FR Veil Provides Low Cost Model to Achieve ASTM E-84 Class A Smoke Index

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Abstract

Low cost pultruded building and structural components have excellent high strength, light weight and corrosion resistant properties. However, upon exposure to open flame or high radiant heat, several troublesome concerns are inherent in these materials with regard to surface flammability, smoke generation and toxicity (FST). These considerations are often subject to prescribed regulatory performance criteria by code governing authorities. For expansion into new market opportunities, of particular interest is having the ability to produce commodity components that will meet the prescriptive ASTM E-84-01, e.g., "Standard Test Method for Surface Burning Characteristics of Building Materials", Class 1 Flame Spread and Class A Smoke Developed Indexes. Commodity components can achieve Class 1 Flame Spread, however, fail in limiting smoke generation. This paper will examine the procedure and technology successfully employed in the development of an economical surfacing veil based system that will provide E-84 Class A Smoke Development behavior. To get around the high development costs of numerous full-scale pultrusion sheet manufacturing and E-84 testing, many small vacuum bagged hand laminated specimens were fabricated to supplement the variety of pultruded specimens. Scanning tests for combustion characteristics and smoke generating properties were accomplished by use of the Cone Calorimeter apparatus. The resultant FST reducing veil can assist pultruders in addressing some of the unsolved and challenging problems associated with meeting prescribed regulatory code requirements. Meeting these prescribed requirements will allow candidacy in new market opportunities where composites have historically been exempt.

1. Introduction

Pultruded components, such as I-beams, box beams, C-channel, sheeting panels, walkway and handrail systems, decking, cable trays, threaded rod and strut, are widely used in corrosive industrial applications. However, the burning behavior of such materials, particularly those that are to be used in an enclosed environment, are of primary concern to end users, regulators and governing authorities. Prescribed code requirements, particularly the ASTM E-84 test protocol requirement for Class A low smoke, has been the regulatory toll composite material producers must meet for entry into broader commercial and industrial acceptance. Historically, pultruded materials have demonstrated undesirable burning characteristics, i.e., flammability at relatively low temperatures, the generation of toxic and acrid smoke, and destructive flame spread. Many reinforced plastics can be designed to have a degree of fire resistance as there are many fire retardant compositions available. Unfortunately, a large number of the more effective commercially available fire retardant resins and additive compounds are bromine based. Bromine is the single most effective flame retardant element in general use. Under a fire load, however, these brominated compounds can produce and liberate extremely toxic fumes such as hydrobromic acid (HBr) and suspect brominated carcinogens. Non-toxic additives, such as aluminum trihydrate (ATH), also known as aluminum trihydroxide (ATH), if used singularly requires very high loading levels to achieve proper fire retardancy. The necessary ATH additive to resin ratios can be so high that the desirable physical properties of an engineered composite product are degraded and can be dramatically diminished.

An unfilled reinforced laminate, e.g., neat resin and reinforcement, will exhibit maximum physical strength characteristics. Polymeric fire retardant additives, or fillers, have numerous problems associated with their use in a variety of ways. For example, during fabrication of a laminate product, a polyester thermoset resin must have a sufficiently low viscosity to soak or wet-out the glass reinforcements prior to curing. This wet-out is necessary upon curing to achieve a sufficient cross-link density of the resin; mechanically encapsulating the reinforcements; maximize the chemical bonding to the sizing on the reinforcements; and, to insure there will be no resin dry areas. However, when a fire retardant powder additive such as ATH is mixed into the resin in the necessary quantities for acceptable fire retardancy, e.g., perhaps as much as 60 parts ATH in 100 parts of total additive / resin mix by weight, the resin viscosity increases dramatically as the styreneated resin wets-out the additive. As a result the higher viscosity resin has difficulty, or, no longer has the ability to fully saturate the reinforcements. To overcome this higher viscosity processing problem with polyester resins, styrene typically is added to the mixed composition to lower the viscosity back to a lower necessary working viscosity range. Consequently, the resin contains a disproportionate, higher quantity of styrene. Additionally as discussed, the heavily filled finished part will exhibit undesirable physical characteristics such as reduced flexural and shear strength. Upon exposure to open flame, the required ATH fire retardant loading does reduce the likelihood of a part to combust by liberating bound water, however, this mechanism is marginally efficient. As the thermal decomposition of the laminate continues, the additional styrene makes a major contribution as a combustible fuel source, providing a greater affinity towards flammability. In addition, styrene is an egregious smoke producing compound, which significantly adds to the overall smoke production of the part. Therefore, with ATH as a sole fire retardant, there are processing problems, which yield weaker parts and which have the characteristic of generating larger quantities of acrid smoke.

For a reduced fire retardant additive loading, an alternative to ATH is a combination of decabromodiphenyl ether oxide (DBDPE) with antimony trioxide (ATO), e.g., less than 20 parts total of DBDPE and ATO per 100 parts of total resin / additive mix. As powders, an additional quantity of styrene is typically still necessary to offset and reduce the buildup in viscosity. When compared with ATH during a fire insult scenario, the brominated fire retardant package is more efficient at reducing the flammability of a substrate. However, the bromine based fire retarding chemical combustion mechanism proceeds along much different reaction lines and sequences than those of ATH. The brominated constituent package operates by competing with oxygen in the ionization phase of the combustion reaction that reduces the availability of oxygen at the substrate surface. This fire retarding mechanism, by design, produces large quantities of soot and char with accompanying dense, acrid smoke. Although effective as a flame retardant, the smoke generated by pyrolysing brominated compounds can render an environment biologically toxic. For example, byproducts of the decomposition of decabromophenyl ether (DBDPE) can form brominated acids and many other brominated byproduct compounds which have significant toxicity.

The ASTM E-84-01 test, e.g., the Standard Test Method for Surface Burning Characteristics of Building Materials, is often referred to as the “tunnel test” and is often cited by building material code regulators. It was developed over time to gauge the relative burning behavior of a subject material, as compared to red oak. This is accomplished by measuring and reporting two observations that occur during exposure to an open flame source within a chamber. One is the flame spread along a specimen and is assigned a Flame Spread Index (FSI) value. The second measurement is the smoke obscuration in the optical scale for human vision and is assigned a Smoke Development Index (SDI) value. At a minimum, fiberglass reinforced building components and related structural support assemblies are typically required to meet the E-84-01 Class 1 Flame Spread Index e.g., 25 or less, and is achievable with popular fire retarding additive compounds. The low smoke Class A Smoke Developed Index (SDI), e.g., defined by convention as less than 450, is extremely difficult to achieve with low cost polyester resins. For commodity composite materials, companies testing material to the E-84 protocol almost exclusively focus on the FSI, e.g., flame value, and ignore the SDI, e.g., smoke development value, as this is usually 950+ out of a possible 1000. Stainless steel and aluminum don’t combust and will not form smoke, although they have other negatives. Many opportunities and markets, which use these metal component materials, cannot employ pultruded components where regulators deem E-84 low smoke characteristics a requirement.

The methodology and results described herein are a review of the technology which lead to the successful production of inexpensive pultruded parts with novel smoke characteristics. In an economical fashion, the program goal was to provide a technically sound fabrication system that would enable pultruders to fabricate low cost components that will meet the ASTM E-84-01 Class A Smoke Developed Index criteria, e.g., SDI less than 450, with non-toxic fire retarding constituents. This was achieved by the development and implementation of a low cost veil based system. By carefully assessing baseline combustion data trends in a qualitative manor and adjusting the composition and design makeup of the material, the veil system was refined in both FST effectiveness and manufacturing processability. Hand laminated placards, tested by the method of Cone Calorimetry, provided sufficient insight to evolve the system to its present refinement, which provides excellent smoke suppression properties when tested in accordance with the ASTM E-84-01 protocol. Employing this system requires no changes in chemistries, reinforcements, manufacturing techniques or line speeds. The applicability of this system to the pultrusion process can be summarized as follows:

- As the fire retarding constituents are non-hazardous, the veil system can be stored as any composite glass fabric material.
- The veil system may be slit in accordance with any width requirement as any standard glass mat or woven fabric.
- Widths have been produced to 72 inches.
- Lengths are generally determined by permissible roll diameters.

- The fire retarding powder composition within the fabric will not dust or flake during production practices.
- All polyester and vinyl ester resins are fully compatible with the veil system, however, this paper will focus on commodity polyester resin only.
- The veil system has a glass rich side which, it is recommended, goes against the die to obtain traditional surface characteristics.
- The veil system does not require pre-wetting or dipping of the fabric into a resin bath. The veil system will wet-out correctly and properly when fed directly into the die from its roll.
- No changes are necessary with regard to pre-former alignment or orientation.
- The veil fabric can accommodate extremely small edge radii without cracking, loss or corruption of the FST chemical composition layer.
- Die temperature zones may be run at temperatures up to 450 degrees Fahrenheit with no deterioration in the systems processability or effectiveness.
- The veil, being white in color, can be pigmented to virtually any color.
- All organic peroxide initiators and blends thereof work properly and correctly without any special consideration or adjustment.
- The surface characteristics of a finished part incorporating the veil system possess the sheen and texture of a typical, commercially available pultruded part.
- Being an integral component within the resin matrix, the system exhibits excellent flexural movement without fear of de-lamination.
- When exposed to open flame or high radiant heat, the system swiftly chars, swells and forms a cementitious layer, e.g., cement, reinforced by the glass filaments of the veil system.
- The reinforced cementitious structure exhibits excellent “basket strength” and structural integrity as compared to halogenated resins or traditional fire retarding additives after prolonged exposure to open flame or high radiant heat.

2. Discussion and Test Results

Coating polyester laminates with certain intumescent coatings will dramatically reduce the ability of a laminate to combust or generate smoke. The following four ASTM test protocols illustrate the effectiveness of a fire retarding and smoke suppressing intumescent coating that was applied to a non-fire retardant, vinyl ester (VE), glass, cored sandwich panel. Without the coating, the cored panel surface skins burn vigorously while generating large volumes of black smoke. Because of these observations, no baseline flammability or smoke generation tests were performed on the uncoated panels. Additionally, no toxic gas analysis was performed on the uncoated panels due the observed poor flame and smoke characteristics.

In Fig. 1 are the results of an ASTM E-162, e.g.: Standard Method of Test for Surface Flammability of Materials Using a Radiant Heat Energy Source, on the cored laminate. This test is used to predict flame spread characteristics of a specimen under specific test conditions. As listed, the laminate attained a calculated Average Flame Spread Index of 10.61. Again, without the benefit of the intumescent coating, the panel would have burned vigorously.

In Fig. 2 are the results of an ASTM E-662, e.g.: the Standard Test Method for Specific Optical Density of Smoke Generated by a Solid Material, on the described VE cored laminate. This test is used to determine the quantity of smoke generated by solid materials and assemblies up to and including one inch. The apparatus measures optical density within a chamber by means of a photometric scale similar to the optical scale for the human eye. As listed, the densities in the non-flaming and flaming modes are low at all times. A general rule observation prediction rule is to add the result values of the flaming and non-flaming modes at twenty minutes. The value should be below two hundred as a predictor for achieving an ASTM E-84 Smoke Development Index of Class A, e.g., less than 450. Again, without the coating, the combusting laminate would have produced large volumes of black smoke where it would not qualify as a Class A assembly.

In addition to flammability and smoke, the toxicity of thermally generated gases, biologically poisonous compounds and acrid smoke is of concern. In Fig. 3 are the results of a Boeing Specification Support Standard BSS 7239 Test Method for Toxic Gas Generation by Materials on Combustion test on the subject cored VE panel. During this test the specimen is exposed to a specified open flame for four minutes and analyzed by using gas detection tubes. The intumescent coating protected the under-laminate without any significant generation of hydrochloric acid (HCl), cyanide (HCN), carbon monoxide (CO), etc.

Not included in the BSS 7239 Toxic Gas analysis protocol is the quantity of brominated compounds present in the smoke generated by a subject specimen such as hydrobromic acid (HBr). As discussed, brominated substances in smoke can quickly render an environment biologically toxic. In addition, some bromine compound decomposition products have been identified as suspect cancer causing agents. As discussed decabromodiphenyl ether (DBDPE) and antimony trioxide (ATO), a heavy metallic compound, are often the fire retardant package of choice for polyester resins. However, brominated compounds are receiving intense scrutiny from government health and environmental regulatory agencies regarding their future availability and use. The base FR intumescent composition tested to the fire, smoke and toxicity protocols, was analyzed for total bromine content by Second Ion Mass Spectrophotometry. The tests were performed at the University of Massachusetts, Lowell, MA. The analysis results identify the composition contains a total of twenty five parts per million of bromine. This represents trace backround residuals from several constituents in the intumescent composition.

The secondary over coating of pultruded parts with an intumescent coating has numerous drawbacks. It requires regulated paint application and drying areas. Coatings can be scored, scratched or chipped at any point, including after end-use site installation. For general, cost effective fire proofing, it's questionable the end markets would accept a costly, secondary coating. However, an integrated surface layer within a composite, comprised of the dry active constituents contained in the intumescent coating discussed above would be a low cost benefit to engineers and fabricators in their efforts to meet regulatory life safety code requirements such as the ASTM E-84-01 Class 1 Fire and Class A Smoke Indexes. A design was envisioned in which the FR powder would be affixed with a minimal quantity of adhesive to one side of a standard glass pultrusion veil wherein it could be "pulled" just as a standard commercial veil. A description summarizing the rationale and design of the fabric is detailed in the following paragraphs.

Surfacing veils and mats are a standard component in most pultrusion laminate schedules for several reasons such as aesthetics. Incorporating the dry fire retardant (FR) powder into a glass surfacing fabric would allow the inter-laminate integration with no changes in the standard pultrusion manufacturing process. A glass fabric is preferred for fire retarding and smoke suppressing properties over a polyester fabric for several reasons. Polyester (PE) fabric provides an additional fuel source; it contributes to increased surface flammability characteristics; and, significantly contributes to the production of smoke. The dry FR powder would be held in and on one side only of the glass fabric with an extremely small quantity of adhesive binder. With the other side glass rich, the construction would allow the glass fabric surface to be pulled against the die in a standard fashion. Meanwhile, the fire retardant side would be forced to the surface of the part by the resin and reinforcement pressure, ensuring complete wet-out. There would be no need to run the FR fabric through a pultrusion bath.

No effective, general purpose fire barrier surfacing fabric, which could be easily fabricated into the surface of a laminate, with no processing or formulation changes had been available as an FR design option for pultrusion. Such a fabric, for example, could greatly benefit pultruders researching and evaluating ATH in their efforts to acquire the ASTM E-84-01 Class 1/A credential. This would allow a reduced additive loading level for improved physical properties. Therefore, a product was developed to provide a non-toxic, fire and smoke suppressing intumescent fabric to assist in the passage of prescriptive test protocols.

The non-woven surfacing mat described in this document has a thickness averaging 23/1000 inch (23mil). In generic polyester resins, with a styrene content of forty percent or less and glass reinforcement, a single ply surfacing veil is sufficient for greatly improved fire and smoke characteristics. A multi-layer stacked fabric schedule is also an option, however this is beyond the scope of this paper. Due to its versatility, the fabric may be employed in a variety of fabrication processes in addition to pultrusion, such as filament winding, compression molding, resin transfer molding, vacuum assisted resin transfer molding, press molding, thermoplastic reinforced films and other secondary processes. When incorporated into a thermoplastic profile under heat and pressure, the cloth can be thermoformed and re-formed at processing temperatures over 450 degrees Fahrenheit.

The integrated powder composition contains more than ten constituents and is thermally activated. By being active, the composition has a latent ability to intumesce or foam out of a laminate when a specific temperature is reached. In the present embodiment, that temperature is around 550 degrees Fahrenheit. For example, at this temperature, and above, the cured or hardened resin/composite structure with ATH as the inter-laminate fire retardant resists combustion, is self-extinguishing without the direct application of a flame extinguisher and produces a substantially smaller quantity of less toxic smoke than a similar structure not employing the fire and smoke suppressing mat.

The additive powder is a combination of five functional groups or families of compounds: 1.) Catalyst, 2.) Carbonific, 3.) Blowing agent, 4.) Inorganic binder, and 5.) Ceramic. Each of these groups contributes a specific property to the formulation, and each is critical to the success of the composition in overcoming the disadvantages associated with prior art toxic, and non-toxic, fire retardants.

When incorporated into the surface of a laminate substrate, and upon exposure to open flame or high radiant heat, the active material operates stepwise in the following orderly pathway:

First, the catalyst decomposes to release a strong acid by-product. The by-product dehydrates the pyrolysing resin and reacts with the carbonific to form initiator based esters. After this series of reactions and decompositions, the original strong acid by-product of the catalyst decomposition is released for further reaction to continue the cycle. Unsaturated compounds are formed with subsequent charring.

Second, as the temperature rises, the catalyzed carbonific begins to decompose along a much different route and at much lower temperature than would occur for a non-catalyzed carbonific. The carbonific binds with the dehydrated polymer to lock a forming carbonaceous layer to the substrate and the subsequent structure begins to add integrity to the charred surface layer. Additionally, the decomposition of the carbonific constituents produces large quantities of char and water, as well as, carbon dioxide. The original strong acid by-product of the catalyst decomposition continues to be regenerated as the reaction cycle continues.

Third, in concert with the decomposing carbonific constituents, the blowing agent breaks down to yield large volumes of non-flammable, oxygen replacing gases. Additional char is produced. Aided by the water vaporization pressure, e.g., steam, the carbonaceous surface swells and bubbles, forming a swollen insulative and infrared protective heat shield.

Fourth, the inorganic binder constituents, a singularly unique feature of the fire retarding composition, react in the presence of the generated steam vapor. These compounds immediately proceed through a hydration reaction and form a cementitious, e.g., cement, structure as the surface swells. This structure, traps and holds soot from the polymer decomposition and mechanically holds the carbonaceous layer in place. These constituents also add to the rigidity and strength of the swollen char by combining with the reinforcement fabric filaments. This fortified, structural matrix reflects infrared (IR) radiation and is not easily dislodged by high velocity flame fronts, or a high pressure stream of water. Furthermore, it dramatically suppresses smoke and afterglow.

Fifth, after the reaction cycle is complete, the ceramic components dispersed throughout the cementitious and carbonaceous barrier keep even higher temperatures and higher velocity pressure gradients from penetrating the laminate by means of infrared reflection, e.g., emissivity.

Although beyond the scope of this paper, the fabric potentially could be comprised of specialized high temperature glass, carbon, arimid, ceramic, basalt or other commercially available fabric material. Additionally, an FR cloth can be produced for other applications with woven, non-woven, mat, felt or needled media, or combination of these various materials.

3. Development and Test Results

There are many standard testing methods and protocols established by code governing authorities. The ASTM E-84-01 tunnel test is a prescriptive test, generally accepted, such that test results with higher values for flame spread and smoke obscuration are indicative of a greater fire hazard and dangerous smoke. Again, the objective of this development program was to obtain the ASTM E-84-01 Class 1 Flame Spread Index, but more importantly, the Class A Smoke Developed Index credential on a pultruded laminate specimen using a cost effective, non-brominated, non-toxic fire retardant system.

Initially, a fabric as described herein was produced in a width and length sufficient to pultrude. This preliminary model was to investigate the fire retarding and smoke suppressing merits of the fire retardant fabric against a panel tested without the fabric. Two identical polyester resin flat sheet panels were fabricated on the same machine by a major pultruder. Both panel laminates were produced with the identical styrenated polyester resin, decabromodiphenyl ether (DBDPE) and antimony trioxide (ATO) fire retardant package and standard commodity glass reinforcements. The only difference between the two specimens was one panel had a polyester veil, the other contained the fire retarding and smoke suppressing surfacing fabric. The resin to bromine / antimony ratios were designed and documented to achieve a flame spread index (FSI) of twenty five with the polyester veil. Due to the flammable nature of the resin, its high smoke generation properties and the loading of the bromine package, no consideration was given in the mix receipt to address the smoke index (SDI) result. The pultruded specimens were thirty six inches wide by one quarter inch thick commercially available flat sheet with a fifty two percent glass content by weight.

Both panels were tested to the ASTM E-84-01 protocol by Southwest Research Institute, San Antonio, TX. The comparative results for flame spread and smoke obscuration are listed in Fig. 4. As seen from the Table, the flame spread ratio and smoke obscuration results for the new material are about ¾ of that of the typical prior art result. This is a significant reduction. The FR glass veil alone enabled the commodity flat sheet to get to nearly fifty percent reduction to the Class A Smoke Index value of less than four hundred fifty.

Smoke obscuration measurement by the ASTM E-84-01 protocol is based upon the attenuation, e.g., change in the concentration, of a white light beam by smoke accumulating in a chamber. Results are derived from measuring optical density as absorbance within the chamber. The photometric scale used to measure smoke by this method is similar to the optical density scale for human vision. Hence, obscuration can result from combustion byproduct species such as particulate acrid soot, or gaseous water vapor.

The fire retarding composition used in the surfacing mat generates large quantities of non-toxic water, which contributes to the cementitious structure, but also obscuration of the white light source of the E-84 test apparatus. It was important to evaluate certain characteristics of the invention to verify the cementitious structure was formed swiftly and positioned correctly to help neutralize resin combustion and maximize smoke entrapment. Particulate smoke matter generated by pyrolyzing polymers is primarily biologically toxic, as opposed to water vapor. Fire engineers can measure the total quantity of particulate smoke constituents, based on mass of particulate smoke per total mass loss, by an ASTM E-1354 Cone Calorimeter instrumental analysis. This apparatus uses red laser spectrophotometry to measure the mass of particulate smoke generated during the combustion of a sample specimen. Thus the actual particulate smoke can be measured without interference of a water vapor constituent. This testing method, which uses 4 inch x 4 inch placards, generates baseline values for smoke production rates and peak heat release rates which can qualitatively illustrate evolutionary improvements in fire retardancy and a reduction in smoke generation characteristics. Although no intention was given to specifically correlating the Cone instrument results to the E-84 results, the Cone was chosen as the preferred screening test apparatus as it is convenient, cost effective, accurate and would show general trends in the improvement of the FR fabric by a number of measurements through the development phases. (Please Note: Time to ignition considerations are beyond the scope of this paper as the crux of this treatise is the desired attainment of a non-toxic, pulrtuded commodity specimen which will meet ASTM E-84-01 Class 1(A) flame and smoke requirements.) All Cone testing listed and referred to in this document were performed at 50 kW/m^2 and were performed at Worcester Polytechnic Institute, Worcester, MA. A development assumption was made that all placard specimen smoke results would be correlated by mass using an assigned or calculated mass correlation factor. This would offer a model as to whether the fabric was suppressing smoke relative to the mass of combustible matter within the laminate substrate.

Comparative tests were performed to measure the difference in actual particulate smoke generation of a brominated panel verses a panel that incorporated a non-toxic, non-brominated fire retardant. To determine the difference, a section of the actual brominated panel with polyester veil described in Fig. 4 was machined into a specified Cone placard dimension and thickness. A flat panel was pultruded by the manufacturer cited earlier, on the same machine, with the same glass laminate schedule as described in Fig. 4 with a prototype FR surfacing fabric. This FR veil panel was machined to a Cone placard matching the mass of the brominated placard. As seen from Fig. 5, the release of particulate smoke from a pultruded specimen employing the smoke suppressing surfacing mat and non-toxic additive, is about one half the results of a typical commodity grade panel employing a polyester veil and brominated fire retardant package. Standard glass veils which do not contain fire retardant have been commercially available for many years. There is no published evidence to suggest a virgin glass veil, by itself, could reduce the production of smoke by one half.

In development for two years, the FR mat evolved through five distinct variations. As the glass mat and fire retarding composition remained constant, each variation improved the adhesive binder and manufacturing process, as well as, processability in pultrusion. However, to explore a wide variety of mat weights and orientations, and to assess the results by Cone Calorimeter analysis, hand fabrication with vacuum bagging was chosen to expedite development. It was deemed the variance inherent in the process with the high reinforcement content, would be within an acceptable tolerance. Each specimen fabricated in this manor had the identical resin system and woven glass reinforcement schedule. Again, the exercise was to investigate the Cones peak heat and total smoke as trends in a qualitative manor. The testing cited in this paper is not a complete listing of all development program testing.

Fig. 6 lists a total of five test results on four vacuum bagged specimens and the pultruded, brominated specimen described in Fig. 4 and Fig. 5. The chart illustrates the Cone results of three placards, e.g., Samples 1,2 and 3, fabricated with the final mat embodiment, e.g., Generation 5. Sample 1 glass up had the glass rich side of the FR mat out as it would be used in pultrusion. Sample 2 FR out had the FR composition side out. Sample 3 double coat employed two mats back to back as a sandwich construction, with the glass rich side out as in pultrusion, and the glass rich side of the inner mat against the inter-laminate woven roving.

These were compared to an earlier tested placard from the Generation 4 mat embodiment, e.g., Standard, and the original brominated flat sheet with polyester veil described in Fig. 4 and Fig.5. The FR mat weights were 36.2 grams per square foot for Samples 1, 2 and 3, and 32.4 grams per square foot for the Generation 4 Standard. The results indicate the glass out orientation of Sample 1 showed a very good peak heat release value and an improvement over the earlier Generation 4 embodiment. Even though the vacuum bagged specimens had lower glass content than the brominated pultruded placard, e.g., 41% verses 55%, the overall improvement in performance contributed by the FR mat is noteworthy.

As adhesive binder technology, manufacturing process technique, necessary constituent masses, and proper pultrusion processing of the fabric were finalized, a non-brominated flat sheet was pultruded for ASTM E-84-01 testing. The exercise was to pultrude a commercially acceptable part; use ATH as the primary fire retardant additive in the resin; have the resin cost model be below $0.70 per pound; to achieve a Class 1 Flame Spread Index of twenty five or less; and, to achieve a Class A Smoke Development Index of less than four hundred fifty. The resin constituent composition was: a commodity grade iso-polyester resin; ATH; a liquid phosphorus FR material; pigment dispersion; mold release; UV inhibitor; methyl methacrylate; and, a three stage initiator package. Final formula viscosity was approximately 2,200 centipoise. The cost of the mix totaled $0.64 per pound which is well within the acceptable range of a low cost commodity formula. This formula is available upon request.

Fig. 7 lists a total of five test results on three vacuum bagged specimens, and two pultruded specimens. The chart illustrates additional Cone testing results on two different vacuum bagged specimens with the "glass out" orientation, e.g., Sample 2 and 3, to acquire more data on the combustion characteristics and enable an averaging of results with the formally tested Sample 1. Note however the weight of the Sample 1 mat was 36.2 grams per square foot, whereas the weight of Samples 2 and 3 was 33.0 grams per square foot. The composition of the placards was identical with the exception of the 3.2 grams of fire retardant per square foot. In every category, although the results show an improvement over earlier developmental embodiments, a distinct reduction in fire retarding and smoke suppression capabilities can be seen by this variance in FR.

Fig. 7 also lists two pultruded placard test results. One is the brominated specimen with polyester veil listed earlier in Fig. 4 and Fig. 5. This specimen is now used as the "Standard" as the original development goal was to produce a non-toxic fire retardant surfacing material. The second pultruded specimen was produced using the ATH resin formulation described above. This specimen was produced with the low fire retardant loading of 33.0 grams per square foot total weight. The FR fabric / ATH specimen is described as Sample 4. Correlating by the defined equal mass model, the calculation shows the placard as generating 29.4 percent total particulate smoke of that of the brominated placard described in Fig. 4, 5 and 6. What this clearly illustrates is a dramatic reduction in the propensity or ability of the part to generate smoke. Based upon this Cone test result, this reduction was deemed so significant as to mandate the fabrication of another part by pultrusion and formally test it to the E-84-01 protocol.

The ATH 0.25 inch thick panel was fabricated with the FR fabric on one side of the flat sheet only. The 24 foot x 2 foot panel specimen was shipped in four sections to Southwest Research Institute, San Antonio, TX and ASTM E-84-01 tested. The four panels were placed on the test tunnel in correct orientation and the test was conducted. During the testing procedure, it was observed the E-84 apparatus flame penetrated through the center seam and contributed to an increased flame spread area. Smoke was observed entering the chamber through the seam, originating from the unprotected back surface. At the conclusion of the test, it was verified by observation that a significant area on the backsides of the panels showed surface combustion had occurred. Figure 8 lists the final test results and posts the light obscuration and flamespread graphs. <u>Please refer to the Fig. 8 report and the detailed discussion of the graphs at the conclusion of this paper.</u> Despite the panel seams presenting a significant penalty, the actual measured results were an Unrounded Flame Spread Index of 23.3 and an Unrounded Smoke Development Index of 351.4, well within the project requirement criteria.

4. Conclusion

The development objective of producing a low cost, non-toxic surfacing fabric which will enable pultruders to acquire the Class A Smoke Development Index (SDI) credential was achieved. As verified by passage of the E-84-01 test requirements, this FR veil fabric markedly reduces the capability of a pultruded laminate to combust or generate smoke when exposed to an open flame.

Figure - 1
Intumescent Coating ASTM E-162 Standard Method of Test for Surface Flammability of Materials Using a Radiant Heat Source

AVG FLAMESPREAD FACTOR (FS)	=	1.26		
AVERAGE HEAT OF EVOLUTION (Q)	=	8.40		
AVERAGE FLAME SPREAD INDEX (Is)	=	10.61		
FLAMESPREAD INDEX RANGE (Is)	=	8.28	TO	12.91

Figure – 1 contains the results of an ASTM E-162 test on a non-fire retardant vinyl ester resin / cored / glass sandwich panel that had an intumescent coating applied to it. As listed, the laminate attained a calculated Average Flame Spread Index of 10.61.

Figure – 2
Intumescent Coating ASTM E-662 Standard Test Method for Specific Optical Density of Smoke Generated by a Solid Material

OPTICAL DENSITY TEST RESULTS SUMMARY			
		NON-FLAMING	**FLAMING**
Ds 1.5 min.	average:	0.6	3.9
Ds 4.0 min.	average:	0.4	30.1
Dm(corr)(20.0 min.)	average:	4.7	178.3

Figure – 2 contains the results of an ASTM E-662 test on a non-fire retardant vinyl ester resin / cored / glass sandwich panel that had an intumescent coating applied to it. Generally, if the non-flaming and flaming average values at 20 minutes are added together and have a result below 200, the specimen will likely have an ASTM E-84 Smoke Development Index of <450.

Figure – 3
Intumescent Coating Boeing Specification Support Standard BSS 7239 Test Method for Toxic Gas Generation by Materials on Combustion

Gas	**Corrected PPM[1]**	**Corrected PPM[2]**	**Average PPM**	**Std. Deviation PPM**	**U.S. Passenger Rail Requirements For Interior Use (PPM)**
CO	270	200	235	49.497	< 3500
HCN	5	5	5	0	< 150
SO2	0	0	0	0	< 100
HCL	1	1	1	0	< 500
HF	0	0	0	0	< 200
NO	40	20	30	14.42	< 100
NO2	4	2	3	1.414	< 100

Figure – 3 contains the results of a BSS 7239 Toxic Gas analysis illustrating no appreciable or significant toxins are generated by the intumescent coating material on combustion.

Figure - 4
ASTM E-84-01 Standard Test Method for Surface Burning Characteristics of Building Materials Results from Two Pultruded Laminates

Property	FR Glass Mat	Polyester Veil
Flame Spread Index	19.2	25.0
Smoke Developed Index	751	985

Figure – 4 contains the comparative results for flame spread ratio and smoke obscuration acquired from an ASTM E-84-01 test on two identical brominated resin pultruded panels, differing only in the surfacing fabrics. The FR Glass Mat panel contained an early version of the fire retarding veil fabric. The Polyester Veil panel contained a standard polyester surfacing veil. A dramatic and noteworthy reduction in both flame spread and smoke production occurred by simply swapping the surfacing veil fabric.

Figure - 5
Cone Calorimeter Tests at 50 kW/m^2 Performed on the Pultruded Specimens Described in Figure – 4

Property	FR Mat & Laminate	Typical Brominated Laminate
Initial Mass	40.6 g	40.6 g
Final Mass	23.6 g	26.2 g
Smoke Obscuration		
Avg. Smoke Yield (g/g)	.057	.106
Total Smoke Release (g)	13.979	26.130

Figure – 5 contains the Cone test results at 50 kW/m^2 obtained from placards cut from the pultruded laminates described in Figure – 4. Although the initial masses were identical and final masses similar, the smoke released by the specimen employing the FR, e.g., fire retarding, mat fabric is approximately one half that of the specimen employing the polyester veil. As both laminates were identical brominated resin laminates, the results indicate an efficient entrapment of particulate smoke by the FR surfacing fabric. The 2.6 gram difference in final mass of the specimens suggests greater charring caused by the flammable polyester veil fabric.

Figure – 6
50 kW/m^2 Cone Calorimeter Test Results Comparing Three Specimens with Three Different FR Veil Orientations to an Earlier Standard Veil and the Brominated Specimen Described in Fig. 4 and 5

Sample /Test #	Placard Initial Mass(g)	Mass Correlated Conversion Factor	Correlated Total Smoke Release(g)	Correlated Average Smoke Production (g/m²/s)	Duration of Test (s)	Peak Heat (kW/m²) Release	Time (s) to Ignition
Standard Generation 4 Veil	85.5	1.00	23.98	.034	691	225	41
Sample 1 glass up FR glass mat out	80.7	1.06	21.20	.018	1198	91	25 & 430*
Sample 2 TSWB out FR glass mat down	81.6	1.04	19.88	.020	1058	123	46
Sample 3 Double coat FR mat sandwich construction	82.2	1.06	16.16	.012	1349	110	56
Pultruded Bromine Panel Polyester veil	40.6	2.04	53.31	.144	465	185	46

Figure – 6 contains the tabulated Cone test results of an earlier Standard / Generation 4 veil placard and three current Generation 5 veil placards, as well as, the pultruded, brominated specimen with polyester veil described in Figures 4 and 5. This exercise was to investigate smoke generation and peak heat results by orienting the veil in different fashions. The Standard / Generation 4 and Sample 1 had the FR veils glass rich side out, on the surface, with the FR smoke suppressing composition material down into the laminate. Sample 2 had the FR smoke suppressing composition out, on the surface, with the glass down into the laminate. Sample 3 was a sandwich construction with a layer of veil, glass rich side down, with a second veil, glass rich side up adjacent to the lower veil, in effect producing an FR smoke suppressing sandwich layer. The Standard and Samples 1, 2, 3 were fabricated by vacuum bagging. As the Cone apparatus uses mass for standard measurements, it was assumed for this model and study, qualitatively, that decomposition product masses can be correlated by employing a mass correlation multiplication factor based upon the starting masses of the specimens with a defined "standard". (Note: Correlation is not extended to test duration, peak heat or time to ignition.) The correlated results show the current Generation 5 veil embodiment shows significant improvement over the earlier Generation 4 veil regardless of orientation. A general property of the FR veiled specimens is a substantial and beneficial improvement in all measurement categories, clearly visible when compared to the pultruded, brominated resin specimen with polyester veil described in Figures 4 and 5. Please refer to page five of this document for a more detailed description of the table.

Figure – 7
50 kw/m^2 Cone Calorimeter Test Results of the Pultruded, Brominated Panel Described in Figures 4, 5 and 6 Verses Three Vacuum Bagged FR Veil Placards and a Pultruded, ATH Panel Described in Figure 8's ASTM E-84

Sample /Test #	Placard Initial Mass(g)	Mass Correlated Conversion Factor	Correlated Total Smoke Release(g)	Correlated Average Smoke Production (g/m²/s)	Duration of Test (s)	Peak Heat (kW/m²) Release	Time (s) to Ignition
Standard Pultruded Br Veil, Polyester	40.6	1.00	26.13	.071	465	185	46
Sample 1 Vacuum Bag FR mat Wt.: 36.2 g/ft²	80.7	0.50	10.00	.009	1198	91	25 & 430*
Sample 2 Vacuum Bag FR Mat Wt.: 33.0 g/ft²	81.8	0.50	13.09	.012	953	140	29 & 271*
Sample 3 Vacuum Bag FR Mat Wt.: 33.0 g/ft²	81.9	0.50	11.40	.013	859	172	55 & 126*
Sample 4 Pultruded FR Mat Wt.: 33.0 g/ft²	93.6	0.43	7.67	.007	967	160	50 & 181*

Figure – 7 contains the tabulated Cone results of five tested specimens. The Standard on this chart is assigned to the pultruded, brominated panel described in figures 4, 5 and 6. Samples 1, 2 and 3 test placards were fabricated by vacuum bagging with the FR veil glass rich side up as recommended for pultrusion. A fourth sample 4, was cut from the pultruded laminate, containing ATH as the primary fire retardant and described in figure 8, that was ultimately ASTM E-84-01 tested. All FR veil placard specimens denoted above demonstrated an improvement over the brominated Standard placard. This would suggest, or predict, a more favorable result in the ASTM E-84-01 test. Note the weight of the FR veil varies between sample 1 and samples 2, 3, 4. One could draw the assumption that a pultruded panel with a 36gram/ft^2 weight would provide better results than a pultruded panel with a 33gram/ft^2 weight. The ATH panel tested to the ASTM E-84-01 protocol had a 33gram/ft^2 FR veil, glass out in its surface. The FR veil is now "standardized" to a weight of 36grams/ft^2.

Figure – 8

Southwest Research Institute ASTM E-84-01 Investigation of the Surface Burning Characteristics of a Pultruded Glass Fiber/Polyester Resin Laminate with Fire Retardant and Smoke Suppressing Surfacing Veil

[redacted]

SWRI PROJECT NO.: 01.06058.01.145
TEST DATE: APRIL 11, 2003
DAILY TEST NO.: 1

TEST RESULTS (ROUNDED TO NEAREST 5)

FLAME SPREAD INDEX (FSI):	25
SMOKE DEVELOPED INDEX (SDI):	350

TEST DATA

UNROUNDED FSI:	23.3
UNROUNDED SDI:	351.4
FS*TIME AREA (Ft*Min):	45.4
SMOKE AREA (%*Min):	206.2
FUEL AREA (°F*Min):	5109.2

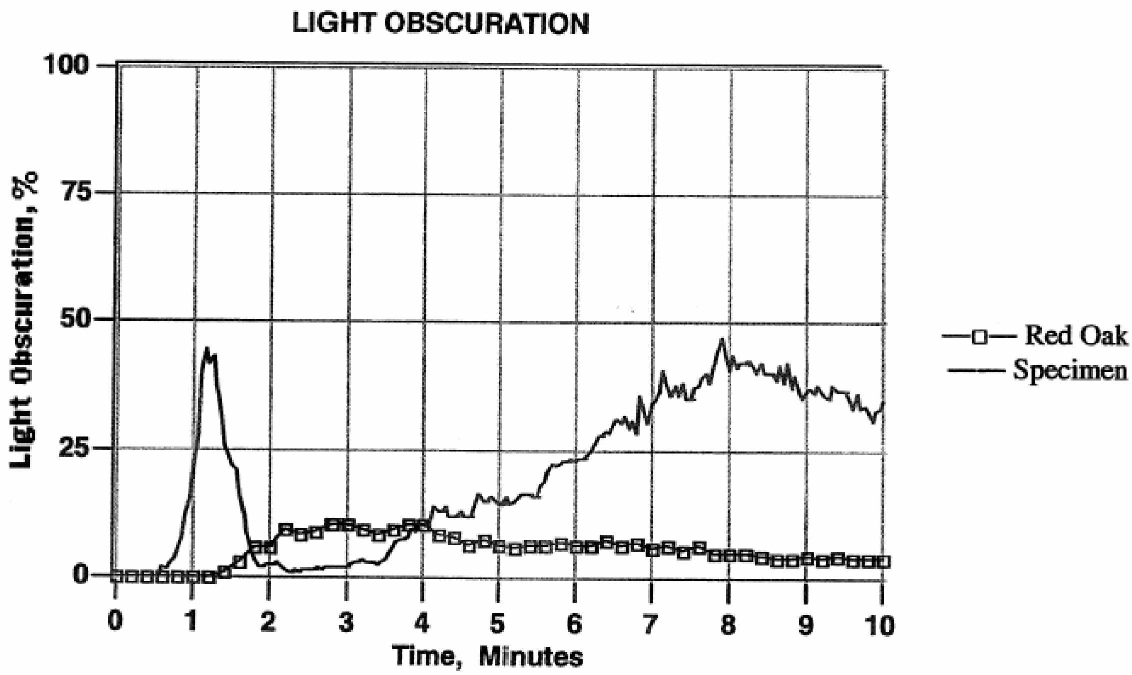
OBSERVATIONS DURING TEST

IGNITION TIME (Min:Sec):	0:38
MAXIMUM FLAME FRONT ADVANCE (Ft.):	6.5
TIME TO MAXIMUM ADVANCE (Min:Sec):	9:51
MAXIMUM TEMP. AT EXPOSED TC (°F):	598
TIME TO MAXIMUM TEMP. (Min:Sec):	9:51
TOTAL FUEL BURNED (Cu. Ft.):	53.0
DRIPPING (Min:Sec):	None
FLAMING ON FLOOR (Min:Sec):	None
AFTERFLAME TOP (Min:Sec):	0:54
AFTERFLAME FLOOR (Min:Sec):	None

Please Note: Please refer to the graphs on the following page. Explanation follows graphs.

ASTM E 84-01 REPORT

[redacted]
SWRI PROJECT NO.: 01.06058.01.145
TEST DATE: APRIL 11, 2003
DAILY TEST NO.: 1



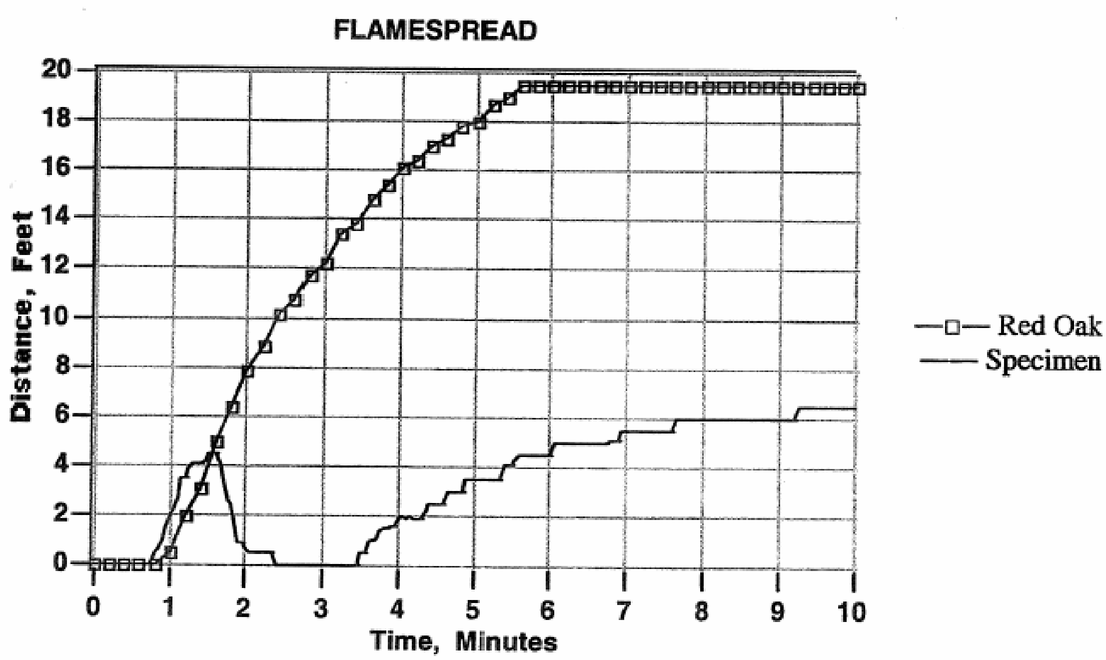


Figure – 8 is a copy of the ASTM E-84-01 test performed by the Southwest Research Institute on an FR veiled, non-brominated, iso-polyester pultruded flat sheet specimen. The fire retardant constituents incorporated into the resin were ATH and a small quantity of phosphate. The cost of the final resin mix was $0.64 / lb. This formula, with specific instructions, is available upon request. Please refer to page 7 of this document for a list of the resin mix formula constituents.

Light Obscuration: Please refer to the Light Obscuration, %, verses Time, Minutes graph on the preceding page. At approximately 30 seconds, obscuration begins to register. However it peaks at approximately 1 minute 10 seconds, at close to 40% light obscuration. In this early phase of the surface burning scenario, several events occur. One is a flash-off of the pyrolysing polyester resin located on outer the surface of the panel specimen and is, for example, consistent with the initial event sequence exhibited by a laminate panel with bromine as the primary fire retardant. Another event is the formation of the swollen char and the reinforcing cementitious structure produced by the FR veil. This structure stays in place during the entire duration of the test. After development, the structure quickly entraps particulate smoke within the cement layer. Obscuration then drops to near 0%. At about 3 minutes the light obscuration begins to slowly rise. The trapped smoke and soot particulate packs tighter and tighter, cutting off oxygen to the under-laminate and reducing the propensity and capability of the panel to combust or generate smoke. (Note: For comparison, when a brominated panel is tested to the ASTM E-84-01 protocol, the smoke obscuration starts at the same time as the flame spread and typically goes to almost 100% light obscuration immediately, staying at that obscuration value until the end of the test.) Over the next 5 minutes, the high temperature and thermal intensity of the open flame, does force particulate smoke from the resin laminate. Combined with the smoke is liquid vapor, generated by the fire retarding constituents. This combination developed an obscuration maximum value of approximately 45% around 7 minutes 50 seconds. However, at just before the 8 minute mark, the smoke suppressing charred surface structure had packed so tight with smoke particulate, it eclipsed the ability of the laminate to generate increasing quantities of smoke. From this 45% obscuration value, the percent light obscuration dropped continuously to a low 30's value at the conclusion of the test. (Note: The final results of the test were inadvertently skewed by the sample specimen supplied for the test. The test specimen was a combination of four panels 12 feet x 2 feet. During the test procedure, flame penetrated the center seam of the specimen, combusting the back of the panel which did not have the FR surfacing veil. Smoke was observed entering the chamber through the seam, originating from the unprotected back surface. Despite the panel seams presenting a sizable penalty, the project was successful.) After calculation of the Smoke Developed Index, the Unrounded SDI was 351.5, with a rounded SDI value of 350. Please refer to page 7 of this paper for additional and supplemental information.

Flamespread: Please refer to the Flamespread, Distance, Feet verses Time, Minutes graph on the preceding page. At approximately 48 seconds flame spread began to form. The flame spread moved to about 4 feet 6 inches at approximately 1 minute 40 seconds, then receded to zero. This flame spread event closely mimicked the early light obscuration scenario noted above. At the 3 minute 30 second time, the flame spread slowly crept down the panel for the remainder of the test to approximately 6 feet 6 inches. The test specimen was tested in a combination of four panels, 12 feet x 2 feet. During the testing procedure, it was observed the E-84 apparatus flame penetrated through the center seam and contributed to an increased flame spread area as air leaked into the tunnel chamber. At the conclusion of the test, it was verified by observation that a significant area on the backsides of the panels showed surface combustion had occurred. After calculation, of the Flame Spread Index, the Unrounded FSI was 23.4, with a rounded FSI value of 25. Please refer to page 7 of this document for additional information.

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