) and high-crosslinked terephthalic (Vipel®F774) resins meet the current UL 1316 standard for glass-fiber-reinforced-plastic (FRP) tanks and pass the UL 1746 Parts 2 and 3 standard. This paper reviews the UL data on Vipel®F764 and Vipel®F774 resins.

BACKGROUND
Since fuel stations upgraded to new construction standards effective December 1998, the number of leaks detected at gasoline filling stations dropped from 2.6% to 0.07%. Leaks, spills and incomplete combustion can account for these leaks or spills into the environment.

Typically, oxygenated fuels contain alcohols and ethers. Methyl tertiary butyl ether (MTBE) was a promising additive to fuel because it was low cost and maintained an acceptable octane rating for fuels. As far as underground gasoline tank manufacturers are concerned, MTBE did not pose any problem by affecting FRP laminates with respect to flexural strength and flexural modulus retention. Even with this significant decrease in leaks, there are plans by the State of California to ban the use of MTBE as an additive for fuel within two years because:

a) MTBE takes longer to break down in the environment than other oxygenates such as alcohols (methanol, ethanol, etc).

b) MTBE has a high vapor pressure. It is expected that MTBE-enriched condensate will collect within the vapor recovery system or vent system. If the vapor systems are not liquid-tight, the MTBE-enriched condensate could escape into the Environment. The ban on using MTBE as an additive in gasoline is now being debated nationally.

Because it is believed that alcohol will continue to be used extensively as an oxygenating additive in fuels, UL imposes tough requirements on the use of resins for the construction of underground gasoline storage tanks and related equipment. In order to meet the UL 1316 and 1746 Parts 2 and 3 requirements, a typical composite must retain a specific percentage of the original flexural strength and modulus at 38°C in a number of environments at specific temperatures.

Until recently, an individual fabricator obtained recognition from UL to manufacture a wholly composite or composite-wrapped steel tank. This also applied when a fabricator wanted to change resin suppliers. A complete set of corrosion testing was required. UL now allows the raw material manufacturers to have resins and glass reinforcements directly recognized. This is accomplished in the following manner:

1) A resin manufacturer submits composites directly to UL. Composites are prepared for corrosion, hot air, impact testing, permeation, light and water exposure.

2) UL tests the composites, and if the requirements are met, recognition will be provided. Any fabricator can use the corrosion data on a specific resin that the resin manufacturer has tested.
3) UL also added an extra option. Now the resin manufacturer can test the samples at 10°C higher temperature and provide recognition in one-half the time. This means that the corrosion resistivity testing runs at 48°C rather than 38°C, and the hot air oven testing is done at 80°C rather than 70°C.

EXPERIMENTAL
UL TESTING
Vipel®F764 and Vipel®F774 resin samples were made with the same styrene content, ~54% non volatiles. Laminates were made at the AOC lab with Vipel®F764 and Vipel®F774 using 450 and 600 gram per square meter chopped strand mat. The resins were promoted with 0.125% cobalt 12%, catalyzed with 1.0% MEKP, cured for 24 hours at ambient temperature and post cured for 4 hours at 100°C. The laminates were shipped to UL testing.

In order to meet the UL 1316 and 1746 Parts 2 and 3 requirements, a typical composite must retain a specific percentage of the original flexural strength and modulus at 38°C in a number of environments at specific temperatures. These standard conditions are listed in Table #1 and the accelerated test conditions are listed in Table #2. ASTM Reference fuel C is a 50/50-volume blend of isooctane and toluene. AOC was confident that its two new resins, Vipel®F764 and Vipel®F774, would meet all the demanding chemical environments of both the UL 1316 standard for glass fiber reinforced tanks and UL 1746 Parts 2 and 3 standard for external corrosion protection systems for steel underground storage tanks with the accelerated test which is 10°C higher.

RESULTS AND DISCUSSION
UL TESTING
The following results were tabulated after test completion. Some of the test results are on graphs 1-18. The falling ball impact, flexural strength and flexural modulus retention for the Vipel®F764 and Vipel®F774 resins are very similar. The only challenges were with the blends of ASTM Reference Fuel C with methanol and ethanol. Please note the following:

1) The blends of ASTM Reference Fuel C with additional methanol or ethanol are more aggressive than either pure product.

2) Both resins perform quite well to sodium hydroxide (pH 12) for a short period of time (90 days).

3) There is a significant amount of data that is not recorded in this report such as several other chemical environments tested, accelerated weathering tests and permeation (pass or fail) low temperature impact.

4) UL recognition is extended to the use of the Vipel®F764 and Vipel®F774 resins with 8 alternative rovings, specific methyl ethyl ketone peroxide and cumene peroxide blends.

CONCLUSIONS
1) The new AOC resins for underground gasoline storage tanks meet all the minimum related requirements of the accelerated UL corrosion, hot air, impact testing, permeation, light and water exposure testing according to UL 1316 Glass-Fiber-Reinforced Plastic Underground Storage Tanks for Petroleum Products, Alcohols, and Alcohol-Gasoline Mixtures and UL 1746 External Corrosion Protection Systems for Steel Underground Storage Tanks. The fabricator can choose which one is best for a given process.

2) Storage Tanks. The fabricator can choose which one is best for a given process.

3) Based on all of the available data, the final conclusion is that the Vipel®F764 resin and the Vipel®F774 resin are interchangeable.
## Details on Casting Preparation

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<th>ENVE</th>
<th>HCT</th>
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<tr>
<td><strong>Curing system</strong></td>
<td>0.3% Cobalt 6%</td>
<td>0.22% Cobalt 6%</td>
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<tr>
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<td>0.05% Diethylaniline</td>
<td>2% MEKP</td>
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<td><strong>Postcure Schedule</strong></td>
<td>24 hrs RT, 3 hrs 100°C and 1 hr 150°C</td>
<td>24 hrs RT, 3 hrs 100°C</td>
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