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# EXPANDABLE GRAPHITE AS A FIRE RETARDANT IN UNSATURATED POLYESTER RESINS

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## ABSTRACT

Expandable graphite flake has been demonstrated to be an effective intumescent flame retardant additive for an unsaturated polyester resin. Results show that the expandable graphite flake could decrease the flammability of the crosslinked polyester resin when added at a level of 10 pph. The expandable graphite was particularly effective when used in conjunction with ammonium polyphosphate as a synergist.

## INTRODUCTION

Chemical intumescent systems have been used as flame retardants for over 50 years. Typically based on phosphates, melamine, and pentaerythritol, these intumescent systems rely on heat induced decomposition to generate a char layer that insulates the substrate from the heat source. As such, they are most useful as coatings for flammable materials. When added into many materials, however, the expansive force of chemical intumescent systems is often insufficient to generate an effective char layer. For example, thermoset phenolic or unsaturated polyester resins cannot be protected by the incorporation of chemical intumescent systems.

Expandable graphite flake is now being used in a growing number of applications as an intumescent fire retardant additive, as an expansive agent, and as a smoke suppressant. Ford et al. used expandable graphite in oriented strandboard panels to reduce the flame spread<sup>1</sup>. Hutchings et al. developed an especially effective intumescent coating containing expandable graphite that reduced the flame spread and smoke of highly combustible fibreboard panels.<sup>2</sup> Most intumescent putties, caulks and firestop systems now rely on expandable graphite to provide the expansive force necessary to close off gaps and holes during the course of a fire. Expandable graphite is also used in various polyurethane foams<sup>3</sup> to pass the rigorous tests required of aircraft seating and construction insulation.

The fire retardant properties of a number of thermoplastic polymers with expandable graphite and synergists was published by Okisaki.<sup>4</sup> To this point, however, there has been no published work on the fire retardancy of compositions based on crosslinked polymers (e.g. unsaturated polyester resins) and expandable graphite. This work was carried out to determine if the high intumescent force of expandable graphite could improve the flame retardant characteristics of unsaturated polyester resins. Formulations of unsaturated polyester resins with different loadings of expandable graphite and various synergists were prepared, and the self-extinguishing character of the materials compared.

## EXPANDABLE GRAPHITE FLAKE

Expandable graphite is manufactured using natural crystalline graphite flake. Deposits of crystalline graphite are numerous and found around the world, usually as inclusions in metamorphic rock, or in the silts and clays that result from their erosion. Graphite is recovered from the ore by crushing and flotation, and is usually beneficiated to give graphite flake that is 95-98% carbon.

Crystalline graphite consists of stacks of parallel planes of carbon atoms. Because no covalent bonding exists between the layers, other molecules can be inserted between them. This process, known as intercalation, is essential for the production of expandable graphite. In the commercial process, sulfuric acid is inserted into the graphite, after which the flake is washed and dried. The intercalant is trapped inside the graphite lattice, so the final product is a dry, pourable, non-toxic material with minimal acidity.

When the intercalated graphite is exposed to heat or flame, the inserted molecules decompose to generate gas. The gas forces apart the carbon layers and the graphite expands. The expanded graphite is a low density, non-burnable, thermal insulation, often referred to as a "worm" because of its curved shape (Figure 1).

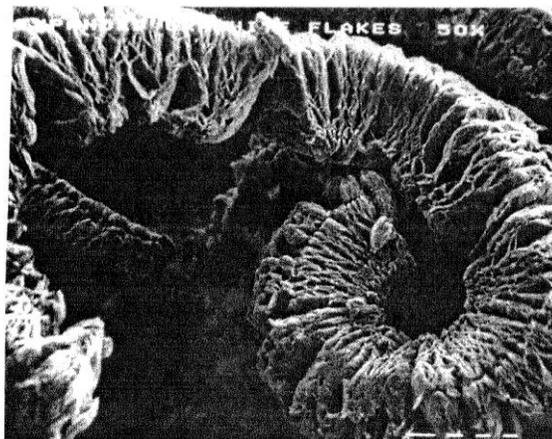


Figure 1: Scanning Electron Micrograph of Expanded Graphite Flake

The expandable graphite used in this study was GRAFGUARD<sup>®</sup> Grade 220-80N, commercially available from GrafTech International, Inc.<sup>5</sup> of Cleveland, Ohio, USA. In the grade nomenclature, "220" refers to the temperature (in 0c) at which the graphite begins to expand, "80" is the mesh size (177 micron or larger), and "N" refers to a neutral flake. GrafTech has manufactured expandable graphite since the 1960s, and offers a variety of expandable graphite products for many different applications.

## **FIRE RETARDANCY OF UNSATURATED POLYESTER RESINS**

For many applications, there is a need for unsaturated polyester resins [UPRs] to be fire retardant or self-extinguishing. Fiber-reinforced plastic (FRP) materials containing UPRs are of particular concern, since much of this material is used in critical applications such as aircraft, shipbuilding, and building construction.

Information on the fire retardancy of UPRs is given in many sources, e.g. in a book on UPRs and in a review article<sup>67</sup>. The flammability mechanisms of polymeric materials including UPRs, along with information on useful fire retardants and testing methods, has been presented in a book by the author.<sup>8</sup>

Chlorine and bromine compounds (e.g. HET acid, tetrachlorophthalic anhydride, tetrabromophthalic anhydride, dibromoneopentyl glycol) can be built into the UPR molecule, or added to the UPR directly as pentabromoethylbenzene or various chloroparaffins. The mechanism of fire retardancy involves the formation of Cl or Br radicals which suppress the chemistry of flame propagation. Antimony trioxide is often used to enhance the fire retardant efficiency of halogen compounds. However, the use of halogenated compounds and antimony oxide has come under some criticism due to the possible formation of toxic or corrosive combustion products.

Aluminum trihydroxide  $Al(OH)_3$  and magnesium hydroxide  $Mg(OH)_2$  exhibit a different mechanism of fire retardancy. Both materials evolve water at high temperatures, thus decreasing the temperature of the substrate while diluting the

combustible pyrolysis gases. The primary disadvantage of these fire retardants is that they require high loadings to be effective. This makes impregnation of the fibre reinforced composite more difficult while reducing its final physical properties. The metal hydroxides do have an important advantage in that they can significantly decrease the evolution of smoke.

A still different mechanism of fire retardancy is observed when red phosphorus and phosphorus compounds (e.g. triethyl phosphate or ammonium polyphosphate) are used. The oxidation and pyrolysis of these compounds result in the formation of polyphosphoric acid. The acids tend to promote charring of the plastic during heating, which acts to reduce burning. Moreover, the char formation decreases the concentration of gaseous hydrocarbons due to pyrolysis. The concentration of phosphorus is usually much less than that required for the Al or Mg hydroxides. In fact, if the amount of the phosphorus-containing fire retardants is too large some properties of the UPRs may be adversely affected and processing problems may arise.

There have been many acidic metal compounds suggested for use as flame retardants. The fire retardant mechanism of these compounds may be similar to that of phosphorus-containing compounds. In addition to the well-known zinc borates, tin compounds [zinc stannate  $ZnSnO_3$  and zinc hydroxystannate  $ZnSn(OH)_6$ ] have also been suggested as possible fire retardants and smoke suppressants<sup>9</sup>

As mentioned above, a flame retardant system must reduce the generation of smoke as well as suppress the flame propagation. In addition to Al and Mg hydroxides and the borates and stannates, molybdenum trioxide ( $MoO_3$ ) is a very efficient smoke suppressant<sup>10</sup>. The effect of the various smoke suppressants depends on the temperature of pyrolysis.<sup>11</sup>

Combinations of various fire retardants can exhibit an elevated efficiency when the mechanism of fire retardancy is different. For example, halogen compounds form synergistic systems with  $Al(OH)_3$  or phosphorus compounds. Halogen-free systems containing  $Al(OH)_3$  with red phosphorus or ammonium polyphosphate can be quite effective.<sup>12</sup> Phosphorus-phosphorus synergism was found when triethyl phosphate was added together with melamine polyphosphate.<sup>13</sup> Because of these kinds of observations, it may be that expandable graphite and other flame retardants will also combine to generate especially effective flame retardant systems.

## **MATERIALS AND METHODS**

### **MATERIALS**

"Polimal 109" unsaturated polyester resin was obtained from Chern. Works "Organika-Sarzyna", Nowa Sarzyna, Poland. The resin is a general-purpose, halogen-free, system made of maleic anhydride, phthalic anhydride, 1,2-propylene glycol and styrene. The cold curing system consisted of methylethylketone peroxide and cobalt octoate.

Fire retardants and synergists used in the study included the following:

GRAFGUARD<sup>®</sup> 220-80N Expandable Graphite Flake, GrafTech International Inc.,  
12900 Snow Road, Cleveland, OH 44130, USA <http://www.graftech.com>  
Aluminum trihydroxide, FlameGard ATH MI5B, Alcoa Industrial Chemicals  
Ammonium polyphosphate, Exolit AP 422, Clariant  
Red phosphorus (paste), Exolit RP 654, Clariant  
Pentabromoethylbenzene, Alwido, Gliwice/Poland  
Antimony trioxide, Inorganic Chemicals Co., Warsaw/Poland

## PREPARATION OF TEST BARS

The liquid UPR was mixed with the fire retardant(s) and 1 phr Aerosil 200 (to avoid sedimentation). The components of the curing system were added, and the compositions were cast into 4 mm x 10 mm x 100 mm steel forms. The curing was carried out by holding the cast pieces at 20°C for 24 hours, followed by a postcuring treatment at 80°C for 2 hours.

## TESTING METHOD

Preliminary evaluations of the test samples indicated that the Limiting Oxygen Index (LOI) was relatively insensitive to the amount of expandable graphite. Subsequently, the fire performance of the bars was tested by heating the samples in a horizontal position using a gas flame for 60 seconds, then monitoring the self-extinguishing (afterflame) time and the remaining non-burnt length of the bar (up to 80 mm). This test corresponds to the Polish Standard PN-82/C-89023 [see ISO 1210:1992 (E) "Plastics-determination of the burning behavior of horizontal and vertical specimens in contact with a small-flame ignition source"].

## RESULTS AND DISCUSSION

The first series of specimens was prepared with GRAFGUARD<sup>®</sup> expandable graphite flake as the only fire retardant. Amounts of GRAFGUARD<sup>®</sup> from 0-30 phr (parts by weight per hundred parts resin) were added to the resin. The results in Table 1 show that the samples self-extinguished beginning with 7.5 phr GRAFGUARD<sup>®</sup>. At 10 phr GRAFGUARD<sup>®</sup>, immediate extinguishing occurs (0-1 sec afterflame time after removing of the gas burner).

**Table 1. Effect of GRAFGUARD<sup>®</sup> on the Fire Behavior of UPR**

Sample No.	GRAFGUARD <sup>®</sup> phr	Behavior in fire			
		Self-extinguishing	Afterflame time, sec	Non-burnt length, mm	LOI, %
1-I	-	No	280	0	19.5
2-I	5	No	365	0	21.6
3-I	7.5	Yes	7	78	-
4-I	10	Yes	0	80	23.3
5-I	15	Yes	0	80	23.3
6-I	25	Yes	0	80	-
7-I	25	Yes	0	80	-
8-I	30	Yes	0	79	-

At some of the lower loading levels of GRAFGUARD<sup>®</sup> there was observed some "sparking" of the graphite during expansion. Presumably, this was the result of the graphite expanding through the extremely rigid polyester, causing some small particles of the resin to be ejected from the sample. In a few cases, the sparks were hot enough to ignite a sheet of filter paper placed 20 cm below the burning bar.

## ALUMINUM TRIHYDROXIDE

Samples were prepared that combined GRAFGUARD<sup>®</sup> with aluminum trihydroxide [ATH] as a potential synergist (Table 2). It is well known that when ATH is used as a fire retardant, it must sometimes be added at levels as high as 60 phr to be effective. For UPRs where ATH was used at moderate levels both with and without GRAFGUARD<sup>®</sup>, there was actually an increase in the afterflame duration. Higher levels of ATH were not tested because of the detrimental effects on the resin properties.

**Table 2. Combined Effect of GRAFGUARD® and Al(OH)<sub>3</sub> [ATH] on the Fire Behavior of UPR**

Sample No.	Fire Retardants, phr		Behavior in fire			
	GRAFGUARD®	ATH	Self-extinguishing	Afterflame time, sec	Non-burnt length, mm	LOI, %
1-I	0	0	No	217	0	19.5
1-II	0	15	No	331	0	-
2-I	5	0	No	365	0	21.6
2-II	5	10	No	510	0	-
3-II	5	15	No	394	24	-
4-I	10	0	Yes	0	80	23.3
4-II	10	5	Yes	0	80	-
5-II	10	10	Yes	0	80	-
6-II	10	15	Yes	0	80	23.6
5-I	15	0	Yes	0	80	23.4
7-II	15	15	Yes	3	79	-
8-II	20	15	Yes	3	80	-

**PHOSPHORUS COMPOUNDS**

Another series of samples was prepared comprising GRAFGUARD® with red phosphorus [RP] (Table 3). RP could only be used in amounts less than 0.5 phr due to its adverse effect on curing. At this level, RP had a negligible (or even harmful) effect on the self-extinguishing properties of the UPR/ GRAFGUARD® compositions. Results for this combination of RP and GRAFGUARD® were uncertain and irreproducible.

**Table 3. Combined Effect of GRAFGUARD® and Red Phosphorus [RP] on the Fire Behavior of UPR**

Sample No.	Fire Retardants		Behavior in fire		
	GRAFGUARD®	RP Paste (45%P)	Self-extinguishing	Afterflame time, sec	Non-burnt length, mm
2-I	5	0	No	365	0
1-III	5	0.125	No	615	0
2-III	5	0.25	No	240	62
3-III	5	0.5	No	110	70
4-I	10	0	Yes	0	80
4-III <sup>1)</sup>	10	0.125	Yes	0	80
5-III <sup>1)</sup>	10	0.25	Yes	10	72
6-III <sup>1)</sup>	10	0.5	Yes	15	60
7-III	-	0.5	No	100	55

<sup>1)</sup> low reproducibility

Phosphorus in the form of ammonium polyphosphate (APP) exhibited the best self-extinguishing properties when combined with expandable graphite (Table 4). Whereas APP by itself at 15 phr was not self-extinguishing and had an afterflame time of 40 seconds, the addition of 5 phr GRAFGUARD® gave immediate self-extinguishing. No sparks were observed at this concentration of additives. In addition, at a loading level of 10 phr GRAFGUARD® + 15 phr APP, the amount of smoke produced was reduced significantly. Thus, the combination of GRAFGUARD® and APP is distinctly synergistic in this unsaturated polyester resin system.

**Table 4. Combined Effect of GRAFGUARD® and Ammonium Polyphosphate [APP] on the Fire Behavior of UPR**

Sample No.	Fire retardant, phr		Behavior in Fire		
	GRAFGUARD®	APP	Self-extinguishing	Afterflame time, sec	Non-burnt length, mm
2-I	5	0	No	365	0
1-IV	5	5	No	13	73
2-IV	5	10	Yes	10	75
3-IV	5	15	Yes	0	80
4-IV	10	0	Yes	0	80
4-IV	10	5	Yes	0	80
5-IV	10	10	Yes	0	80
6-IV	10	15	Yes	0	80
7-IV	0	15	No	40	55

### BROMINATED ADDITIVE

Very recent experiments involve a composition consisting of GRAFGUARD® and pentabromoethylbenzene [PBEB] with antimony trioxide (Sb<sub>2</sub>O<sub>3</sub>, ATO). The use of GRAFGUARD® with brominated additives was investigated because of the possibility that expandable graphite could reduce the amount of brominated additive required. Table 5 shows the results obtained on this system to date. It is apparent that the self-extinguishing properties appear at a relatively low concentration of the fire retardants. Zero burning time was found at loadings as low as 5 phr GRAFGUARD® and 3 phr PBEB with 2 phr ATO.

**Table 5. Combined Effect of GRAFGUARD®, Pentabromoethylbenzene [PBEB] and Antimony Trioxide [ATO] on the Fire Behavior of UPR**

Sample No.	Fire retardant, phr			Behavior in Fire		
	GRAFGUARD®	PBEB	ATO	Self-extinguishing	Afterflame time, sec	Non-burnt length, mm
1-I	5	0	0	No	365	0
1-V	5	3	2	Yes	0	74
2-V	5	5	2.5	Yes	0	78
3-V	5	10	3	Yes	7	80

### CONCLUSIONS

Expandable graphite flake added to unsaturated polyester resin in the amount of 7.5 phr or more makes the resin self-extinguishing. The use of expandable graphite with ammonium polyphosphate further improves the fire retardant behavior of UPR. GRAFGUARD® added at 5 phr with 15 phr APP inhibits burning of the sample while eliminating any afterflame (immediate self-extinguishing). Moreover, GRAFGUARD® and APP together suppress the formation of smoke. Good fire retardancy can also be obtained by adding expandable graphite to a brominated fire retardant and antimony trioxide. Sparks generated by pieces of the rigid resin ejected by the expansion of the graphite are eliminated with APP or (PBEB + ATO) when applied in a proper ratio.

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