GRAFGUARD®
Fire Retardant Additive

"Expandable Graphite Flake as an Additive for a New Flame Retardant Resin"

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INTRODUCTION

Chemical intumescent systems have been used as flame retardants for nearly 50 years. The effectiveness of these flame retardants depends on the heat-induced decomposition of the organic components, and the creation of a char layer that insulates the substrate from the heat source. However, as intumescents are required to address more severe and diverse applications, new approaches are needed that provide improved performance over conventional systems. Expandable graphite flake is a radically different intumescent additive that has found use in a number of flame retardant applications. **Expanding up to 100 times its original thickness, the graphite flake generates a greater insulative layer than many intumescents**. Unlike the carbon char layer formed with chemical intumescents, the graphite char formed from expandable flake retains the superior heat resistance of graphite. In addition, **graphite flake is the only intumescent that expands with sufficient force to allow its use in rigidized systems**, such as those employing cured phenolic resins.

The intumescent properties of expandable graphite flake are the basis for its use in a growing number of flame retardant applications. For some uses, such as firestops, putties and seals, the primary purpose of the graphite is to generate expansion. Other applications take advantage of both the expansion and the insulative properties of the graphite. For example, the expansion of graphite flake dispersed in polyurethane foam acts to smother burning, as well as to insulate the foam from the heat source. In a construction application, expandable graphite distributed in the outer layers of oriented strandboard has been shown to reduce the flame spread(1), also by expansion and insulation. As with intumescent coatings, the best efficiency was demonstrated when the expanded graphite layer was concentrated on, or just below, the surfaces of the board.

As part of the effort to develop more effective flame retardants, the effect of expandable graphite flake was investigated as an additive for intumescent flame retardant resins. Two new intumescent resin systems were developed as part of this study, and their performance was compared to that of another intumescent resin. One of the new resin systems exhibited much better flame retardant activity than the other two materials.

The performance of the resin systems with and without expandable graphite is reported here based on cone calorimeter and ASTM E-84 (tunnel) testing. For each resin system, the addition of expandable graphite improved the performance by increasing the amount of char developed. **Formulations using expandable graphite were found to**:

- Increase the time to ignition
- Reduce heat release and mass loss
- Reduce smoke and flame spread

MATERIALS

<u>Expandable Graphite Flake</u>

Crystalline graphite flake is the starting material for the manufacture of expandable graphite. Deposits of crystalline graphite are found throughout the world. The graphite is usually found either as inclusions in various metamorphic rocks, or concentrated in the silts and clays that result from their erosion. Graphite is recovered from the ore by crushing and flotation, and beneficiated to give graphite flake that is 94-98% carbon.

Crystalline graphite consists of stacks of parallel planes of carbon atoms, as shown in Figure 1. Because no covalent bonding exists between the planes, 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. Since the intercalant is sealed within the graphite lattice, the expandable graphite is a dry, pourable material with only minimal acidity. The expandable graphite flake used in this study was GRAFGUARD™ Grade 373, manufactured by GrafTech International LTD.

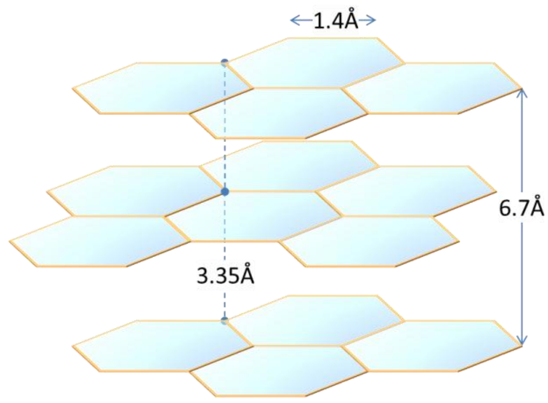

Figure 1: Crystal Structure of Natural Graphite Flake

When the intercalated graphite is exposed to heat or flame, the inserted molecules decompose to generate gas. The graphite layer planes are forced apart by the gas and the graphite expands. The expanded graphite is a low-density, non-burnable, thermal insulation that can reflect up to 50% of radiant heat. It is often referred to as a "worm" because of its long, twisting shape. A typical segment of an expanded graphite worm is shown in Figure 2.

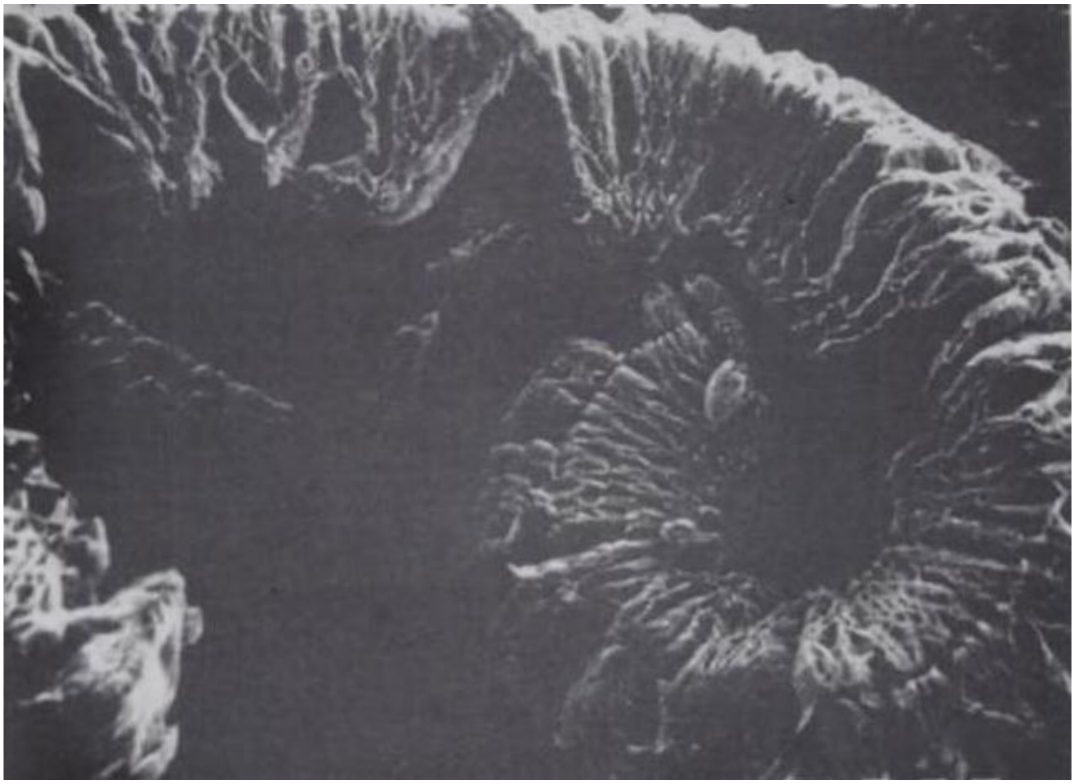

Figure 2: View of Expanded Graphite, magnified 50 times

In order to be useful as a part of an intumescent system, the expansion of intercalated graphite must occur at the relatively low temperatures that are typical of small-scale fires. This prevents the protected substrate from burning and contributing to an increase in the total heat flux. The temperature-induced expansion of expandable graphite can be monitored using thermal mechanical analysis (TMA). Figure 3 shows a TMA plot for the graphite flake used in this study. The first 10% of expansion occurs by 235°C. Half of the expansion is completed by 260°C, with 90% expansion reached at 300°C. Thermal gravimetric analysis shows that the expansion is accompanied by a continual mass loss. The inverse relationship of expansion and mass loss shows the correlation of expansion to the generation of gases from the intercalated flake. Special processing can make expandable graphite that exhibits initial expansion temperatures of 170°C to 350°C.

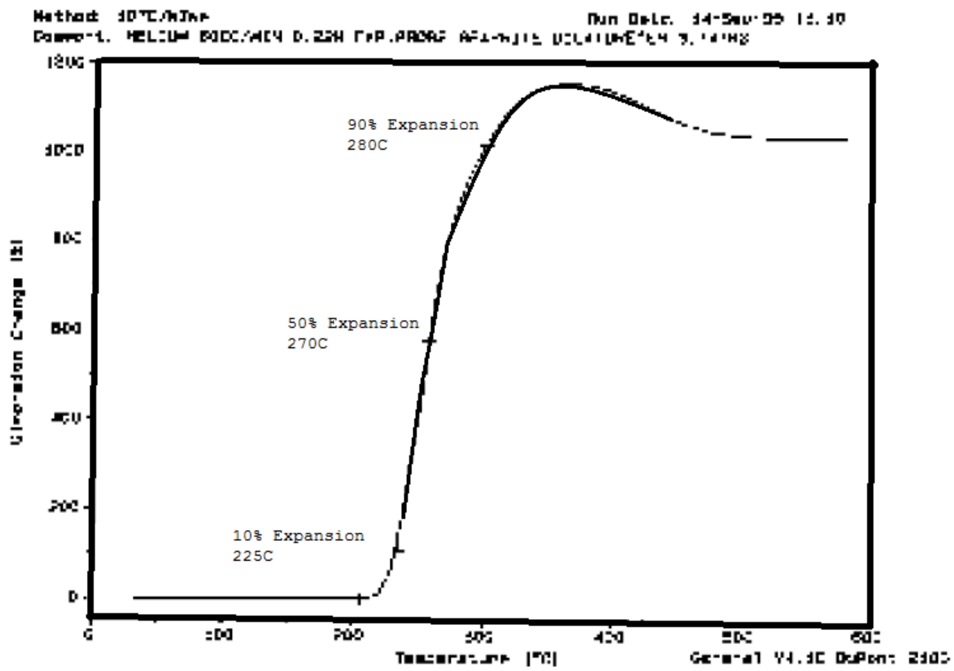

Figure 3: Thermomechanical Analysis (TMA) Plot for GRAFGUARD™ Grade 373

Graphite flake must be used in conjunction with a carrier system in order to be an effective flame retardant additive. Upon expansion, the expanded graphite possesses very little strength or adhesion. A binder is necessary to maintain the integrity of the char layer and its bond to the substrate.

Intumescent Resins

Georgia-Pacific Resins Inc. (GPRI) has been working in conjunction with GrafTech to develop a resin system that could be used as a binder with expandable graphite. As part of this effort, GPRI developed several chemical intumescent formulations that exhibited significant flame retardant efficiency of their own. Based on a proprietary formulation, the most effective GPRI resin system (designated as GP2) consists of a resin component and a curing agent. The two components can be combined at room temperature to give a solution with a viscosity of under 500 centipoise. The shelf life of the resin component is one month at room temperature, while the curing agent is stable for at least 1 year. The pot life of the mixed solution is 6-8 hours.

The intumescent resin system can be easily applied by brush or rollcoating, or further diluted with water for spray application. The mixture can be cured overnight at ambient temperature, or at 90°C for as little as 20 minutes. The film dries to a hard, clear finish. The surface resists abrasion and demonstrates excellent adhesion to the substrate.

The expansion of the cured resin system was monitored by TMA, and is shown in Figure 4. The initial 10% of expansion occurs at 255°C, with the midpoint at 260°C and 90% of expansion complete by 280°C. The resin expansion lies totally within the 235°- 300°C range of the expandable graphite, suggesting that the two components could intumesce together to form a composite char layer.

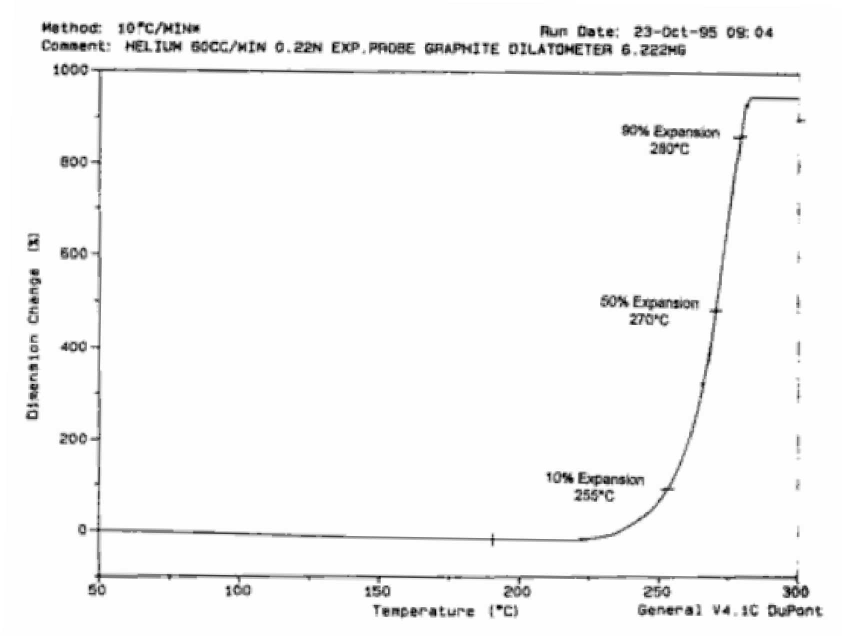

Figure 4: Thermomechanical Analysis (TMA) Plot for GP2 Intumescent Resin

SAMPLE PREPARATION

A number of formulations of intumescent resins were evaluated by GPRI. Discussed in this work are results for a preliminary system, designated as GP1, and a more effective formulation, GP2. For comparison, the flame retardant properties of another intumescent resin (Resin A) was also evaluated.

Samples for cone calorimeter testing were 4-inch square, 7/16-inch thick pieces of oriented strandboard (OSB). Two grams of an intumescent resin were applied by brushing to the non-textured side of the board. This loading corresponds to an application rate of about 18 grams per square foot (coverage rate of250 ft^2/gallon). For samples containing expandable graphite, the graphite was mixed in with the resin prior to application on the board. The loading of the graphite/intumescent mix was increased so that the amount of intumescent remained constant at two grams. All samples were cured at 90°C for 20 minutes. The dried film thickness was about 0.005 inch.

Samples of the GP2 intumescent resin with and without expandable graphite flake were prepared for evaluation by the ASTM E-84 method. The method of preparing the resin mixtures was the same as that used for the cone calorimeter samples. The initial tests were conducted using six pieces of2' x 4' x 7/16-inch thick oriented strandboard from a specific manufacturer. The resin was brushed on to the smooth side of the OSB and on any cut edges that would be exposed to the tunnel. The application rate was 27 grams/ft^2. For samples prepared with graphite, one-third of the resin was replaced by graphite to maintain an overall application of 27 grams/ ft^2. Panels were cured at 90°C for 30 minutes. A second set of OSB samples was prepared in a similar manner, except the resin mixture was applied to the rough side of OSB obtained from a different manufacturer.

Another series of E-84 tests was carried out using Hushboard sound-deadening fiberboard manufactured by Georgia-Pacific. Panels measured 2' x 4' x I/2-inch thick, and six panels were used for each 24-foot test. The amounts of intumescent resin and graphite used for the tests are shown in Table I. All cut edges exposed to the tunnel were also coated. The panels were cured at 90°C for 30 minutes.

Table I: Compositions of Coating Applied to Fiberboard

Component (g/ft^2)	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**
GP2 Resin	27	18	9	18	12	6	3	0
GRAFGUARD™ 373	0	0	0	9	6	3	6	0

RESULTS AND DISCUSSION

The flame retardant effect of the various resin systems on wood-based materials was determined by Cone Calorimeter (ASTM E-1354) and Steiner Tunnel (ASTM E-84) testing conducted by Omega Point Laboratories, San Antonio, Texas.

ASTM E-1354 (Cone Calorimeter) Testing

Cone Calorimeter data for the resin systems are given in Table II. Data were collected for longer than 600 seconds if there was no combustion during the initial ten minute test. However, all peak heat release and mass loss data in the table are based on 10 minutes.

Table II: Cone Calorimeter Fire Test Results

Resin Component	**Resin (g)**	**Expandable Graphite (g)**	**Time to Ignition (sec)**	**Peak Heat Release (kW/m^2)**	**Mass Loss (%)**
Resin A	2	0	203	67	32
Resin A	2	1	443	37	15
GP1	2	0	165	68	31
GP1	2	0.7	623	<10	8
GP1	2	0.7	410	24	11
GP2	2	0	720	<10	11
GP2	2	1	1020	<10	6

35 kW/m2 incident heat flux

The Resin A intumescent generated less than 1/8-inch of expansion, and there was significant cracking along the surface that led to rapid ignition. Addition of expandable graphite dramatically improved the expansion and physical characteristics of the char. The expanded layer was free of cracks and had good rigidity. The GP1 resin behaved similarly to the Resin A material, although better performance was observed upon the addition of expandable graphite.

For the GP2 resin, the developed char layer was more expansive than for Resin A or GP1. With the addition of expandable graphite, the char depth was nearly one inch with good rigidity, no cracking, and good adhesion to the OSB. Interestingly, intumescence was observed to occur in two stages. An initial rapid expansion within the first minute was due primarily to the graphite, with a smaller contribution due to expansion of the resin. The second expansion was slower and more gradual, and appeared to be due to slow heat penetration to the remaining underlying resin. A cross section of the char showed a higher proportion of expanded graphite toward the upper char surface, with more GP intumescent near the substrate. The insulation of the resin by the expanded graphite likely contributes to the special synergy of this system.

The decrease in mass loss upon the addition of graphite is a direct result of delayed ignition. Mass loss is an important factor that relates to structural failure in fires, and so improvement in this area can be very important. By comparison, flame retardant treated plywood loses 20% of its mass under similar test conditions.

ASTM E-84 (Tunnel) Testing of Oriented Strandboard

Based on results from Cone Calorimeter testing, large scale ASTM E-S4 testing was carried out using oriented strandboard as the substrate. Results were obtained using two different manufacturers of OSB and are recorded in Table III.

Table III: Tunnel Test Results for Oriented Strandboard using GP2 Resin

Oriented Standboard	Resin (g/ft^2)	Expandable Graphite (g/ft^2)	Time to Ignition (sec)	Flame Spread Index	Smoke Index
Source A	27	0	201	10	100
Source A	18	9	275	5	20
Source B	27	0	190	20	210
Source B	18	9	262	10	55
B (Control)	0	0	25	220	95

As with the cone calorimeter testing, the use of expandable graphite improved the performance of the intumescent resin. By comparison, the samples of resins without graphite showed 1/2 the char depth and were deeply channeled directly above the burner. This was reflected in a significantly shorter time to ignition, higher flamespread index, and higher smoke index. The 75% reduction of smoke when using expandable graphite is an important benefit that might find use in other flame retardant systems. Although the mechanism of the reduction has not been determined, it has been shown that expanded graphite is efficient in absorbing some gases at high temperatures(2).

Examination of the char produced 10 feet from the burner showed two distinct regions in the expanded layer. The top portion consisted of graphite worms held in place by expanded resin. Underneath this layer was a 1/8-inch thick, semi-expanded layer of orange char, composed mostly of the GP2 intumescent. In the most intense regions of the flame, this orange char had expanded further to give a total char thickness of about 1/2 inch. This is similar to the two-stage expansion observed in the cone calorimeter testing.

The most significant burning of the substrate occurred at the edges between the 4-foot long panels. Probable end use of these intumescent resin systems would be on 8-foot panels. The flamespread index of eight-foot long panels would probably be less than that observed for these tests.

ASTM E-84 (Tunnel) Testing of Fiberboard

Fiberboard is a medium density cellulose fiber material often used for office partitions. The material is highly flammable, and represented a severe trial of the flame retardant properties of the GP2 intumescent system.

Table IV shows the loadings of intumescent resin and expandable graphite used on the fiberboard. At the 27 g/ft^2 and 18 g/ft^2 loadings, Class A (<25) flamespread indices were obtained. Again, the addition of graphite reduced smoke by about 75%, while lowering the flamespread index. However, it was noticed that there was not much rigidity to the expanded worms, nor was there much evidence of an expanded layer of the GP2 resin. For the lower loaded panels, there was little difference in results between the panels treated with and without expandable graphite This was probably due to the porous nature of the fiberboard, which caused the wet resin to be drawn into the board during application. Very little resin remained on the surface to bind the graphite, especially at the low loading levels. Much of the expanded graphite blew off the boards during the test, clearly demonstrating the need for a binder in order for the expanded graphite to be effective. As with any porous substrate, the use of a sealer prior to the application of the resin could dramatically improve the efficiency of the intumescent system.

Table IV: Tunnel Test Results for Fiberboard using GP2 Resin

Resin (g/ft^2)	Expandable Graphite (g/ft^2)	Time to Ignition (sec)	Flame Spread Index	Smoke Index
27	0	90	20	185
18	9	224	10	40
18	0	93	20	80
12	6	154	15	25
9	0	34	40	80
6	3	55	35	85
3	6	65	35	30
0	0	11	285	90

CONCLUSIONS

The addition of expandable graphite flake was found to increase the flame retardant effectiveness of intumescent resin systems. The use of graphite improved the physical characteristics of the char by increasing the amount of the insulative layer and reducing crack formation. A newly-developed intumescent resin using expandable graphite as an additive showed markedly improved results for time to ignition, heat release, mass loss, and flamespread. The smoke index for the resin/graphite system was reduced by 75% compared to that obtained for the intumescent resin alone.

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