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# TECHNICAL PAPER



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## Comparison of Low HAP Resin Alternatives for Replacement of High Styrene Orthophthalic Resins

### ABSTRACT

With the implementation of the marine Maximum Achievable Control Technology (MACT) less than a year away and the implementation of the MACT for other composite applications to follow soon after, fabricators will be required to use resins with low Hazardous Air Pollutant (HAP) content in their fabrication processes. Most of the low HAP resins currently being offered to fabricators are made from Dicyclopentadiene (DCPD) based resins. A majority of fabricators can use these DCPD based resins in their fabrication process successfully. However, some fabricators cannot or will not use these resins because of concerns about secondary bonding and/or the rigidity of these resins. These fabricators are currently using low reactive orthophthalic resins in their fabrication process. In most cases their fabrication procedure requires extended open time between lamination steps. In this paper the secondary bonding ability of the traditional orthophthalic (ortho) resin will be compared to that of the low HAP DCPD based resins.

Data on the effects reductions in styrene content have on traditional orthophthalic resins will be presented. Why this approach to meeting the MACT standards HAP requirements does not work will be demonstrated. A new low HAP orthophthalic replacement resin will be evaluated. This resin will be compared to traditional high styrene orthophthalic resins and low styrene DCPD resin in regards to cure, mechanical, and secondary bonding properties.

### BACKGROUND

The MACT standards for the composite and marine industries have now been finalized. The Marine MACT goes into effect August 22, 2004. The Composite MACT goes into effect April 21, 2006. The maximum HAP content for non-atomized mechanical application is 38.4% in the Composite

MACT and 35% in the Marine MACT. In most laminating resins the only HAP present is styrene.

For most of the fabricators currently using DCPD based resins, meeting the MACT requirements does not present a major problem. The resins they use either already meet the HAP requirement or a slight decrease in styrene content would bring their resins into compliance. Any change required in their resins would be minor and could be easily adjusted for in their fabrication process.

However, for those fabricators currently using orthophthalic base resins, meeting the HAP requirements of either MACT standard presents a major challenge. Simply reducing the styrene level will not work with these resins. The typical HAP (styrene) content of a traditional orthophthalic resin is 45%. A reduction of styrene content to 35% or even to 38.4% will increase the viscosity of the resin and reduce the heat distortion of the composite significantly. (Figure 1) In almost all instances the current orthophthalic resins user will not be able to use their resin and will be required to switch to a different resin type to meet the MACT requirements.

### OBJECTIVES

The objective of our work was to evaluate and compare the two most feasible options that are available to a fabricator, currently using a high HAP orthophthalic resin, to meet the HAP requirements of the MACT standards. We focused on comparing the performance of a low HAP DCPD resin and an orthophthalic replacement resin in the areas of most concern to the fabricators currently using orthophthalic resins. We evaluated liquid and cure properties, mechanical values, application issues, osmotic blistering and secondary bonding. For all evaluations, a comparison was made between the low HAP options and the traditional low and medium reactive orthophthalic

resins currently in use. Our primary goal was to provide the fabricator with information that will allow him to choose the best low HAP resin to fit his process.

### EVALUATION OF LOW HAP OPTIONS

Since they are currently in wide spread use, we first examined the low HAP DCPD resins as an alternative to the high HAP content orthophthalic resins. Many of the fabricators currently using orthophthalic resins are reluctant to use DCPD based product as a means to meet the MACT requirement. They have two major concerns about DCPD based resins. The ability of the DCPD resin to achieve good secondary bonding, particularly over an extended time and/or the rigidity of parts made with many of the DCPD based products currently available.

To evaluate secondary bond we ran laboratory tests to measure the strength of the bond of a laminate applied to a laminate cured under varying conditions. These bonding tests were run using the following procedures:

- 1) A 6 in. X 12 in. laminate is made at a 33% glass content using 4 oz. of mat with the resin catalyzed at 1.5% with MEKP.
- 2) The laminate is allowed to cure over different time periods and under different conditions as specified. This may be at room temperature, at elevated temperatures, and/ or exposure to sun or UV light.
- 3) A piece of Mylar is placed on the upper 2 inches of the cured laminate.
- 4) A second laminate of the same size but using 2oz of mat is applied on top of the cured laminate and the Mylar.
- 5) This laminate is allowed to cure for a minimum of 1 week.
- 6) The Mylar between the laminates is remove.
- 7) A wedge is inserted where the Mylar has been removed.
- 8) The secondary laminate is peeled off of the first laminate as well as it can be done. (Figure 2)

After the secondary bond tests have been conducted a score reflecting the amount of bonding that occurred is given to each laminate. Half of the score is based on the percent of the secondary laminate that could not be removed from the first laminate. The other half of the score is based on the amount of the surface of the first laminate that is comprised of visible glass fibers. The higher the score the better the bonding. A score of 0 would indicate no secondary at all.

Secondary bonding was evaluated after 1 day, 3 days, 1 week, and 1 month of exposure of the bottom laminate.

We used three types of exposure of the bottom laminate before we applied the top laminate:

- 1) Inside at 77 °F/25 °C
- 2) Inside at 100 °F/38 °C
- 3) At 77 °F/25 °C with intermittent sun exposure (8 hours in the sun for the 24 and 72 hour exposures, 16 hours for the one week exposure and 24 hours for the one month exposure)

Previous work was done testing secondary bonding on resins with varying amounts of DCPD resin base and surface preparation<sup>1</sup>. While there is some secondary bonding achieved with DCPD resins, it is inferior to that achieved with the orthophthalic resins. This difference is most prominent after exposure to sunlight. Over time the difference in the secondary bond strength between orthophthalic and DCPD based resins become less significant. However, the DCPD based resins always have reduced secondary bonding, under all exposure conditions, when compared to the secondary bonding achieved with orthophthalic resins. There is some improvement the bonding when the DCPD resin is blended with 50% of an orthophthalic-based resin. Even then, the secondary bonding is not as good as is achieved with traditional orthophthalic resins. With 50% orthophthalic base content, it is difficult to achieve the desired viscosity and still meet the MACT requirement for HAP content.

As demonstrated by their domination of the open mold market in the US, the traditional DCPD based res-ins, despite their lower secondary bond strengths, can be used successfully in most applications. Some changes in the composite structure

or fabrication methods may be required when using DCPD resins. Their wide spread use is evidence of the ability of many fabricators to successfully adjust their part design and/or fabrication process to compensate for the reduced secondary bond strength achieved when using resin containing significant amounts of DCPD base resin.

A second reason often given by fabricators for not using the DCPD based low HAP resins is concern about mechanical properties. Fabricators currently using orthophthalic resins find their resins typically provide a good elongation while maintaining good modulus and strength values. Resins with these properties are considered to be tough resins. It has been demonstrated that the use of a tough resin will significantly reduce the amount of cosmetic cracking in composites.

Some changes in the composite structure or fabrication methods may be required when switching from orthophthalic resins to DCPD based resins. Typically these would include, but not limited to an increased glass % and changes in design to reduce laminate flexing. For those fabricators that cannot make such adjustments, the traditional DCPD resin can toughen significantly by blending in a flexible resin. By using the right combination and amounts of DCPD resin and flexible resin, mechanical properties very similar to those of the orthophthalic resins can be achieved. (Figure 3) Because this resin still contains more than 50% DCPD base resin, it would still have the lower secondary bonding typically seen with traditional DCPD based low HAP resins.

Some manufacturers will be unable or unwilling to modify their process or part design enough to enable them to compensate for the lower secondary bond strength achieved with the DCPD based resins. For those fabricators a low HAP orthophthalic replacement resin that has properties that are the same or similar to those of the orthophthalic resins they are currently using would be required. We targeted as our goals for such a resin, the properties of the current orthophthalic resins currently being used. In evaluating potential orthophthalic replacement resins the following resin characteristics were considered:

- 1) Liquid Properties (Viscosity and Thix Index)
- 2) Cure properties (Gel time, Interval, and Peak Exotherm)
- 3) HDT
- 4) Mechanical Strength ( Flexural and Tensile)
- 5) Modulus (Flexural and Tensile)
- 6) Tensile elongation
- 7) Secondary bond strength
- 8) Workability
- 9) Profile
- 10) Osmotic blister resistance

We targeted the viscosity at 550cps at 50rpm on an RVT viscometer. Although the composite MACT allow for a HAP content of 38.4% with non-atomized mechanical application we targeted the more stringent 35% maximum of the Marine MACT. We did so with the understanding that a large amount of the orthophthalic resins currently being sold is sold through distribution. It is not always possible to know what the end use will be for the resin and distributors like to limit the number of resins they have to stock. Therefore, we determine it was best to target the 35% HAP level of the Marine MACT that would also meet the 38.4% maximum styrene content requirements of the Composite MACT. As seen in "Figure 4" the viscosity and thix index achieved with the orthophthalic replacement resin is similar to that of the traditional orthophthalic resin.

For gel and cure properties we targeted those properties typically achieved with the current low to moderate reactive orthophthalic resins in the market-place. With varying amounts and type of promoters, a wide range of gel and cure properties can be achieved with any resin type. We evaluated resins with similar gel times and promoter systems. The orthophthalic replacement resin had cure properties very similar to those of the traditional orthophthalic resin. (Figure 4)

As stated in the background section of this paper, simply removing styrene from a standard orthophthalic resin does not work because of excessively high viscosity and low HDT values. Attempts were made to address both these issues by a reduction in molecular weight with an increase in the amount of unsaturation (reactivity) in the polymer. While the higher reactivity did help most of the mechanical properties, HDT in particular, the improvement was not enough to bring the properties

up to those of the typical orthophthalic resin. Further reductions in molecular weight and reactivity were made and were determined to have little to no effect on viscosity and greatly reduced the mechanical properties.

It was determined a change in the polymer would be required to achieve the mechanical properties desired and still get the target viscosity while maintaining the maximum styrene content of 35%. Different types and amounts of reactants were evaluated as to their effect on mechanical properties and viscosity. After evaluating over two dozen different polymers, a polymer that would provide the desired properties was discovered. The properties of this polymer dissolved in 35% styrene were very similar to those of the current 42-45% styrene resins currently in use. The HDT value of the resin was in fact significantly higher than the HDT of the orthophthalic resin. (Figure 5)

Secondary bonding was evaluated using the same testing procedure as was used in evaluating the secondary bonding of the DCPD based resins. Since the secondary bonding is the key reason for development of this resin it was of critical importance that the secondary bonding be much better than seen with the DCPD resins and similar to that of typical orthophthalic resins. The results of the secondary bonding are listed in (Figures 6-8).

Once the mechanical, liquid properties and secondary bonding properties were achieved, an evaluation of the workability, profile, and blister resistance was undertaken. We defined workability as the ability of the resin to wet out the glass and the effort required to consolidate the laminate and remove the entrapped air. The workability of the orthophthalic replacement resin was compared subjectively to that of the traditional orthophthalic resin. The workability was similar to that of the orthophthalic resin. Because of the lower styrene level the time to complete glass wet-out was slightly longer than achieved with the orthophthalic resin.

Profile was evaluated using a 6oz laminate behind 20mil of gel coat applied to a glass plate. The profile was compared immediately upon de-mold and after 24 hours post cure at room temperature. The profile achieved with the orthophthalic replacement resin was better than that achieved with the orthophthalic resin.

To eliminate the variability seen when testing gel coated laminates, the osmotic blister resistance was run on

castings. This test was run at 100°C. The time to first blister formation and the extent of the blistering after a set time of exposure was recorded. This testing showed that while the blister resistance of the orthophthalic replacement resin was not as good as seen with the low HAP DCPD based resin it was superior to that achieved with the current high HAP orthophthalic resins it would replace.

The ultimate test of any new resin is the performance of that resin in an actual production environment. Trial amounts of the orthophthalic replacement resin were made to customer's specification and run in their fabrication shops. In all instances this resin was used in replacement of the orthophthalic resin currently being used. The orthophthalic replacement resin was used successfully in all trials. Because of the significantly lower styrene level of the orthophthalic replacement resin some adjustments in the pressure and tip of the spray equipment were required to get the desired spray pattern.

## CONCLUSION

For a majority of the fabricators currently using orthophthalic resins, a change in polymer of the resin they are using will be required for them to meet the MACT requirements for HAP content. Three resin options are available to these fabricators to meet the MACT requirements for HAP content.

- 1) Currently available DCPD based low HAP resins. For those fabricators that can make adjustments in their processes and parts to compensate for the reduced secondary bonding and rigidity of these resins
- 2) Flex modified DCPD resins. For those fabricators that need the tougher mechanical properties of orthophthalic resin but can make adjustments in their processes and parts to compensate for the reduced secondary bonding.
- 3) Orthophthalic replacement resin. For those fabricators that are unwilling or unable to make any modification in their process or parts to compensate for lower secondary bond strength and/or rigidity.

## REFERENCES

Hewitt, John, Secondary Bonding with Low Styrene DCPD Based Resins  
Presentation of Northeast Composites Conference  
Portland, Maine June 26, 2001

<b>Effects of Styrene reduction on traditional ortho resins</b>			
Molecular Weight	Standard	Standard	Reduced
% Styrene	45	35	35
HDT °C	68	60	50
Viscosity	500	1250	750
TI	2.5	2.5	2.5

Figure 1.



Figure 2.

		Traditional DCPD Blend	Traditional Ortho	Flexural Modulus DCPD
<b>TYPICAL LIQUID PROPERTIES</b>				
Styrene %		35 Max	45	35 Max
Viscosity		450	650	550
TI		3.0	2.0	2.5
<b>TYPICAL CAST MECHANICAL PROPERTIES</b>				
Flexural Strength	Psi/Mpa	14,000/97	18,000/124	17,000/117
Flexural Modulus	Psi x 105/Gpa	5.9/1	5.7/4.0	5.4/3.8
Tensile Strength	Psi/Mpa	8,500/59	10,000/69	9,500/66
Tensile Modulus	Psi x 105/Gpa	5.7/3.9	5.8/4.0	5.1/3.5
Elongation	%	2.0	2.4	2.6
HDT	°F/°C	194/90	153/68	185/85

Figure 3.

	Traditional DCPD Blend	Traditional Ortho	Traditional Ortho	Ortho Replacement
<b>TYPICAL LIQUID PROPERTIES</b>				
Styrene %	35 Max	45	45	35 Max
Viscosity	450	450	650	575
TI	3.0	2.0	2.0	2.0
<b>TYPICAL GEL AND CURE PROPERTIES</b>				
Gel Time (Minutes)	32	30	28	30
Interval	15	17	13	14
Peak Exotherm (F)	310	290	340	300

Figure 4.

		Traditional DCPD Blend	Traditional Ortho	Traditional Ortho	Ortho Replacement
<b>TYPICAL CAST MECHANICAL PROPERTIES</b>					
Flexural Strength	Psi	14,000	20,000	18,000	18,900
Flexural Modulus	Psi	590,000	580,000	570,000	540,000
Tensile Strength	Psi	8,500	12,000	10,000	10,000
Tensile Modulus	Psi	570,000	570,000	580,000	540,000
Elongation	%	2.0	3.0	2.4	2.5
HDT	°F/°C	194/90	149/65	158/70	181/83

Figure 5.

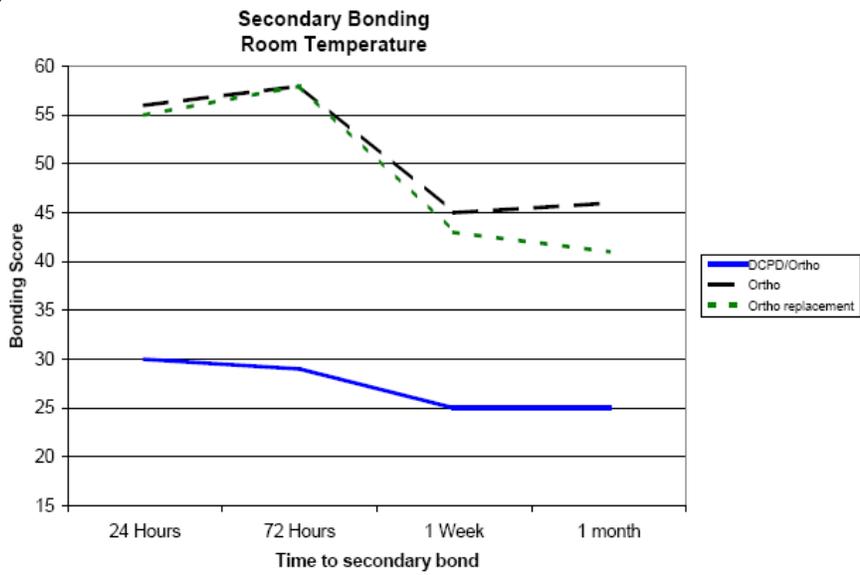


Figure 6.

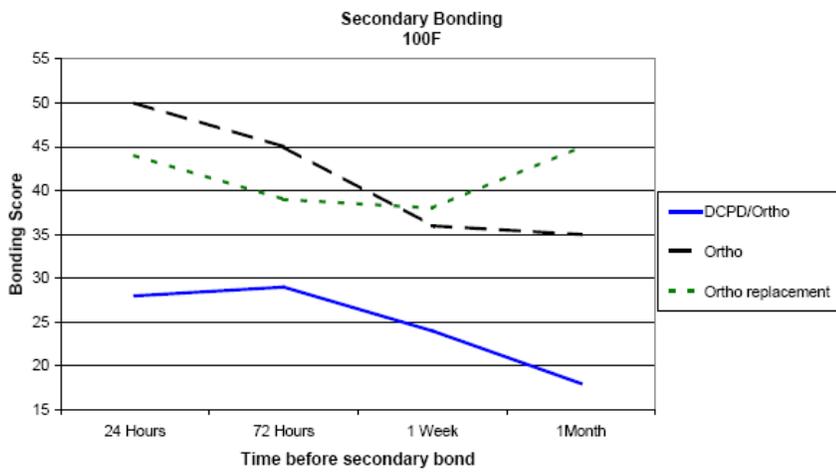


Figure 7.

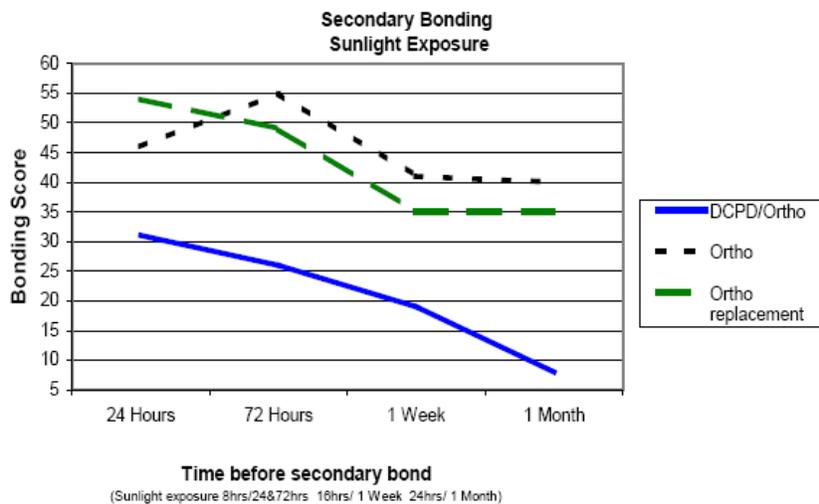


Figure 8.