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Fire Resistant Closed Cell Foams for Aircraft Shelters Technical Review

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PREFACE

This report was prepared by the Georgia Tech Research Institute, Electro Optics Environment and Materials Laboratory, at the Georgia Institute of Technology, Atlanta, GA, for the Fire Fighting Research Section of Air Force Research Laboratory (AFRL/MLQD), Tyndall Air Force Base, Florida, and RBX Corporation, Roanoke, VA, under Air Force Contract F08637-03-C-4009, GTRI/EOEML 97838. This document is a review of the literature as it pertains to intumescence of materials as they apply to closed cells foams and similar polymer based materials.

The Start Date for the overall program was 1 October 2003, and the End Date is June 30 2004. The AFRL/MLQD Project Officer is Mr. Paul Carpenter, the RBX Project Officer is Mr. Lynn Bakker, and the GTRI Principal Investigator is Dr. Juan Vitali.

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EXECUTIVE SUMMARY

The objective of this program is to develop a fire proof shelter material that is lightweight and meets or exceeds current USAF aircraft shelter specifications. The program is focusing on the development of innovative materials that provide passive and active fire protection. The passive material resistance is proposed to be accomplished by a novel approach that includes the phenomenon of intumescence, and the active protection, is propose to be achieved by the inclusion of non-volatile precursors of fire suppressing gases that activate upon exposure to high heat fluxes. These materials are to be incorporated into shelter covers without any loss of mechanical strength or shelf life.

This report outlines the current state of the art in intumescent chemistries and reviews the current literature on the subject. Over 70% of the current use of intumescent materials is based on its application to plastics. However, the intumescent set of chemicals has been shown to be used in elastomers-based materials as well although it is not very frequent. The common composition of an intumescent matrix includes acid catalysts, a carbonizing agent, and a blowing agent. The most commonly used acid catalysts include ammonium polyphosphate, the most common carbonizing agent includes pentaerythritol, and the most common blowing agent used is melamine. The metric of performance of the use of these compounds is based on a first order estimate of the ability for the final material to insulate against a directly impinging flame. Other characterization techniques include the use of thermo gravimetric analyses to determine the rate of decomposition of the materials.

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LIST OF ABBREVIATIONS

AFRL	Air Force Research Laboratory
ASTM	American Society for Testing and Materials
APP	Ammonium Polyphosphate
BP	Burning Percentage
EVA	Ethyl Vinyl Acetate
FR	Fire Resisting or Resistant
HRR	Heat Release Rate
LOI	Limiting Oxygen Index
PE	Polyethylene
PP	Polypropylene
PU	Polyurethane
SI	Smoke Index
TGA	Thermogravimetric Analysis
TTI	Time to Ignition
USAF	U.S. Air Force

LIST OF UNITS

h	hour
kg	kilogram
mg	milligram
m	meter
min	minute
ppm	parts per million

A. SECTION I

TECHNICAL REVIEW

A. Background

Fire is a major cause of casualties in the US military during peacetime. Fire resistant materials are part of the military's strategy to increase readiness while better protecting our war fighters and our material assets. The development of lightweight shelters is critical to the Air Expeditionary Forces (AEF) mission of providing prompt logistics support for forward base operations. Deployable airbase systems are to be developed to reduce airlift, setup times, manpower requirements, and sustaining costs. Structures should also have characteristics that enable these shelters to be flexible, and in the case of containing ignitable fuels and other assets such as aircraft, these structures are required to be fire resistant. A key property in providing resistance to fires is the ability of a structure to withstand heat fluxes for a relative long period of time. In addition to these properties, a surface structure that is capable of generating effective fire suppressing gases that would enable the extinguishment of fires in a shelter structure would be a useful and life saving feature.

Although the concept of intumescence is not new, the use of intumescent matrices in closed cell foams is. The objective of this program is to develop intumescent closed cell foams that are fire proof and at the same time is capable of emitting fire suppressing gases to suppress or extinguish fires. Following is a review of the state of the art in intumescence and preliminary recommendations on the components for an intumescent matrix.

B. Literature Review

Intumescence, from the Latin *intumescere* meaning to swell, has been employed in polymeric systems as an effective halogen-free method of fire retardance. Upon heating, the polymeric material develops a foamed char at the surface that serves as a barrier to heat and mass transfer between the gas and condensed phases. A tremendous variety of polymeric materials have been modified for intumescence. Three general components are needed: (1) char-forming or carbonizing agent, (2) catalyst, typically an acid to decompose the carbonizing agent, and (3) a blowing or foaming agent. The catalyst has often been referred to as a dehydrating agent because many of the carbonizing agents have been polyols that are dehydrated by the acid. In some cases, one or more of these components may already be present in the material, so that imparting intumescence may not always require the addition of all three as separate components in the formulation. For example, polyurethanes and polyamides, which are typical commodity polymers, can act as carbonizing agents.* Thus, only a catalyst and blowing agent would need to be added to materials containing a sufficient fraction of one of these two polymers. When the catalyst and blowing agent are the same material, as is the case with ammonium polyphosphate (APP), then simply incorporating this additive into the formulation may lead to an intumescent material.

For effective intumescence, it is important that the following occur nearly simultaneously, but in this sequence: (1) liquefaction of a char-forming agent, (2) generation of gases for foam formation, and (3) crosslinking for char formation. If formation of the liquid char-forming agent needs activation by

* Le Bras, M.; Bourbigot, S. **Use of carbonizing polymers as additives in intumescent polymer blends.** ACS Symposium Series (2001), 797(Fire and Polymers), 136-149.

the release of an acid catalyst, then this must occur slightly before step (1). Mechanical properties of the liquefied tar and resulting char are important to consider. The tar should be viscous enough that the generated gases do not simply bubble through, but expand under the force of the escaping gases. Crosslinking of the tar should occur simultaneously so that the char is formed at the point of maximum expansion. The char shield should remain intact and its integrity not compromised so that it can protect the underlying substrate. Thus, the char should not crack under strain at the temperatures experienced during combustion. The char should remain viscoelastic and tough during formation.

Thus, component selection and relative fraction in the formulation must be optimized for a given polymeric material. Much of the successful intumescent formulations have been developed empirically, although recent mathematical models hold promise as a more efficient methodology.*

Established intumescent are based on ammonium polyphosphate, melamine phosphates, and pentaerythritol derivatives. All of these materials are hydrophilic, which could be problematic for applications that require water resistance. Non-hydrophilic alternatives include polyol phosphoryl chlorides† and expandable graphite.

Expandable graphite, also called vermicular graphite, is an intumescent material prepared from graphite and sulfuric acid. The sulfuric acid is intercalated between the graphite layers at high pressure. When exposed to temperatures between 160 and 220 °C, the sulfuric acid vaporizes

* Di Blasi, Colomba; Branca, Carmen. **Mathematical model for the nonsteady decomposition of intumescent coatings.** *AIChE Journal* (2001), 47(10), 2359-2370.

† Zhang, Sheng; Horrocks, A. Richard. **Substantive intumescence from phosphorylated 1,3-propanediol derivatives substituted on to cellulose.** *Journal of Applied Polymer Science* (2003), 90(12), 3165-3172.

and causes separation of the graphitic sheets. The result is a bulk volumetric expansion. It serves as both blowing agent and carbonization compound. Polyolefins* and polurethane foams have been made intumescent with expandable graphite. It can be used alone or in conjunction with other compounds.

Intumescent materials are much safer than earlier flame retardant systems that used halogenated materials to reduce gas-phase combustion. The halogen-based flame-retardant systems release toxic smoke and corrosive gases into the air upon combustion. The combustion products of the intumescent systems are no more harmful or toxic than the combustion products of the bulk material. In fact, due to the physical barrier created by the carbonaceous mass, the volume of combustion products is much less than from the combustion of the bulk material alone. Another disadvantage of the halogen-based systems is that these materials are only effective for as long as the halogenated additive is present. Following intumescence, a char shield effectively protects the substrate.

B.1. Catalysts (Acid Source)

These compounds release an acid during thermal decomposition that catalyzes the decomposition of the carbonizing agent. These acid catalysts help promote the formation of carbonaceous char.

Table 1. Acid Catalysts.

Compound	Empirical Formula	Decomposition Temp (°C)
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* Xie, Rongcai; Qu, Baojun. **Expandable graphite systems for halogen-free flame-retarding of polyolefins. II. Structures of intumescent char and flame-retardant mechanism.** Journal of Applied Polymer Science (2001), 80(8), 1190-1197.

Monoammonium phosphate	$\text{NH}_4\text{H}_2\text{PO}_4$	147
Diammonium phosphate	$(\text{NH}_4)_2\text{HPO}_4$	87-147
Ammonium polyphosphate	$(\text{NH}_4\text{PO}_3)_n$	215
Melamine phosphate	$\text{C}_3\text{H}_6\text{N}_6 \cdot \text{H}_3\text{PO}_4$	~300
Urea phosphate	$\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$	130
Diammonium sulfate	$(\text{NH}_4)_2\text{SO}_4$	400

Ammonium polyphosphate (APP) is a commonly used intumescent additive, often in combination with pentaerythritol. The APP acts as both acid catalyst and blowing agent for the carbonizing pentaerythritol. The following have been used as synergistic agents in APP/PER intumescent mixtures: various metallic compounds,* zeolites, clays, fluid catalytic cracking catalyst waste (zeolites and clays),† and boroxo silicone.

Ammonium polyphosphate has been used with pentaerythritol and melamine as an intumescent additive. One noted problem is that this trimixture is hydrophilic and therefore can phase separate from hydrophobic polymers like polypropylene. Methods of compatibilization have proved successful,‡ but it is unclear whether truly necessary for materials that are melt-processed.

* Lewin, Menachem; Endo, Makoto. **Catalysis of intumescent flame retardancy of polypropylene by metallic compounds.** *Polymers for Advanced Technologies* (2003), 14(1), 3-11.

† Esteveao, Luciana R. M.; Nascimento, Regina S. V. **The use of heating microscopy in the study of intumescence in waste catalyst containing polymer systems.** *Polymer Degradation and Stability* (2002), 75(3), 517-533.

‡ Ma, Zhi-Ling; Gao, Jun-Gang; Niu, Hai-Jun; Ding, Hai-Tao; Zhang, Jie. **Polypropylene-intumescent flame-retardant composites based on maleated polypropylene as a coupling agent.** *Journal of Applied Polymer Science* (2002), 85(2), 257-262.

A potential new intumescent additive is calcium gluconate monohydrate. This material expands by loss of water of hydration as well as dehydration of hydroxyl groups, primarily between 120 and 250 °C. As opposed to all of the other intumescent additives, this one is base-catalyzed.*

B.2 Carbonizing Agents

First-generation carbonizing agents are compounds with high carbon and hydroxyl contents, or at least high hydroxyl content upon thermal degradation so that esterification with acids can occur. These materials are referred to as polyols in the literature. Examples include pentaerythritol, starch, and their derivatives; they react with the acids liberated from the acid precursor catalysts. Upon reaction with acids, the resulting esters thermally degrade at higher temperatures to yield water and carbon dioxide for foaming to yield a carbonaceous char.†

* Labuschagne, F. J. W. J.; Focke, W. W. **Metal catalyzed intumescence: characterization of the thermal decomposition of calcium gluconate monohydrate.** *Journal of Materials Science* (2003), 38(6), 1249-1254.

† M. Wladyka-Przybylak and R. Kozłowski, *Fire and Materials*, **23**, 33 (1999).

Table 2. Carbonizing Agents

Compound	Empirical Formula	Carbon Content (wt%)
Erythritol	$C_4H_6(OH)_4$	39
Pentaerythritol	$C_5H_8(OH)_4$	44
Pentaerythritol dimer	$C_{10}H_{16}(OH)_6$	50
Pentaerythritol trimer	$C_{15}H_{24}(OH)_8$	53
Dextrin	$(C_6H_{10}O_5)_n$	44

These polyols often suffer from low compatibility with the host polymeric matrix which can lead to diffusion out of the product, referred to as blooming of the additive. One possible solution is replacement of the polyols with true polymeric carbonizing agents like polyamides or polyurethanes. Polyamides and polyurethanes can be used as the carbonizing agents because of an acid-catalyzed depolycondensation reaction that takes place at elevated temperatures. Upon decomposition a carbonaceous mass is produced. Generally, ammonium polyphosphate (APP) is used as the catalyst in these systems.

B.3 Blowing Agents

These compounds release copious amounts of non-flammable gases (NH_3 , CO_2 , H_2O) during thermal decomposition, thus expanding the carbonaceous layer and forming a “foam” structure. In order to form an intumescent layer, the decomposition temperature of the blowing agent should be near or greater than the decomposition temperature of the catalyst.¹⁻³

Table 3. Blowing Agents.

Compound	Empirical Formula	Decomposition Temp (°C)
Urea	CH ₄ N ₂ O	130
Guanidine	CH ₅ N ₃	190
Dicyandiamide	C ₂ H ₄ N ₄	210
Glycine	C ₂ H ₅ NO ₂	233
Melamine	C ₃ H ₆ N ₆	250

Melamine and melamine derivatives can be used as solitary flame retardants in polyurethane foams. These compounds can act as both catalysts and blowing agents.

C. Typical Examples of Intumescent Polymeric Materials

Polypropylene: APP/pentaerythritol/boroxo silicone

These components have been combined with boroxo silicone in a polypropylene matrix to increase the melt viscosity and char viscoelasticity. This results in better fire retardancy due to decreased dripping.*

Polypropylene: APP/polyamide (nylon 6)/ethyl vinyl acetate copolymer (EVA)

* P. Anna, G. Marosi, S. Bourbigot, M. Le Bras and R. Delobel, *Polymer Degradation and Stability*, 77, 243 (2002).

Ethyl vinyl acetate is a surfactant here to compatibilize APP and the polyamide.*

Polyurethane: APP†

Char formation is favored by chemical reaction of polyurethane with APP. Phosphorus is incorporated in the char as crosslinks between PU chain fragments.

Polyurethane: expandable graphite‡

There is no chemical reaction between the polyurethane and the expandable graphite. Less char is formed as compared to polyurethane:APP. The char consists of separate expanded graphite and degraded polyurethane.

Polypropylene: melamine phosphate- pentaerythritol §

Reactive extrusion of polypropylene with melamine phosphate and pentaerythritol yields a compatible intumescent material. By reacting melamine phosphate with pentaerythritol, an intumescent additive is prepared with all three components for intumescence in a single compound.

* Almeras, X.; Le Bras, M.; Poutch, F.; Bourbigot, S.; Marosi, G.; Anna, P. **Effect of fillers on fire retardancy of intumescent polypropylene blends.** *Macromolecular Symposia* (2003), 198(7th European Symposium on Polymer Blends, 2002), 435-447.

† S. Duquesne et al., *Journal of Applied Polymer Science*, **82**, 3262 (2001).

‡ Duquesne, Sophie; Le Bras, Michel; Bourbigot, Serge; Delobel, Rene; Camino, Giovanni; Eling, Berend; Lindsay, Chris; Roels, Toon. **Thermal degradation of polyurethane and polyurethane/expandable graphite coatings.** *Polymer Degradation and Stability* (2001), 74(3), 493-499.

§ Chen, Yinghong; Liu, Yuan; Wang, Qi; Yin, Huan; Aelmans, Nico; Kierkels, Rene. **Performance of intumescent flame retardant master batch synthesized through twin-screw reactively**

D. Typical Loading Levels

The following system was incorporated into a polypropylene (PP) matrix which resulted in formation of a successful intumescent layer and little change to mechanical properties:*

Based on wt of PP: 23 wt% ammonium polyphosphate (n=700)
 14 wt% pentaerythritol
 13 wt% melamine

A successful flame-retardant layer was formed by adding 40 wt% APP to a soft polyurethane (PU) foam. An intumescent foam-char structure is not formed; however, the material becomes non-dripping and self-extinguishing.†

Two other formulations that have been used on soft PU foams include the following:‡

- 30 wt% total additives with 3:1:1 molar ratio of APP:pentaerythritol:melamine
- 30 wt% total additives with 1-2:1 molar ratio of melamine phosphate:dipentaerythritol

Formulations for soft PU foam which include expandable graphite:

- 15 wt% melamine and 5-10% expandable graphite*

extruding technology: effect of component ratio. *Polymer Degradation and Stability* (2003), 81(2), 215-224.

* S. Chiu and W. Wang, *Journal of Applied Polymer Science*, **67**, 989 (1998).

† S. Duquesne et al., *Journal of Applied Polymer Science*, **82**, 3262 (2001).

‡ B. Kandola, A. Horrocks and S. Horrocks, *Fire and Materials*, **25**, 153 (2001).

- 15-25 wt% expandable graphite and 3 wt% triethylphosphate (decreases CO/CO₂ ratio)[†]

E. Characterization

Thermogravimetric analysis provides mass versus temperature at a constant heating rate. From these data, the degradation onset temperature and profile may be determined, along with the char yield. The degradation onset temperature can be defined as the temperature of 2% weight loss. The degradation profile reveals information on the degradation mechanism.

Heat release capacity[‡] can be measured with a pyrolysis-combustion flow calorimeter. This device is used to separate fuel generation from combustion, as they occur at the surface and in the flame, respectively, in a fire. Samples are heated in an inert gas stream at a fixed heating rate. The evolved fuel gases are swept away and mixed with excess oxygen and completely oxidized at 900 °C. The combustion products are removed from the gas stream and the oxygen concentration and mass flow rate measured. The oxygen consumed is then used to calculate the heat release rate from the sample.[§]

Smoke generation, heat release rate, and total heat release in forced flaming combustion are measured using a cone calorimeter. A standard method is employed and the calculations based on

* H. Horacek and S. Pieh, *Polymer International*, **49**, 1106 (2000).

† M. Modesti, A. Lorenzetti, F. Simioni and G. Camino, *Polymer Degradation and Stability*, **77**, 195 (2002).

‡ Lyon RE. Heat release kinetics. *Fire and Materials* **2000**; *24*(4): 179-186.

§ Hugget C. Estimate of rate of heat release by means of oxygen consumption measurements. *Fire and Materials* **1980**; *4*(2): 61-65.

the oxygen consumption principle.* Most measurements in the literature use a cone calorimeter and follow ISO 5660 and ASTM-E-1354/6 guidelines for the measurement of TTI (time to ignition), BP (burning percentage), and HRR (heat release rate). The TTI of a FR material should be higher than that of a non-FR material. BP and HRR should be minimized when compounded with FR materials.

Another important measurement is the LOI (limiting oxygen index) which measures the necessary amount of oxygen present for combustion. The LOI test follows ASTM-D-2863. When performing the cone calorimeter tests, the general heat flux levels for testing are 25, 35, and 50 kW/m².

Evolved gases can be monitored by infrared or mass spectrometry of the effluent stream from the cone calorimeter or thermogravimetric analyzer.

The thickness of the intumescent layer of these materials when exposed to elevated temperatures has been reported to increase anywhere from 50 to upwards of 500%. This can be monitored with optical microscopy using a heated stage.

* ASTM 1354-90, *Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter*. American Society for Testing of

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