FR Composite Development
Utilizing the Cone Calorimeter

Glade Squires
About Omya

- Global producer of **industrial minerals** - mainly derived from Calcium Carbonate, Dolomite and Perlite
- **Worldwide distributor** of specialty chemicals
- Privately-owned **Swiss** corporation with a **global presence**

**High-quality, innovative products and environmental solutions** to multiple industries:

Construction, Paper, Board, Polymers, Food and Personal & Home Care, Agriculture, Water and Energy.
Commitment since 1884

- Founded 1884 in Switzerland, by Gottfried Plüss and Emma Staufer
- Producing glazing putty, made of fine chalk mixed with linseed oil
Our Global Figures

- 170 locations
- 50 countries
- 9,000 employees
- 70 nationalities
- 10 innovation hubs
- > 4 billion turnover
Global Distribution Sales 2021

Globally ~ CHF 1,5 bn

North America ~ CHF 160 m

Asia Pacific ~ CHF 310 m

Europe ~ CHF 800 m

Latin America ~ CHF 100 m

Middle East & Africa ~ CHF 140 m

Source: 2022 ICIS Chemical Business Magazine
Role of Flame Retardants

Almost all materials that contain flame retardants will ignite and burn to some degree

However, Flame Retardants will…………

• Increase the ignition temperature and, or make a material self-extinguish –
  Prevent Fires From Starting

• Decrease the rate of combustion resulting in lower amounts of heat release to adjacent surfaces and objects –
  Increase Escape Time For Occupants, Save Lives

• Reduce the rate of a fire spreading to avoid or delay flashover –
  Increase Response Time, Reduce Property Loss
Types of Flame Retardants

Halogen
- Bromine
  - Inorganic Bromide salts
  - Bromine containing organic compounds
- Chlorine
  - Chlorine containing organic compounds
- Fluorine
  - Inherently flame retardant polymers, i.e. Teflon™

Non-Halogen
- Phosphorus
  - Elemental Red Phosphorus
  - Phosphoric Acid salts
  - Phosphorus containing organic compounds
- Nitrogen
  - High Nitrogen content organic compounds
- Metal Hydroxides
  - Absorb heat and release water upon decomposition
Halogen Flame Retardants

In general Bromine is twice as efficient as Chlorine on a molecular basis.
Non-Halogen Flame Retardants

Higher load levels required versus Halogen / Antimony systems

Char forming chemical reaction creates insulation from external heat source and barrier for fuel to evolve into combustion zone

Some vapor phase chemical reactions also occur

Heat absorption leads to decomposition and release of Nitrogen gas that dilutes the Oxygen content in the combustion zone, produces intumescence when coupled with a char forming flame retardant

Highly Endothermic Decomposition (absorbs heat)
Magnesium Hydroxide - Mg(OH)$_2$

\[ \text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O} \quad @ \quad 330^\circ\text{C} \]

Alumina Trihydrate – Al(OH)$_3$

\[ 2\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \quad @ \quad 230^\circ\text{C} \]
Synergists and Smoke Suppressants

Halogen FR systems exhibit their greatest efficiency and best economics when Antimony Oxide is added as a Synergist

Usually added at a 3:1 ratio of Halogen to Antimony

As a result of the efficiency of a vapor phase FR system, large amounts of unburnt fuel are present as smoke

Zinc Borate is the most common smoke suppressant / synergist added to reduce smoke

Suppressing higher levels of smoke in more challenging systems, Zinc Hydroxystannate or Zinc Stannate are used

Adding some ATH will also help to control smoke in composites
Reducing Dust Level of Antimony Oxide

Recommendations are being made to reduce worker exposure via inhalation to very fine, micron to sub-micron dust particles of any material.

Antimony Oxide’s particle range is 0.8 microns to 1.5 microns depending on the grade.

Dust level of Antimony Oxide is significantly reduced by “wetting or damping” with 3% or 4% plasticizer.

Measured level of dust can be reduced significantly from over 1% to well below 0.1% with the Antimony Oxide remaining free flowing.

Based on addition level of Antimony Oxide wetted with 4% plasticizer and added at about 8% to a composite system, only 0.3% plasticizer is present in the final product – no noticeable or measurable impact on physical properties.
Dust Levels of Various Grades – Standard Powder and Wetted

<table>
<thead>
<tr>
<th>Grade</th>
<th>Microns</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>0.8 to 1.0</td>
</tr>
<tr>
<td>MT</td>
<td>1.3 to 1.5</td>
</tr>
<tr>
<td>LT</td>
<td>2.0 to 2.5</td>
</tr>
<tr>
<td>Z</td>
<td>8.0 to 13</td>
</tr>
</tbody>
</table>
Fire

Fire consists of five distinct stages - heating, decomposition, ignition, combustion and propagation.
Physical and Chemical Processes of Combustion

FIGURE 2. PHYSICAL AND CHEMICAL PROCESSES IN THE FLAMING COMBUSTION OF POLYMERS

https://www.fire.tc.faa.gov/pdf/05-14.pdf Polymer Flammability U.S. Department of Transportation, Federal Aviation Administration Authors - Richard E. Lyon and Marc L. Janssens

Intumescence Charring

Halogen Antimony
Nitrogen / Water Vapor
Phosphorus / Nitrogen
Metal Hydroxides
Flame Retardant Mechanisms

Chemical

- Halogen + Antimony scavenging free radicals in the vapor phase breaking the chain propagation of combustion
- Phosphorus charring and Phosphorus + Nitrogen intumescence
- Metal Hydroxides absorbing heat and releasing water vapor
- Zinc compounds creating char in the condensed phase

Physical

- Char insulating the substrate and preventing volatilization of fuel
- Nitrogen released dilutes oxygen level in combustion zone
- Water vapor released, cooling and dilution of oxygen level in the combustion zone
Omya’s Flame Retardant Suppliers

Flame Retardants

- Antimony Trioxide (ATO)
- Antimony Trioxide (ATO) – Concentrates
- Flame Retardant Masterbatch
- Decabromodiphenyl Ethane
- Brominated Flame Retardant (Br-FR)
- Magnesium Hydroxides
- Phosphate Ester
- Red Phosphorus-Based Flame Retardants
- Specialty Phosphorus-Based Flame Retardants
- Melamine Cyanurate
- Melamine Phosphate
- Zinc Borate
- Zinc Hydroxy Stannate
- Zinc Stannate
Flame Retardant Wall Panel

Customer produces fiberglass reinforced panels for multiple end uses.

A small percentage of their production needs to meet a Class 1 E84 Steiner Tunnel flammability rating.

Current Class 1 panel uses a Brominated resin and Antimony Oxide to achieve the FR rating.

Other than flame retardancy, the other attributes of a Brominated resin are not needed for this application.

Goal is to develop an equivalently rated panel using their general purpose vinyl ester resin and an additive FR package, Bromine FR and Antimony Oxide.

This way, only one resin needs to be inventoried along with FR additives.
ASTM E84 Flammability Test

ASTM E84, UL 723, are also known as the Steiner Tunnel Test (developed by Albert Steiner in 1944), tests the surface burning characteristics of interior finishes and building materials, specifically of wall and ceiling materials.

Tunnel is 24 inches wide by 24 feet long. Test specimen is 18 inches wide by 24 feet long mounted on the ceiling of the tunnel. Two burners at the front generate 89 kW of heat.

Test measures two key characteristics, flame spread and smoke generation.

Flame spread determines how fast a material will contribute to the propagation of a fire.

Smoke generation determines how much smoke a burning material will contribute during a fire and can visibility be maintained for occupants to escape.
ASTM E84 Flammability Ratings

Both the Flame Spread and the Smoke Development are indices and calculated from the data generated during the actual burn test.

<table>
<thead>
<tr>
<th>Class</th>
<th>Flame-Spread Index (FSI)</th>
<th>Smoke Development Index (SDI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class 1 or Class A</td>
<td>0-25</td>
<td>450 Maximum</td>
</tr>
<tr>
<td>Class 2 or Class B</td>
<td>26-75</td>
<td>450 Maximum</td>
</tr>
<tr>
<td>Class 3 or Class C</td>
<td>76-200</td>
<td>450 Maximum</td>
</tr>
</tbody>
</table>
Cone Calorimeter

Small scale test that measures very specific processes and stages of combustion and fire.

Standard sample size of 100 x 100 mm and less than 50 mm thick.

Heat flux of the ceramic cone heating element is typically set at 50 kW/m$^2$ to simulate the ignition burner heat fluxes in ASTM E84, Steiner Tunnel.

Most important parameters measured are;

Time To Ignition, Heat Release Rate, Peak Heat Release Rate, Total Heat Released, Mass Loss Rate and Total Smoke Produced

These are all part of the various stages of a fire starting and propagating - heating, decomposition, ignition, combustion and propagation
Cone Calorimeter
Developed by the Fire Research Division at NIST in 1982

- Laser photometer beam including temperature measurement
- Temperature and differential pressure measurements taken here
- Soot sample tube
- Exhaust blower
- Soot collection filter
- Controlled flow rate
- Gas samples taken here
- Cone heater
- Spark igniter
- Specimen
- Load cell
- Vertical orientation
Additive FR Formulation

FR-1410 – ICL Industrial

- Chemical name: Decabromodiphenyl Ethane
- Formula: C₃₄Br₁₄H₄
- CAS Number: 84852-53-9
- Bromine Content: 82.0%
- MW: 971.2

Antimony Trioxide - Campine

Typical Properties

- Particle size
  - Average Particle size: 1.3-1.5 μm
  - Sieve refusal (on 45μm / 325 mesh sieve) is specified: max 0.1%

Purity levels

- Sb20.3% is specified: min 99.8%
- Pb, As, Fe are specified:
  - Pb: max 1000 ppm
  - As: max 750 ppm
  - Fe: max 30 ppm

- Target formulation is to achieve 14% by weight Bromine in the resin
  - FR-1410 is 82.0% by weight Bromine
  - Antimony Oxide initially at a 2 to 1 level, Bromine FR to Antimony ratio
Cone Calorimeter Data – Small Test Panels

<table>
<thead>
<tr>
<th>Formulation</th>
<th>FR Current (Thin)</th>
<th>FR 1410 (Thin)</th>
<th>FR Current (Thick)</th>
<th>FR 1410 (Thick)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (mm)</td>
<td>5.13</td>
<td>5.00</td>
<td>9.75</td>
<td>9.10</td>
</tr>
<tr>
<td>Starting mass (g)</td>
<td>42.53</td>
<td>42.70</td>
<td>60.78</td>
<td>50.98</td>
</tr>
<tr>
<td>Finished mass (g)</td>
<td>19.72</td>
<td>19.78</td>
<td>30.40</td>
<td>26.82</td>
</tr>
<tr>
<td>Mass lost (g)</td>
<td>22.81</td>
<td>22.92</td>
<td>30.38</td>
<td>24.16</td>
</tr>
<tr>
<td>t-ignition (s)</td>
<td>30</td>
<td>30</td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td>t-flame out (s)</td>
<td>285</td>
<td>257</td>
<td>568</td>
<td>457</td>
</tr>
<tr>
<td>t-end (s)</td>
<td>390</td>
<td>366</td>
<td>673</td>
<td>564</td>
</tr>
<tr>
<td>Peak HRR (kW/m2)</td>
<td>324.83</td>
<td>273</td>
<td>251.3</td>
<td>379.2</td>
</tr>
<tr>
<td>t-peak (s)</td>
<td>39</td>
<td>33</td>
<td>42</td>
<td>33</td>
</tr>
<tr>
<td>THR (MJ/m2)</td>
<td>38.8</td>
<td>35.4</td>
<td>53.0</td>
<td>45.2</td>
</tr>
<tr>
<td>HRR @ 60s (kW/m2)</td>
<td>232.9</td>
<td>204.2</td>
<td>186.2</td>
<td>196.3</td>
</tr>
<tr>
<td>HRR @ 120s (kW/m2)</td>
<td>189.8</td>
<td>181.7</td>
<td>133.4</td>
<td>145.8</td>
</tr>
<tr>
<td>HRR @ 180s (kW/m2)</td>
<td>175.5</td>
<td>169.5</td>
<td>113.8</td>
<td>129.0</td>
</tr>
<tr>
<td>HRR (avg) (kW/m2)</td>
<td>107.7</td>
<td>105.4</td>
<td>82.2</td>
<td>84.4</td>
</tr>
<tr>
<td>MLR (avg) (g/s s m2)</td>
<td>6.33</td>
<td>6.82</td>
<td>4.72</td>
<td>4.51</td>
</tr>
<tr>
<td>EHC (avg) (MJ/kg)</td>
<td>16.99</td>
<td>15.45</td>
<td>17.45</td>
<td>18.72</td>
</tr>
<tr>
<td>SPR (avg) (m2/s)</td>
<td>0.0613</td>
<td>0.0689</td>
<td>0.0386</td>
<td>0.0348</td>
</tr>
<tr>
<td>SEA (avg) (m2/kg)</td>
<td>1046.3</td>
<td>1099.7</td>
<td>856.5</td>
<td>812.5</td>
</tr>
<tr>
<td>Fuel load (MJ/kg)</td>
<td>9.11</td>
<td>8.29</td>
<td>8.72</td>
<td>8.87</td>
</tr>
<tr>
<td>MARHE (kW/m2)</td>
<td>161.9</td>
<td>153.1</td>
<td>136.7</td>
<td>145.6</td>
</tr>
<tr>
<td>TSP (m2)</td>
<td>23.9</td>
<td>25.2</td>
<td>26.0</td>
<td>19.6</td>
</tr>
<tr>
<td>FIGRA (W/s)</td>
<td>8.631</td>
<td>8.278</td>
<td>7.075</td>
<td>11.794</td>
</tr>
</tbody>
</table>

HRR = Heat Release Rate
THR = Total Heat Released
MLR = Mass Loss Rate
EHC = Effective Heat of Combustion
SPR = Smoke Production Rate
SEA = Specific Extinction Area
MARHE = Max Average Rate Heat
TSP = Total Smoke Produced
FIGRA = Fire Growth Rate
Cone Calorimeter Data – Hand Made Test Panels

Heat Release vs Time: Thick Samples

Heat Release vs Time: Thin Samples
Cone Calorimeter Data – Production Panels

D-75-080 – Thick Panel

D-36-060 – Thin Panel

<table>
<thead>
<tr>
<th>Formulation</th>
<th>D-75-080</th>
<th>D-36-060</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (mm)</td>
<td>9.10</td>
<td>5.50</td>
</tr>
<tr>
<td>Starting mass (g)</td>
<td>62.80</td>
<td>55.51</td>
</tr>
<tr>
<td>Finished mass (g)</td>
<td>31.57</td>
<td>27.05</td>
</tr>
<tr>
<td>Mass lost (g)</td>
<td>31.23</td>
<td>28.46</td>
</tr>
<tr>
<td>t-ignition (s)</td>
<td>23</td>
<td>25</td>
</tr>
<tr>
<td>t-flame out (s)</td>
<td>529</td>
<td>376</td>
</tr>
<tr>
<td>t-end (s)</td>
<td>651</td>
<td>484</td>
</tr>
<tr>
<td>Peak HRR (kW/m²)</td>
<td>463.8</td>
<td>473.0</td>
</tr>
<tr>
<td>t-peak (s)</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>THR (MJ/m²)</td>
<td>58.7</td>
<td>46.4</td>
</tr>
<tr>
<td>HRR @ 60s (kW/m²)</td>
<td>228.2</td>
<td>217.1</td>
</tr>
<tr>
<td>HRR @ 120s (kW/m²)</td>
<td>177.1</td>
<td>172.5</td>
</tr>
<tr>
<td>HRR @ 180s (kW/m²)</td>
<td>150.6</td>
<td>147.1</td>
</tr>
<tr>
<td>HRR (avg) (kW/m²)</td>
<td>93.5</td>
<td>101.0</td>
</tr>
<tr>
<td>MLR (avg) (g/(s*m²))</td>
<td>4.97</td>
<td>6.21</td>
</tr>
<tr>
<td>EHC (avg) (MJ/kg)</td>
<td>18.80</td>
<td>16.29</td>
</tr>
<tr>
<td>SPR (avg) (m²/s)</td>
<td>0.0366</td>
<td>0.0531</td>
</tr>
<tr>
<td>SEA (avg) (m²/kg)</td>
<td>760.7</td>
<td>901.9</td>
</tr>
<tr>
<td>Fuel load (MJ/kg)</td>
<td>9.35</td>
<td>8.35</td>
</tr>
<tr>
<td>MARHE (kW/m²)</td>
<td>165.9</td>
<td>154.6</td>
</tr>
<tr>
<td>TSP (m²)</td>
<td>23.8</td>
<td>25.7</td>
</tr>
<tr>
<td>FIGRA (W/s)</td>
<td>13.4</td>
<td>11.8</td>
</tr>
</tbody>
</table>
Heat Release Rate Comparisons

- Compared to prior tests, both samples showed flame behavior most similar to the thick sample produced with FR-1410 from the previous report. Both samples exhibited generally similar smoke production rates to the same previous sample as well.

- Heat release behavior between the two samples was remarkably similar. Sample D-36-060 exhibited slightly higher peak and average heat release rates, by a nearly negligible margin. The significant difference in thickness between the two samples resulted in sample D-36-060, the thinner of the two, showing a significantly shorter flameout time.
Samples After Burn Test
Conclusions

The Cone Calorimeter is an effective small-scale test that can be used as development tool to predict the fire behavior of a composite material in a full-scale burn test such as the E-84

Time and money saving development tool compared to the cost of running multiple full-scale tests

Measuring the very specific processes and stages of combustion and fire on the Cone Calorimeter can be used to predict full scale fire behavior

Effective tool to match fire performance of an existing, competitive flame retardant product or to improve fire performance and economics of an existing composite material
Thank you!

Our thanks to ICL Industrial Products for the use of their Cone Calorimeter to conduct the burn tests.