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Using Peroxides to Optimize Process Control for Styrene Emissions

By

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Target:

Open molding operations, large part corrosion molders, thick cross sectional profiles, or other high thermal mass parts. Equipment manufactures, resin formulators, and coring vendors.

Abstract:

Several studies in the past have suggested that it is possible to dramatically reduce the over all loss of styrene vapors during the laminating process by simply increasing the thickness of the laminate, thus reducing the number of "open" layers in the laminate schedule. The elimination of an "open surface" step reduces the amount of time the laminate surface is exposed for the styrene to evaporate. The major problem to implementing this procedure in the past was the exotherm generated by the thick thermo mass of the laminate. It is now possible to reduce this exotherm with specialty blended peroxides, thus making this technique practical to use in most laminating shops to reduce styrene emissions without costly mechanical controls. A secondary bonus in this process change is a reduction in labor equal to the number of process steps eliminated.

Introduction:

During the past decade many advances have been made in resin cure initiation (catalyst) technology. Not only have the organic peroxide manufactures improved the quality of the products available, but they have introduced numerous specialty products and blends to

address specific issues in the fabrication process. Whereas in the past there were three or four standard products referred too as "hot", "fast", "general purpose", or "gel coat", there are now over a dozen commercial products that cover a wide range of conditions, processes, and niche applications. Combine that with the trend to blend various peroxides to get even more specific results, and today's production manager has a wide range of choices to optimize his process.

The majority of these advances were made in the interest of obtaining "Better, Faster, Cheaper" results in the fabrication process, many aimed directly at better cosmetics. Other prime concerns were: better roll out, less "sticky"; porosity and pinholes; better, faster overall cure; post cure issues, dimensional stability or reproducibility issues; and adapting to the new "low haps" resins and gel coats mandated by the EPA. This latter concern raised a number of issues all by itself. As the industry worked its way through the emissions reduction process, it was discovered early on that one of the easiest methods to reduce overall styrene evaporation was to simply make the laminate thicker. One or two laminate schedules at $\frac{3}{8}$ - $\frac{1}{2}$ inch emitted far less styrene overall than the equivalent thickness made up of three or four $\frac{1}{8}$ - $\frac{1}{4}$ inch layers. It is simply a matter of exposed surface area. Given the same mold surface, one thick layer has $\frac{1}{2}$ the exposed surface area as two thinner layers made on the same mold by the practice of letting the first laminate gel and cure before starting the second laminate.

A major drawback to this practice, and the reason it was never recommended, is the extreme heat generated by the thicker laminate on curing, more heat than could be handled by the mold. This increased heat also was detrimental to surface cosmetics and caused excessive, non-uniform shrinkage. This study will demonstrate that in many situations these concerns can be alleviated with the proper selection of peroxide blends. Other cases may require changes in resin promotion, but in all cases it seems this method could be a viable approach to help reduce styrene emissions, while at the same time eliminating labor costs associated with making several schedules versus one.

Experimental:

Modern methyl ethyl ketone peroxides (MEKP) formulations are made up of various combinations of four active ingredients: hydrogen peroxide, (H₂O₂) and the monomer, dimer and trimer forms of MEKP. For this study we used a standard high monomer MEKP in combination with cumyl hydroperoxide (CHP). The ratios of these blends are considered proprietary. They are labeled A, B, C, D, etc. Gel times were taken using a Sunshine gel meter, following Norac standard operating procedure (SOP) number 258A. Cure data was developed following Norac SOP 262 (All Norac SOP's are available on request). Laminate temperatures were determined using an infrared probe placed ¼ inch above the laminate surface. Emission testing and calculations were performed in accordance 40CFR Part 63 Subpart WWWW

Graph and Table 1 show laminate peak surface temperatures of a 1X2 layer laminate, a 1X4 layer laminate, etc all the way to a 1X8 layer laminate. Each layer was an 8X8 inch piece of ¾ once mat. Time to Peak, TTP, shows the effect of the thermo mass of the laminate. As the mass is increased, the TTP is faster, and the Peak temperature is also higher with the standard MEKP. This is reversed with MEKP/CHP blend, with the TTP getting longer with a lower peak exotherm. This set was run using a standard Vinyl Ester/DCPD blend marine laminating resin, Resin A for this study

Graph and Table 2 show the same testing done using a standard DCPD marine laminating resin, Resin B for this study.

Graph and Table 3 show the emissions testing of Resin A. Each laminate was constructed in a shallow baking pan to allow for taring and weighing all components of the laminate in accordance with 40CFR Part 63 Subpart WWWW After construction the pan was placed on a scale and readings were taken while the laminate cured. Data collection was stopped after three consecutive reading without any change.

Graph and Table 4 show the results of Resin B.

(See Tables and graphs in Appendix)

Conclusion:

This study supports the thesis of this paper. For the resins tested it is very possible to double or even triple the laminate thickness and still achieve the lower peak temperatures necessary for good cosmetics. The emission data for the thick, 8 layer laminates were not only less than the combined total of the layers, but actually less than any single layer, in one case allowing for a 50% total reduction. This study did not take into consideration the effect of "spraying the chopped glass", only hand lay up. From previous emission studies it is legitimate to assume that the pattern would still hold true. That is one spray application is going to be better than multiple spray applications. However, Norac would caution managers to test the individual application and process before making production parts. In some instances, it may be necessary for the resin manufacturer to adjust the resin promoter system to accommodate this practice. It may also take some testing to determine the optimal MEKP/CHP blend for the thermal mass configuration.

Acknowledgement:

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Graph 1

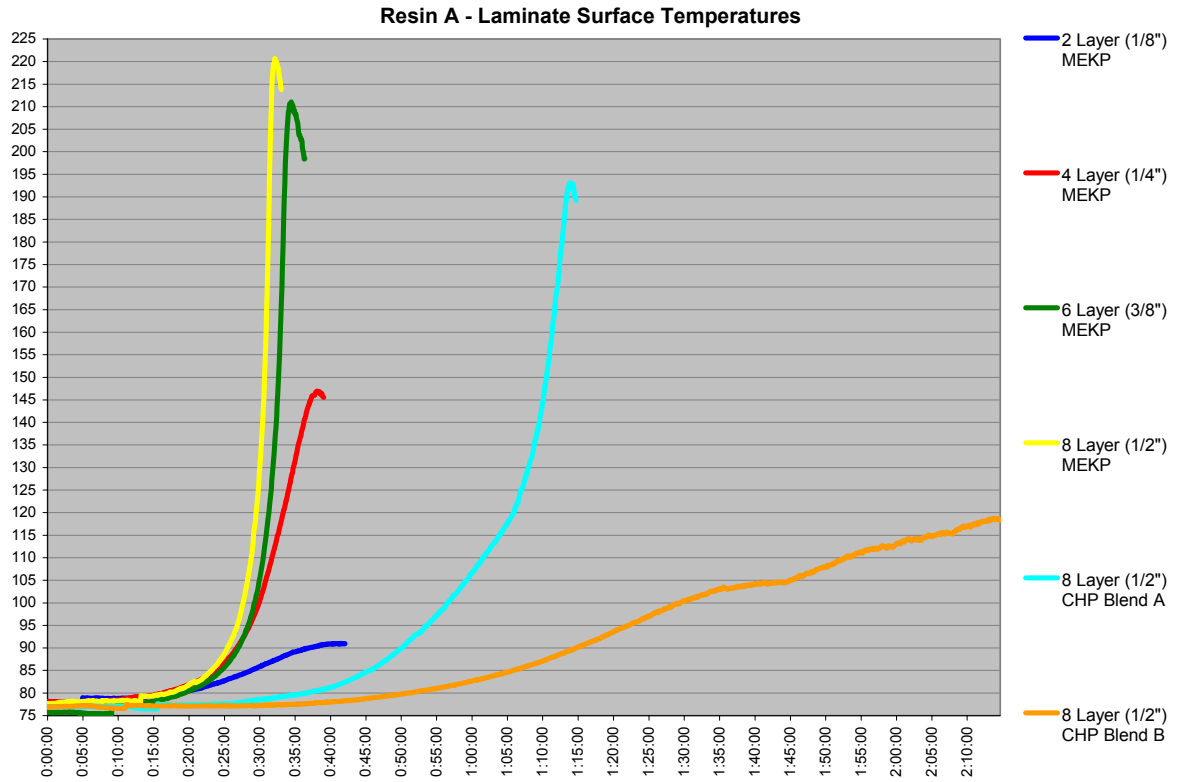


Table 1

| | Time to Peak | Peak Temp. | Peroxide |
|-----------------|--------------|------------|-------------|
| 2 Layers (1/8") | 41.1 Min. | 91°F | MEKP |
| 4 Layers (1/4") | 38.1 Min. | 147°F | MEKP |
| 6 Layers (3/8") | 34.4 Min. | 211°F | MEKP |
| 8 Layers (1/2") | 32.1 Min. | 221°F | MEKP |
| 8 Layers (1/2") | 64.5 Min. | 188°F | CHP Blend A |
| 8 Layers (1/2") | 133.7 Min. | 119°F | CHP Blend B |

All testing was run at 1.50%
 Resin A
 Laminate Size 8"x 8"

Graph 2

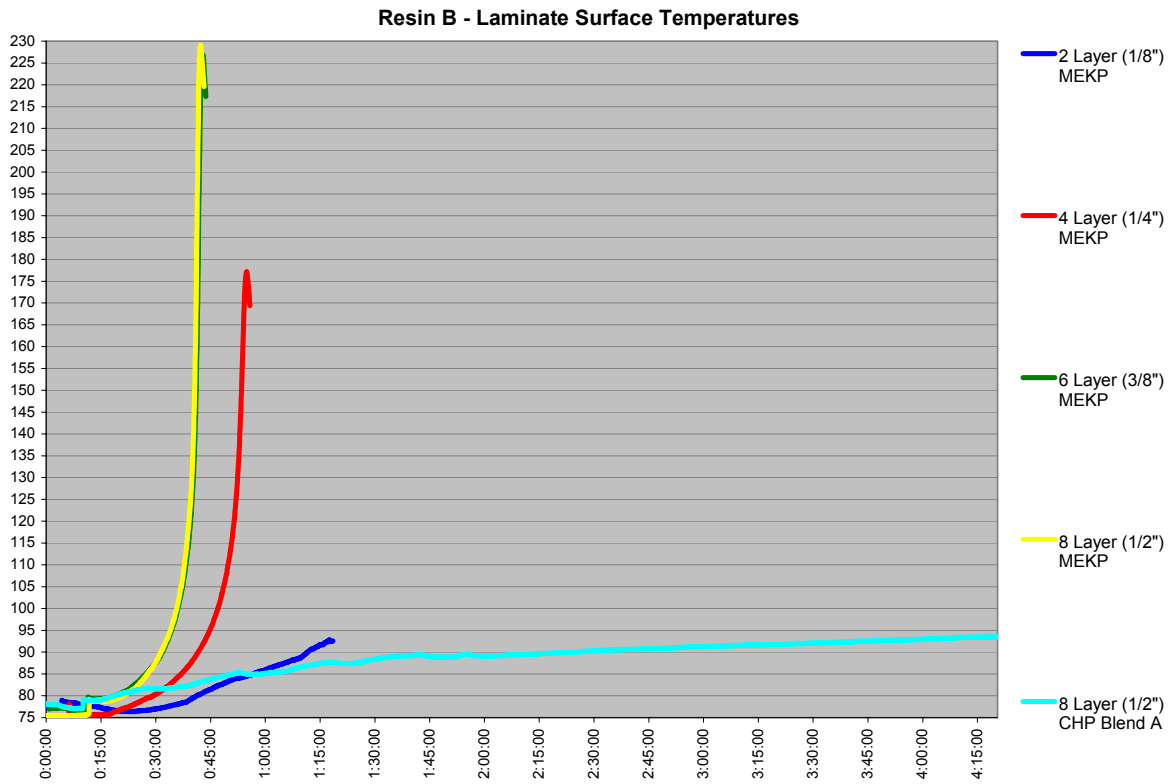


Table 2

| | Time to Peak | Peak Temp. | Peroxide |
|-----------------|--------------|------------|-------------|
| 2 Layers (1/8") | 77.5 Min. | 93°F | MEKP |
| 4 Layers (1/4") | 54.8 Min. | 177°F | MEKP |
| 6 Layers (3/8") | 42.8 Min. | 227°F | MEKP |
| 8 Layers (1/2") | 42.3 Min. | 229°F | MEKP |
| 8 Layers (1/2") | 191.8 Min. | 94°F | CHP Blend A |

All testing was run at 1.50%
 Resin B
 Laminate Size 8"x 8"

Graph 3

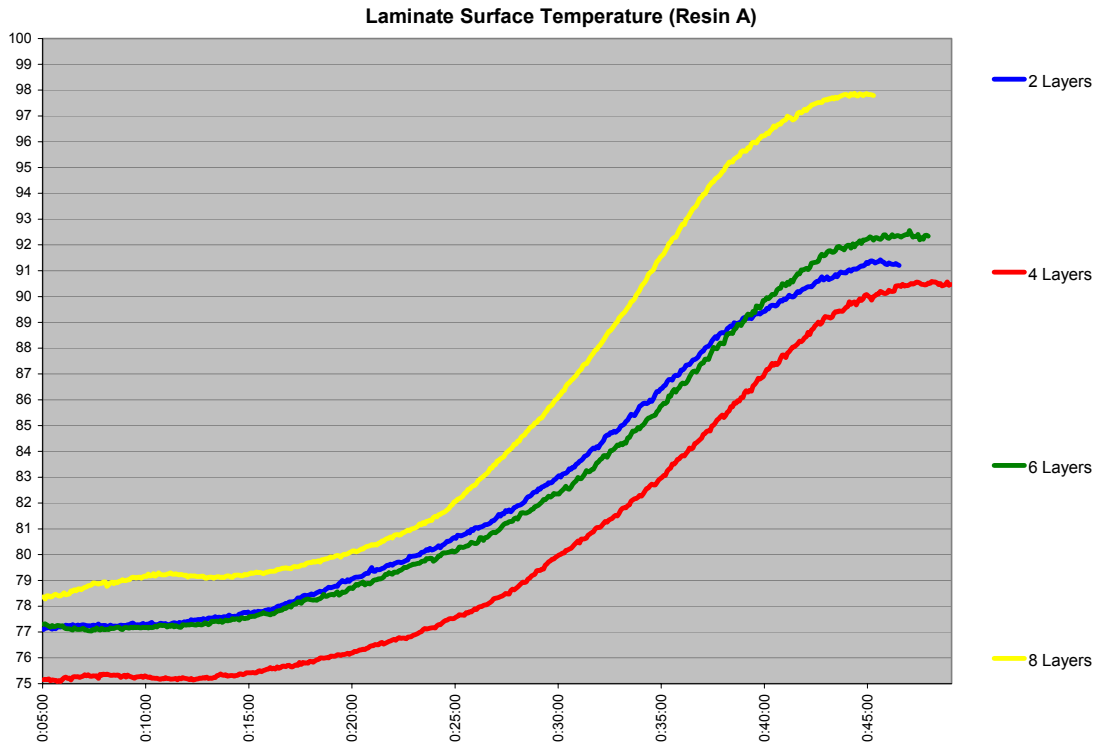


Table 3

| Resin A – Testing Parameters | 2 Layers (1/8") | +2 Layers (1/4") | +2 Layers (3/8") | +2 Layers (1/2") | 8 Layers (1/2") | 8 Layers (1/2") |
|---|--------------------|---------------------|---------------------|---------------------|--------------------|--------------------|
| Tare of Pan & Mylar | 399.62g | 603.92g | 806.68g | 1008.65g | 413.34g | 391.20g |
| Tare of Pan, Mylar & Glass | 472.99g | 674.29g | 876.04g | 1081.77g | 714.46g | 672.16g |
| Tare of Pan, Mylar, Glass & Rolling Media | 475.76g | 676.99g | 878.57g | 1084.79g | 717.33g | 674.59g |
| Gross Weight (With Resin) | 606.73g | 810.15g | 1012.09g | 1223.80g | 1310.12g | 1228.95g |
| Weight of Glass (8"x 8") | 73.37g | 70.37g | 69.36g | 73.12g | 301.12g | 280.96g |
| Initial Resin Weight | 130.97g | 133.16g | 133.52g | 139.01g | 592.79g | 554.36g |
| Temperature | 76°F | 75°F | 77°F | 78°F | 76°F | 80°F |
| Humidity | 39% | 37% | 39% | 34% | 44% | 36% |
| Peroxide Level | 1.50% | 1.50% | 1.50% | 1.50% | 1.50% | 1.50% |
| Peroxide Type | MEKP | MEKP | MEKP | MEKP | CHP Blend A | CHP Blend B |
| Roll-out Duration | 4 Min. | 4 Min. | 4 Min. | 4 Min. | 10 Min. | 10 Min. |
| Starting Weight | 606.73g | 810.15g | 1012.09g | 1223.80g | 1310.12g | 1228.95g |
| Post Roll Out Weight | 605.95g | 808.91g | 1010.91g | 1222.34g | 1306.12g | 1227.12g |
| 15 Min. | 604.82g | 808.09g | 1010.60g | 1221.94g | 1305.60g | 1226.32g |
| 30 Min. | 604.29g | 806.97g | 1009.26g | 1220.20g | 1303.70g | 1225.20g |
| 45 Min. | 603.92g | 806.74g | 1008.65g | 1220.09g | 1302.30g | 1224.30g |
| Final Weight | 603.92g | 806.72g | 1008.65g | 1220.04g | 1301.78g | 1222.22g |
| Peak Temperature | 91°F | 91°F | 93°F | 98°F | 188°F | 119°F |
| Weight Loss % | 2.1% | 2.6% | 2.6% | 2.7% | 1.4% | 1.2% |
| | | | | Total Loss % | 2.5% | 1.4% |
| | | | | | 1.4% | 1.2% |

Graph 4

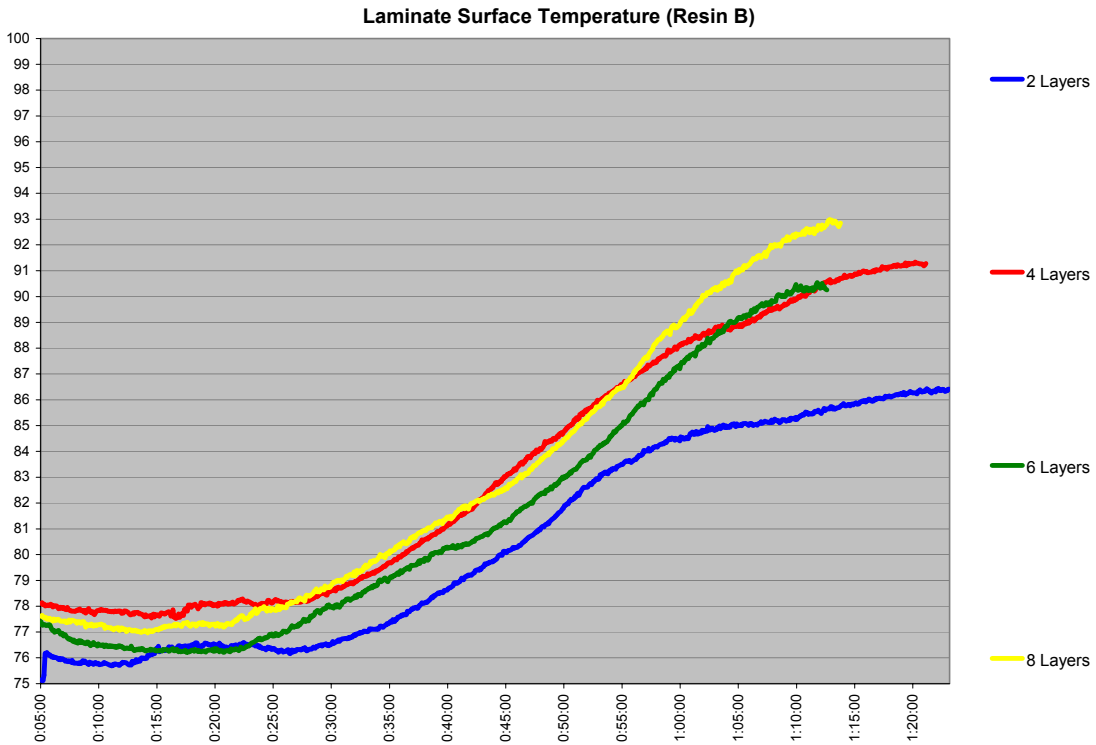


Table 4

| Resin B – Testing Parameters | 2 Layers (1/8") | +2 Layers (1/4") | +2 Layers (3/8") | +2 Layers (1/2") | 8 Layers (1/2") |
|---|--------------------|---------------------|---------------------|---------------------|--------------------|
| Tare of Pan & Mylar | 413.70g | 596.66g | 792.80g | 999.78g | 413.58g |
| Tare of Pan, Mylar & Glass | 482.53g | 670.06g | 868.86g | 1074.80g | 703.35g |
| Tare of Pan, Mylar, Glass & Rolling Media | 485.13g | 672.82g | 871.58g | 1077.47g | 706.31g |
| Gross Weight (With Resin) | 602.64g | 799.51g | 1006.23g | 1216.20g | 1213.28g |
| Weight of Glass (8"x 8") | 68.83g | 73.40g | 76.06g | 75.02g | 289.77g |
| Initial Resin Weight | 117.51g | 126.69g | 134.65g | 138.73g | 506.97g |
| Temperature | 76°F | 77°F | 75°F | 77°F | 77°F |
| Humidity | 41% | 40% | 37% | 37% | 40% |
| Peroxide Level | 1.50% | 1.50% | 1.50% | 1.50% | 1.50% |
| Peroxide Type | MEKP | MEKP | MEKP | MEKP | CHP Blend A |
| Roll-out Duration | 4 Min. | 4 Min. | 4 Min. | 4 Min. | 10 Min. |
| Starting Weight | 602.64g | 799.51g | 1006.23g | 1216.20g | 1213.28g |
| Post Roll Out Weight | | | | | |
| 15 Min. | 599.96g | 796.30g | 1003.35g | 1214.48g | 1209.30g |
| 30 Min. | 598.35g | 794.10g | 1002.25g | 1212.26g | 1207.44g |
| 45 Min. | 597.36g | 792.92g | 1000.88g | 1210.90g | 1205.66g |
| Final Weight | 596.66g | 792.80g | 999.78g | 1210.16g | 1201.90g |
| Peak Temperature | 86°F | 91°F | 91°F | 93°F | 94°F |
| Weight Loss % | 5.1% | 5.3% | 4.8% | 4.4% | 2.2% |
| | | | Total Loss % | 4.9% | 2.2% |