

# COMPOSITE FLAME RETARDANT AND SMOKE SUPPRESSING SURFACING MAT

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## ABSTRACT

An important focus of polymer composite development and application technology is the reduction of surface flammability, smoke generation and toxicity of laminated specimens when exposed to open flame or high radiant heat. In addition to addressing these issues of fire, smoke, and toxicity (FST), it is desirable to enable fabricators to achieve lighter parts with higher physical properties. Surfacing mats or veils have traditionally been specified to provide a pleasing esthetic appearance, as well as, enhance and maximize the corrosion resistance and / or life cycle of a composite part. In these cases, the veiled surface is enriched with a disproportionate quantity of combustible resin compared to the inter-laminate resin to reinforcement ratio. Under a fire load, the use of surfacing veils has historically ensured an increase in surface flammability and early smoke generation of a finished part. The development and availability of a new surfacing mat, now overcomes the noted disadvantages of prior surfacing fabrics when a laminate is exposed to a fire insult scenario. By incorporating this FST reducing fabric *within* a laminate, a fabricator is assured that the outermost surfaces of any part are fire hardened with a reduction in smoke without a toxicity contribution. This is due to the innovative, intumescent and ceramic additive technologies applied to one surface, and partially contained within the profile of a non-woven glass fabric. The composition has a glass rich side to provide traditional processing and options without any changes in technique, mechanicals or chemistries. This mat has been designed with high physical characteristics for use in a variety of mechanized processing techniques such as pultrusion and filament winding. In summary, by employing this FST reducing surfacing mat, a non-toxic, smoke suppressing fire retardant barrier is oriented and positioned where it is needed first and foremost, at the initial point of contact with an open flame or high radiant heat – at the surface.

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## **1. INTRODUCTION**

Resins are petroleum by-products that typically have very harmful burning characteristics, i.e., high flammability at relatively low temperatures, very toxic and acrid smoke, and rapid destructive flame spread. It is well known that the flammability of thermoset resins can be reduced by incorporating flame retardant agents at the raw material manufacturing phase of a resin, or, blended as an additive with the polymer prior to use. However, when bromine based compounds are cooked into a resin, or additives are blended with non-fire retardant resins for improved fire retarding characteristics, a multitude of problems arise.

Thermoset resins are frequently used in the manufacturing of reinforced plastics, fiberglass laminates, and cast plastics requiring high physical strength characteristics. Composite polymer materials are widely used in industrial applications as structural components (i.e.: I-beams, box beams, C-channel, etc.); siding and roofing panels; walkway and handrail systems; roof decking; cable trays, and mechanical parts such as threaded rod and strut. Additionally they are widely used by manufacturers in the automobile, rail and aircraft transportation industries because of their lightweight, high strength characteristics for improvements in economies of range and maneuverability.

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. Many reinforced plastics can be designed to have a degree of fire resistance as there are many fire retardant compound compositions available. Unfortunately, a large number of the more effective commercially available fire retardant resins and additive compounds are bromine based. These compounds produce and liberate extremely toxic fumes under a fire load, such as hydrobromic acid that can cause pulmonary edema. Less toxic additives, such as aluminum trihydroxide (ATH) and magnesium hydroxide are inefficient and require very high loading levels. The necessary additive to resin ratios are so high that the desirable physical properties of the resin and characteristics of an engineered composite product are degraded and can be dramatically diminished. This typically necessitates thicker and heavier profiles to simply equal the physical values of an unfilled part.

All conventional polymeric additives 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 high cross-link density within the finished product; to 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 in 100 parts of total mix, 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 type 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. When the part has been processed and cured, the part contains added, unwanted organic matter that dramatically contributes to smoke generation in a fire scenario. Additionally, the heavily filled part will exhibit undesirable physical characteristics such as reduced tensile, flexural and shear strength. Again, the only way to make up for the reduced physical strength characteristics is to produce a thicker, heavier, more expensive part. Although the excessively high ATH fire retardant loading does reduce the likelihood of the part to combust, ATH reduces combustion by liberating bound water and vitrifying, which is relatively ineffective. Hence, the high loading requirements. As the thermal decomposition of the laminate continues, the additional styrene makes a major contribution as a combustible fuel source, and provides the composite surface with a greater affinity towards flammability. In addition, styrene is an egregious smoke generating compound, which significantly adds to overall smoke production of the part. Therefore, with ATH, there are processing problems, which yield weaker parts, and which have the characteristic of generating larger quantities of toxic particulate smoke.

To reduce the fire retardant loading in a thermoset resin, an alternative to ATH is a combination of decabromodiphenyl ether with antimony, e.g., less than 20 parts per 100 parts of total 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 chemical combustion mechanism proceeds along much different reaction lines and sequences than ATH. The brominated constituent package operates by competing with oxygen in the ionization phase of the combustion reaction. The fire retarding mechanism in a cured resin produces large quantities of soot with accompanying dense, acrid smoke. The formation of these compounds further reduces the availability of oxygen at the laminate surface.

Although, effective as a flame retardant, the smoke generated by pyrolysing brominated compounds renders the environment biologically toxic. For example, a byproduct of the decomposition of decabromophenyl ether is hydrobromic acid. In significant concentration, this vapor phase acid causes pulmonary edema when inhaled. The symptoms exhibit similar biophysiological affects as military trench warfare gases used in the First World War. In addition, many other brominated byproduct compounds are produced, which have significant toxicity, with the possible production of suspect carcinogens.

Therefore, for reasons stated above, the finished surfacing mat described herein, does not include *any* of the following ingredients or classes of compounds: *No* metal compounds of any kind. An

example would be compounds containing such elements as aluminum (Al) or magnesium (Mg). There are *no* heavy metal compounds present in the composition such as those containing Zinc (Zn). No brominated compounds, including decabromodiphenyl ether (Deca-BDE), octabromodiphenyl ether (Octa-BDE), pentabromophenyl ether (Penta-BDE), hexabromocyclododecane (HBCD), decabromobiphenyl ether, polybrominated biphenyls (PBB), tetrabromophthalic anhydride, nor any and all related aliphatic or aromatic brominated substances. No metallic antimony compositions, such as antimony trioxide (Sb<sub>2</sub>O<sub>3</sub>) are constituents as antimony and its compounds have been identified as suspect cancer-causing agents which carry an MSDS Health Rating: 3 – Severe (Poison).

The selection of a suitable smoke suppressant for curable resins is not always predictable. Selection is particularly difficult when flame-retardants are employed, exacerbated by the complex interaction between the resin and the flame retardant agent. Although efficient in suppressing the rate of combustion of finished resin reinforced products, most flame-retardants tend to affect adversely one or more key properties of the resin. For example, many flame retardant additives are ineffective at producing very low density, and low smoke product formulations. It is well known that the flame retardant and smoke suppressive properties of additives in resin formulations varies greatly with the nature of the substrate. Other considerations can also come into play, even where the properties of the fire retardant and smoke suppressive properties of the composition are optimal. These considerations include the effect of the additive on the physical properties, color, molding, and / or other processing characteristics of the base resin. The development of additives for use with resins remains a highly empirical art. Due to this complexity, some companies specializing in functional fire retardant chemistries have largely concentrated on developing highly specific additive combinations for particular resins and end-uses. This development approach is a particular problem when the fire retardant additive powder needs to be combined with strengthening reinforcements such as glass rovings, yarns, cloths, mattes, and knitted fabrics.

An extensive analysis was commissioned and completed for composite fire retardant product options as they relate to fabrication processes; industrial production requirements; legitimate fire engineering practices; local and federal government agencies; environmental and life safety issues and concerns. The conclusion of this study clearly indicated, rather than a single chemical solution, a “systems approach” is desirable and developing, both here in the U.S. and abroad. This “systems approach” is the integration of traditional engineering and design, and, the use of multiple technology options to attain composite components and structures that will meet prescriptive fire, smoke and toxicity test and code requirements. Two examples are: a.) The blending of a low styrene content polyester resin with a lower loading of ATH with a brominated fire retarding compound and adjusting the viscosity with methyl-methacrylate, then covering the finished part with a fire retardant coating, or, b.) Blending a resin with an intermediate level of ATH to attain better physical characteristics, then applying a thick layer of intumescent coating to the part. Coating composites necessitates a secondary production operation. Other systems might include the choice of acrylic polyester or phenolic resins. For reduced surface flammability, no traditional surfacing veil should be used, especially a polyester veil as polyesters are a fuel source and egregious smoke developers.

## 2. MATERIAL SELECTION

In a fire insult scenario, it is the exterior of a laminate part that is exposed to an open flame or high radiant heat source. No surfacing fire barrier reinforcement, which could be easily fabricated *into* the surface of a laminate with no processing or formulation changes had been available as a design option. Therefore, a product was developed to provide a non-toxic, fire retardant, smoke suppressing intumescent glass surfacing reinforcement fabric, to provide to the engineer another material, or system option, 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 (20mil). Additional profile thicknesses can be available as reinforcements are dependent on the particular engineering application and end use. In generic iso-polyester resin, styrene content thirty five percent or less, and glass reinforcement applications, a single ply surfacing veil is generally recommended as part of the fire retarding system. A multi-layer stacked fabric schedule is also an option, however this is beyond the scope of this presentation. The fabric can be positioned at the ends or within a partial section of a part during fabrication for enhanced localized fire and smoke protection. Alternatively, due to its high tensile strength for a non-woven, the fabric can be used as a primary reinforcement material as a skin on a cored sandwich panel or in cellular foam constructions. Due to its versatility, the fabric may be employed in a variety of fabrication processes such as pultrusion, filament winding, compression molding, resin transfer molding, vacuum assisted resin transfer molding, press molding, reaction injection molding, impression molding, B staged prepregs, thermoplastic reinforced films and other secondary processes. When incorporated into a thermoplastic under heat and pressure, the cloth can be thermoformed, vacuum formed, or re-formed at processing temperatures over 285 degrees Centigrade.

The integrated powder composition contains over a dozen constituents and is thermally active. By being active, the composition has a latent ability to intumesce or foam when a specific temperature is reached. In the present embodiment, that temperature of flame or heat retardation is 350 degrees Centigrade. At this temperature, and above, the cured or hardened resin/composite structure 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 containing the fire retarding mat.

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

When incorporated into a fabric 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 temperatures 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 (i.e.: steam), the carbonaceous surface swells and bubbles, forming a swollen insulative and infrared protective heat shield.

Fourth, the inorganic binder constituents react in the presence of the generated water vapor. These compounds immediately proceed through a deposition reaction and form a cementitious structure as the surface swells. This structure, fills with soot from the polymer decomposition, protects 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 radiation (IR) and is not easily dislodged by high velocity flame fronts or fire hose pressures. Furthermore, it 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 and emissivity.

Although beyond the scope of this treatise, the fabric potentially could be comprised of specialized high temperature glass, carbon, arimid, ceramic, rock fiber or other commercially available fabric material. The cloth can be woven, non-woven, mat, felt, needled, or a sandwich structure of any of these cloth constructions, or, a composite design combination of these various materials.

### **3. EXPERIMENTAL**

There are many standard testing methods and protocols established by code governing authorities, which are used to determine fire hazards and surface burning characteristics of building materials. The ASTM E-84 tunnel test is a prescriptive test protocol, 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. To identify the fire retarding and smoke suppressing merits of the fire retardant mat, two identical polyester resin flat sheet panels were pulled on the

same machine by a major pultruder. Both panel laminates were produced with the identical styrenated polyester resin, decabromodiphenyl ether and antimony trioxide fire retardant package, and standard commodity glass reinforcements. The only difference between the two specimens was one panel had a popular polyester veil, the other contained the fire retarding and smoke suppressing glass surfacing mat. The resin to bromine / antimony ratios were designed and documented to achieve a flame spread of twenty five only with the polyester veil. Due to the flammable nature of the resin, its high smoke generation properties and the high loading of the bromine package, no consideration was given in the mix receipt to address the smoke index result. The pultruded specimens were thirty six inch wide by one quarter inch thick commercially available flat sheet with a fifty two percent glass content. All other constituents and construction were identical. The comparative results for the ASTM E-84 test protocol, were obtained at Southwest Research Institute, San Antonio, TX, are listed in Table A.

**Table A**

<b>Property</b>	<b>FR Glass Mat</b>	<b>Polyester Veil</b>
Flame Spread Ratio	19.2	25.0
Smoke Obscuration Index	751	985

As seen from the Table, the flame spread ratio and smoke obscuration results for the new material are about  $\frac{3}{4}$  of that of typical prior art result. This is a significant reduction. The glass mat, compressed to several thousands inch, enabled the commodity flat sheet composition to get to nearly fifty percent reduction to the Class A Smoke Index of less than four hundred fifty.

Smoke obscuration measurement by the ASTM E-84 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 such combustion byproduct species as particulate matter such as 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 obscuring of the white light source of the E-84 test apparatus. As particulate smoke matter generated by pyrolyzing polymers is biologically toxic, as opposed to water vapor, fire engineers can measure the total quantity of toxic particulate constituents by an ASTM E-1354 Cone Calorimeter instrumental analysis. This apparatus uses red laser spectrophotometry to measure the actual specific mass of particulate smoke generated during the combustion of a sample specimen in comparison to the total mass loss of the test specimen. It does not register or measure water vapor. Thus the actual toxic smoke can be measured without interference of a water vapor constituent.

A comparative test procedure was designed to measure the difference in actual particulate smoke generation of a brominated panel verses a panel that incorporated a non-toxic fire retardant.

To determine the difference, a section of the actual brominated panel described in Table A was machined into a specified Cone placard size and dimension. A second flat panel, pultruded by the same manufacturer, on the same machine, with the same glass laminate schedule as described in Table A, was fabricated employing the fire retarding and smoke suppressing powder composition incorporated into the surfacing glass mat as the resin fire retardant package. The second panel was machined to a Cone placard matching the mass of the brominated placard. The two specimens were tested at Worcester Polytechnic Institute, Worcester, MA.

**Table B**

<b>Property</b>	<b>FR Mat &amp; Laminate</b>	<b>Typical Brominated Laminate</b>
Initial Mass	40.6 g	40.6 g
Final Mass	23.6 g	26.2 g
<b>Smoke Obscuration:</b>		
Ave. Smoke Yield (g/g)	.057	.106
Total Smoke Release (g)	13.979	26.130

As seen from Table B, 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.

#### **4. CONCLUSION**

Noteworthy and distinct improvements in both flame spread and smoke generation of a pultruded laminate are now possible with a delightfully simple substitution. Merely replacing a traditional surfacing veil with a new and innovative FST reducing glass surfacing mat. This will markedly reduce the capability of a laminate to combust or generate toxic smoke when exposed to an open flame or high radiant heat. No other changes are required.