FR Composite Development Utilizing the Cone Calorimeter

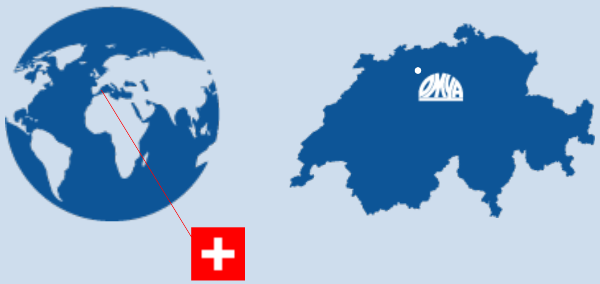
Glade Squires

THINKING OF TOMORROW

omya.com

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**



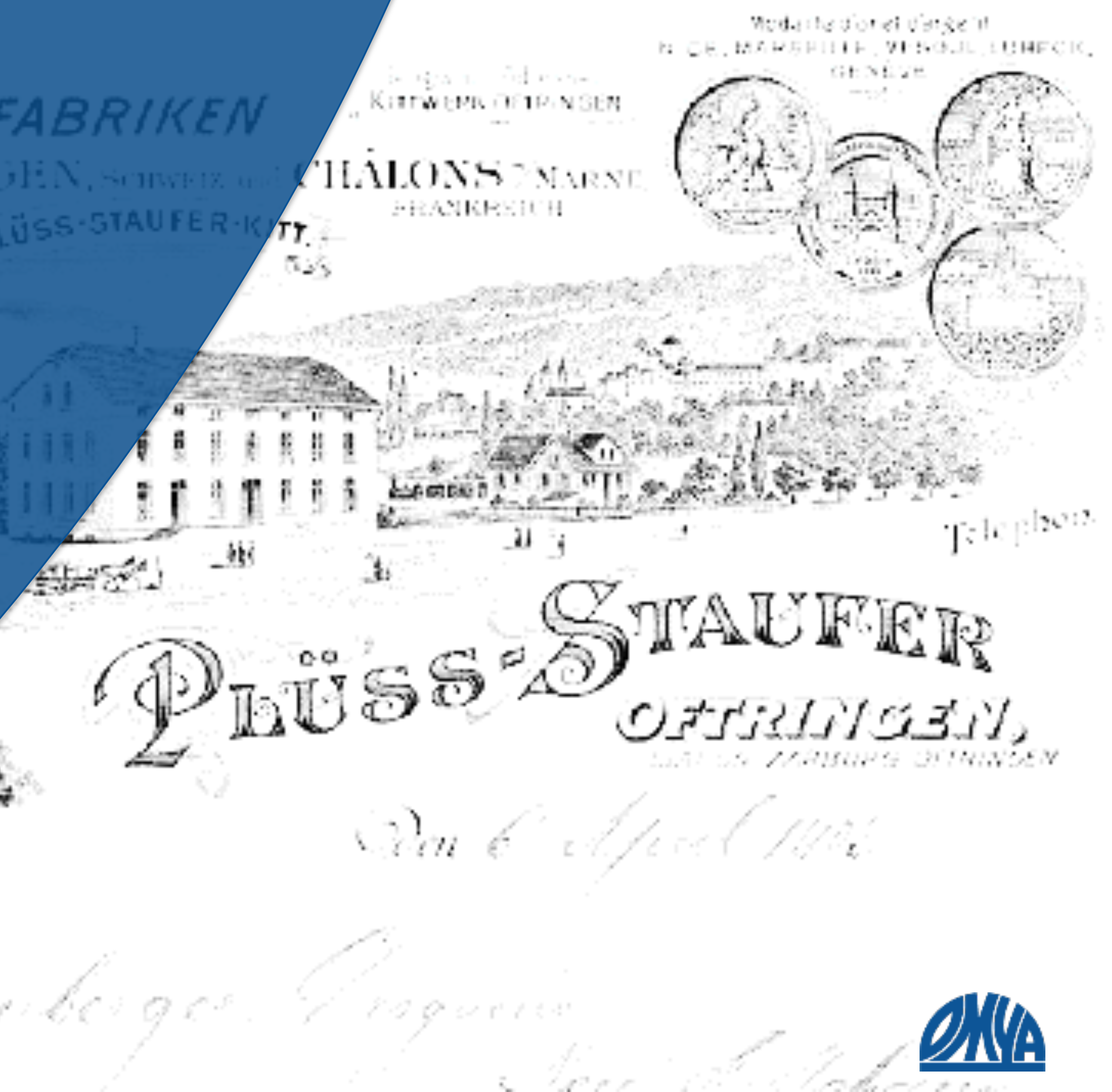
High-quality, innovative products and environmental solutions to multiple industries:

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

Bromine

- **Additive**
  Singular, Bromine containing organic molecules
- **Reactive**
  Bromine containing organic molecules with one or more chemically reactive groups
- **Oligomeric Polymeric**
  Long chain bromine containing organic compounds / Brominated resins

Chlorine

- **Additive**
  Singular, Chlorine containing organic molecules
- **Reactive**
  Chlorine containing organic molecules with one or more chemically reactive groups
- **Oligomeric Polymeric**
  Long chain Chlorine containing organic compounds, PVC, Chlorinated resins

Non-Halogen Flame Retardants

Higher load levels required versus Halogen / Antimony systems

Non- Halogen

Phosphorus

Elemental Red Phosphorus

Phosphoric Acid salts

Phosphorus containing organic compounds

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

Nitrogen

High Nitrogen content organic compounds

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

Metal Hydroxides

Absorb heat and release water upon decomposition

Highly Endothermic Decomposition (absorbs heat)

Magnesium Hydroxide - $Mg(OH)_2$

$Mg(OH)_2 \rightarrow MgO + H_2O$ @ 330°C

Alumina Trihydrate – $Al(OH)_3$

$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$ @ 230°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

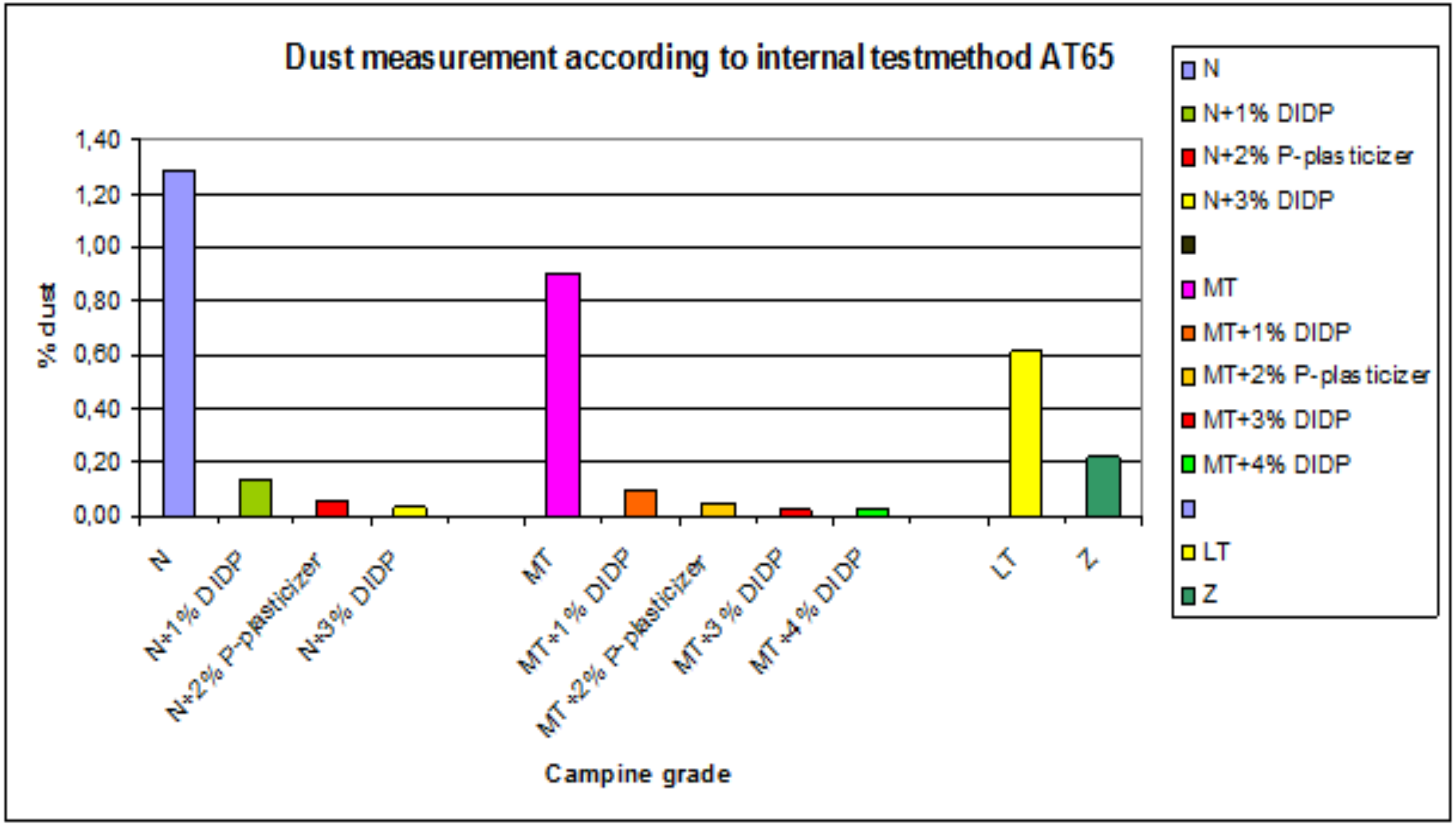
Antimony Oxide's particle range is 0.8 microns to 1.5 microns depending on the grade

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

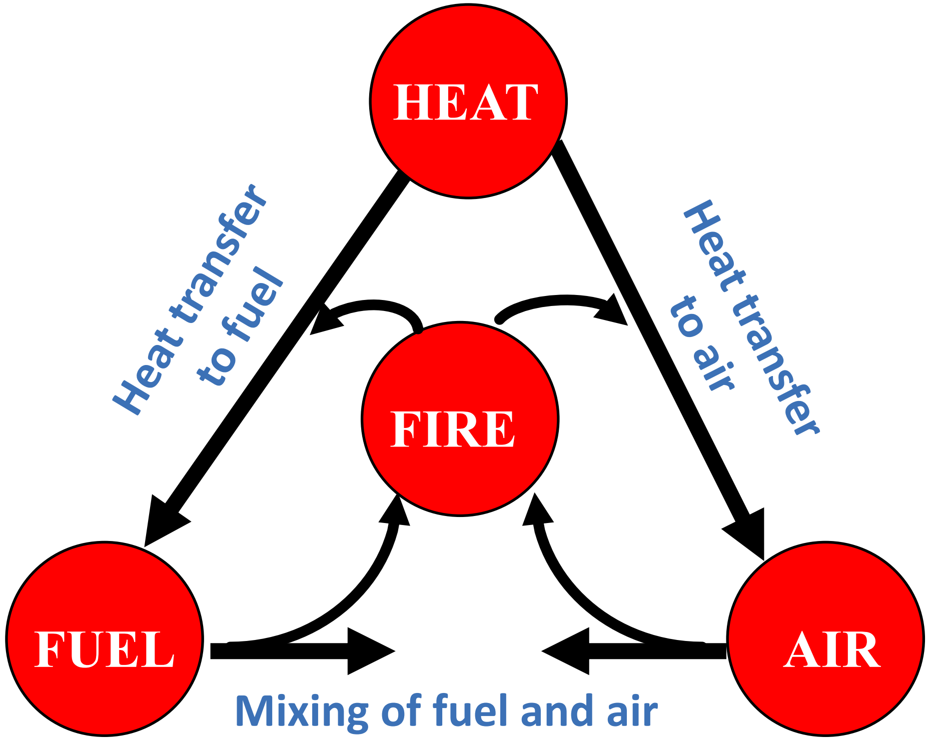
Dust Levels of Various Grades – Standard Powder and Wetted



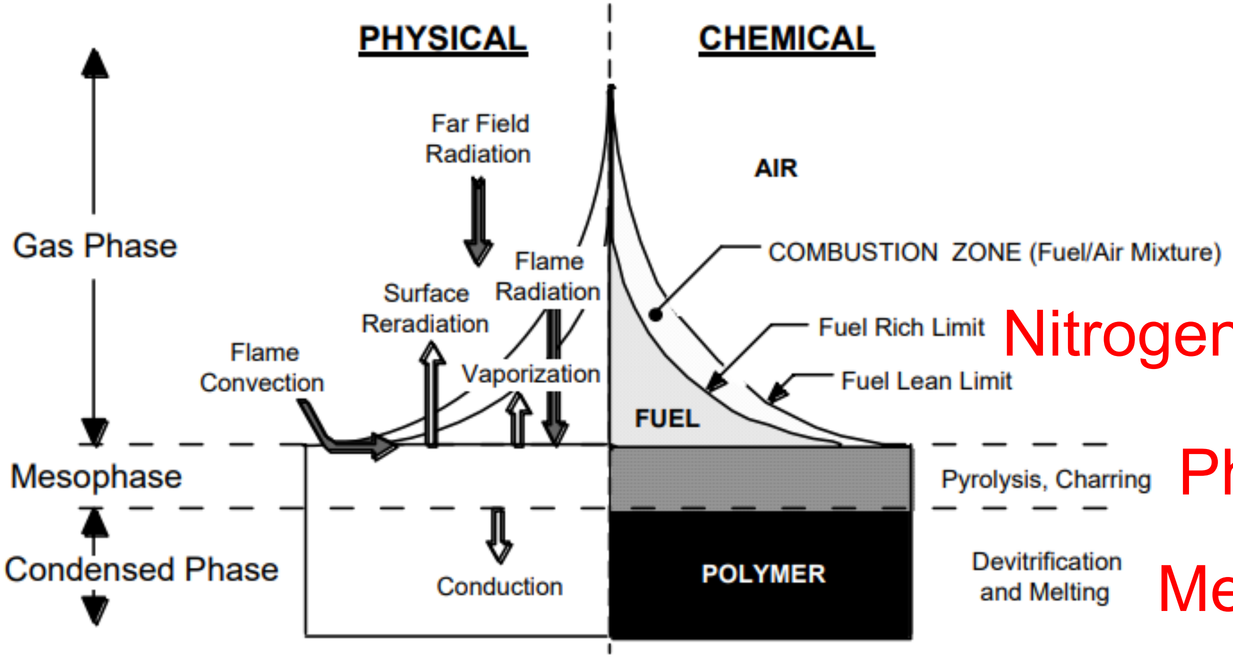
Grade	Microns
N	0.8 to 1.0
MT	1.3 to 1.5
LT	2.0 to 2.5
Z	8.0 to 13

Fire

Fire consists of five distinct stages - heating, decomposition, ignition, combustion and propagation



Physical and Chemical Processes of Combustion



Halogen Antimony

Nitrogen / Water Vapor

Intumescence

Charring

Phosphorus / Nitrogen

Metal Hydroxides

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

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

Campine

ICL Industrial Products
Where needs take us

Italmatch Chemicals

Larderello Group

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.

	Flame-Spread Index (FSI)	Smoke Development Index (SDI)
Class 1 or Class A	0-25	450 Maximum
Class 2 or Class B	26-75	450 Maximum
Class 3 or Class C	76-200	450 Maximum

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.

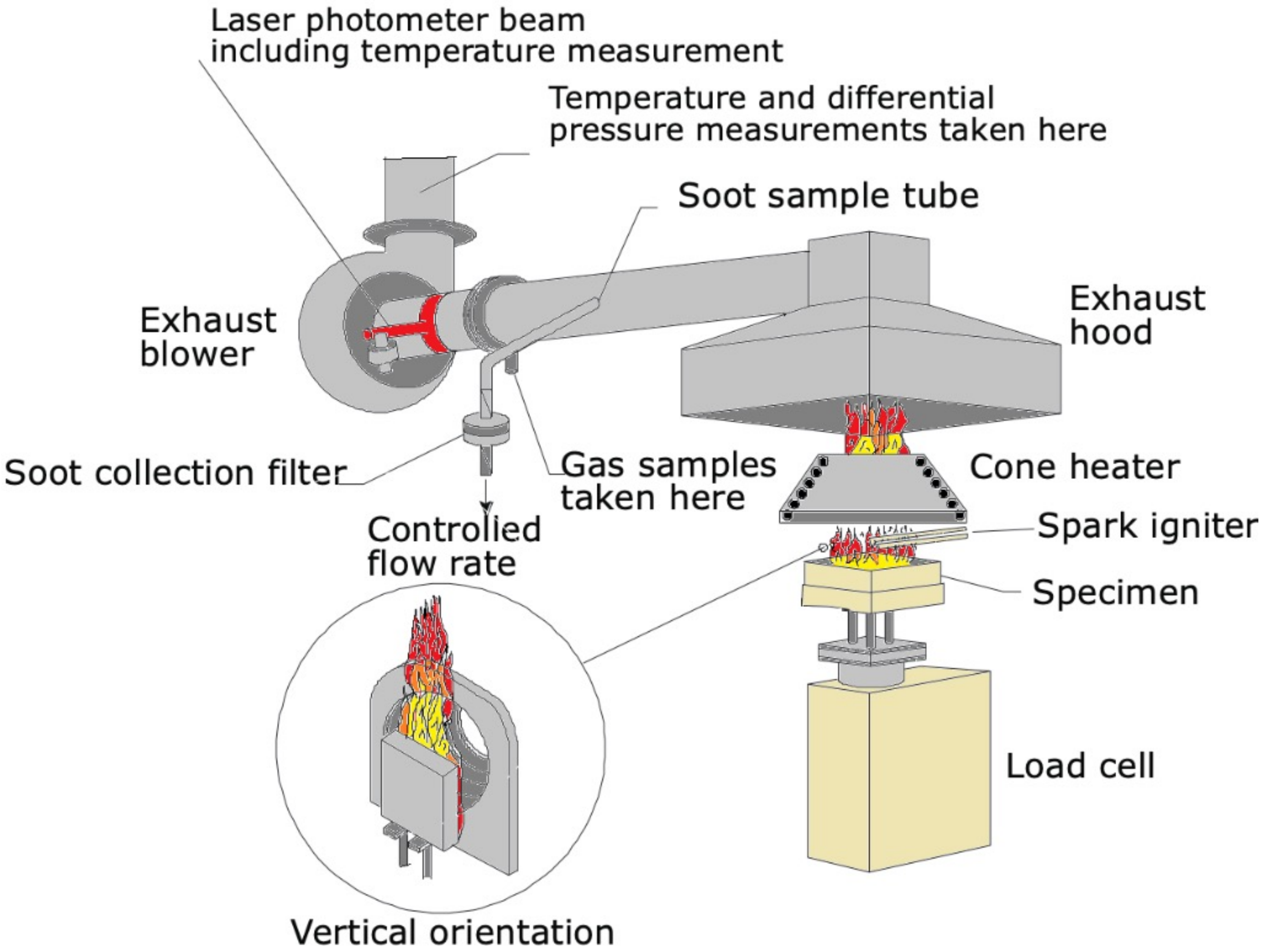
Most important parameters measured are;

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

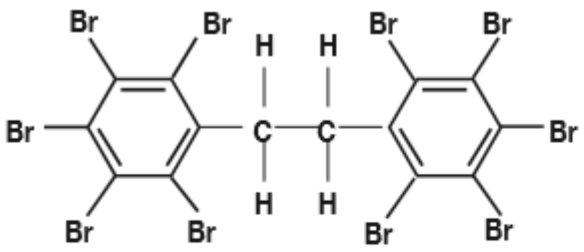
Developed by the Fire Research Division at NIST in 1982



Additive FR Formulation

FR-1410 – ICL Industrial

Chemical name:	Decabromodiphenyl Ethane
Formula:	$C_{14}Br_{10}H_4$
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

- Sb203% is specified: min 99,8 %
- Pb, As, Fe are specified :
  - Pb: max 1000ppm
  - 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 to1 level, Bromine FR to Antimony ratio

Cone Calorimeter Data – Small Test Panels

Formulation	FR Current (Thin)	FR 1410 (Thin)	FR Current (Thick)	FR 1410 (Thick)
Thickness (mm)	5.13	5.00	9.75	9.10
Starting mass (g)	42.53	42.70	60.78	50.98
Finished mass (g)	19.72	19.78	30.40	26.82
Mass lost (g)	22.81	22.92	30.38	24.16
t-ignition (s)	30	30	28	28
t-flame out (s)	285	257	568	457
t-end (s)	390	366	673	564
Peak HRR (kW/m2)	324.83	273	251.3	379.2
t-peak (s)	39	33	42	33
THR (MJ/m2)	38.8	35.4	53.0	45.2
HRR @ 60s (kW/m2)	232.9	204.2	186.2	196.3
HRR @ 120s (kW/m2)	189.8	181.7	133.4	145.8
HRR @ 180s (kW/m2)	175.5	165.5	113.8	129.0
HRR (avg) (kW/m2)	107.7	105.4	82.2	84.4
MLR (avg) (g/(s*m2))	6.33	6.82	4.72	4.51
EHC (avg) (MJ/kg)	16.99	15.45	17.45	18.72
SPR (avg) (m2/s)	0.0613	0.0689	0.0386	0.0348
SEA (avg) (m2/kg)	1046.3	1099.7	856.5	812.5
Fuel load (MJ/kg)	9.11	8.29	8.72	8.87
MARHE (kW/m2)	161.9	153.1	136.7	145.6
TSP (m2)	23.9	25.2	26.0	19.6
FIGRA (W/s)	8.631	8.278	7.075	11.794

HRR = Heat Release Rate

THR = Total Heat Released

MLR = Mass Loss Rate

EHC = Effective Heat of Combustion

SPR = Smoke Production Rate

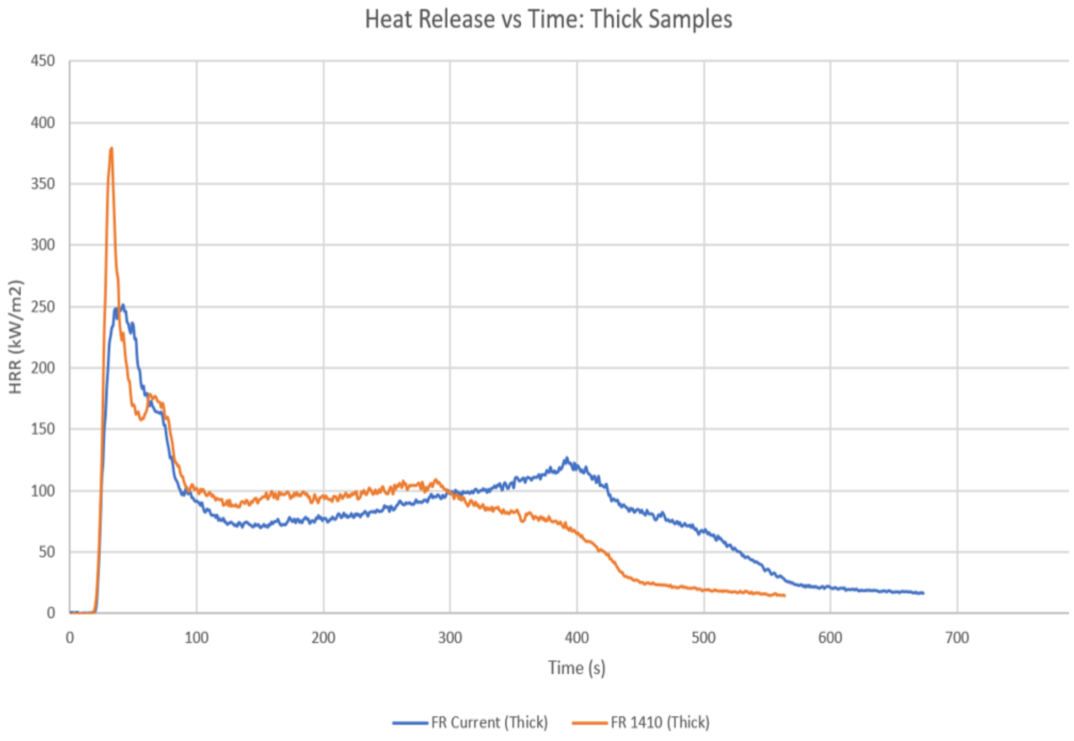
SEA = Specific Extinction Area

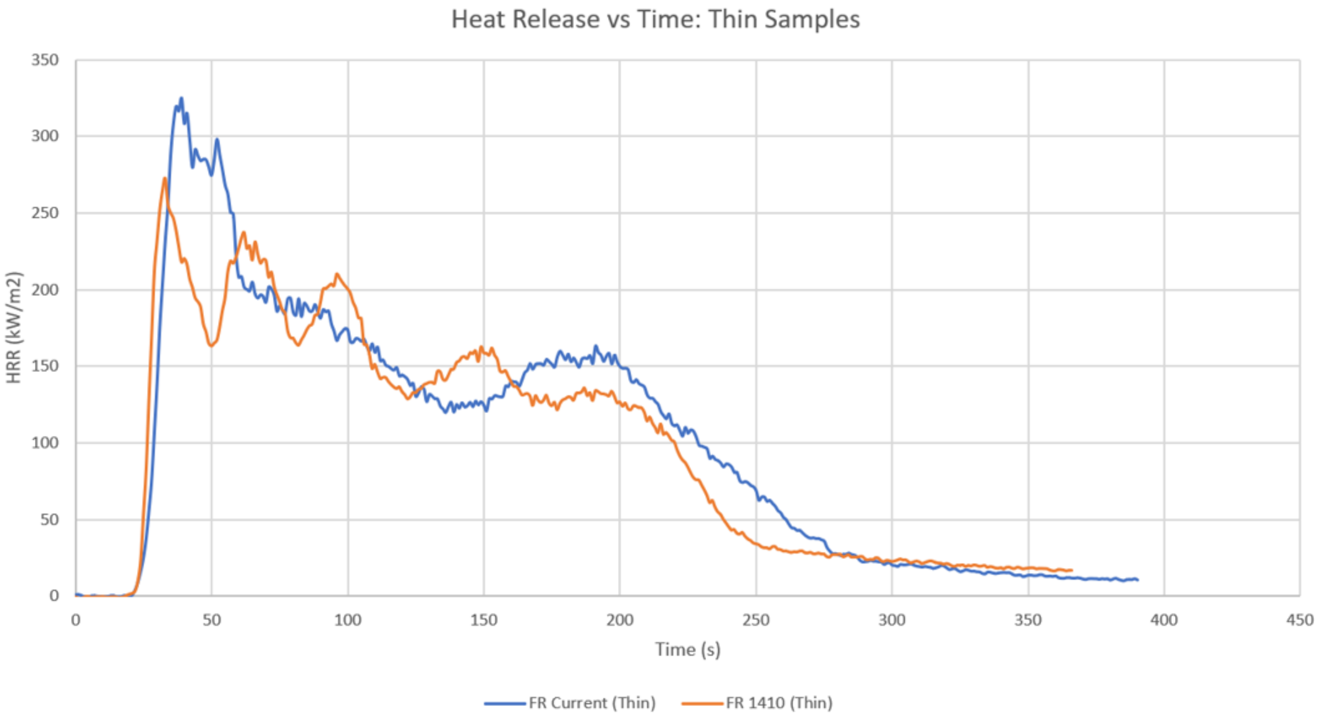
MARHE = Max Average Rate Heat

TSP = Total Smoke Produced

FIGRA = Fire Growth Rate

Cone Calorimeter Data – Hand Made Test Panels





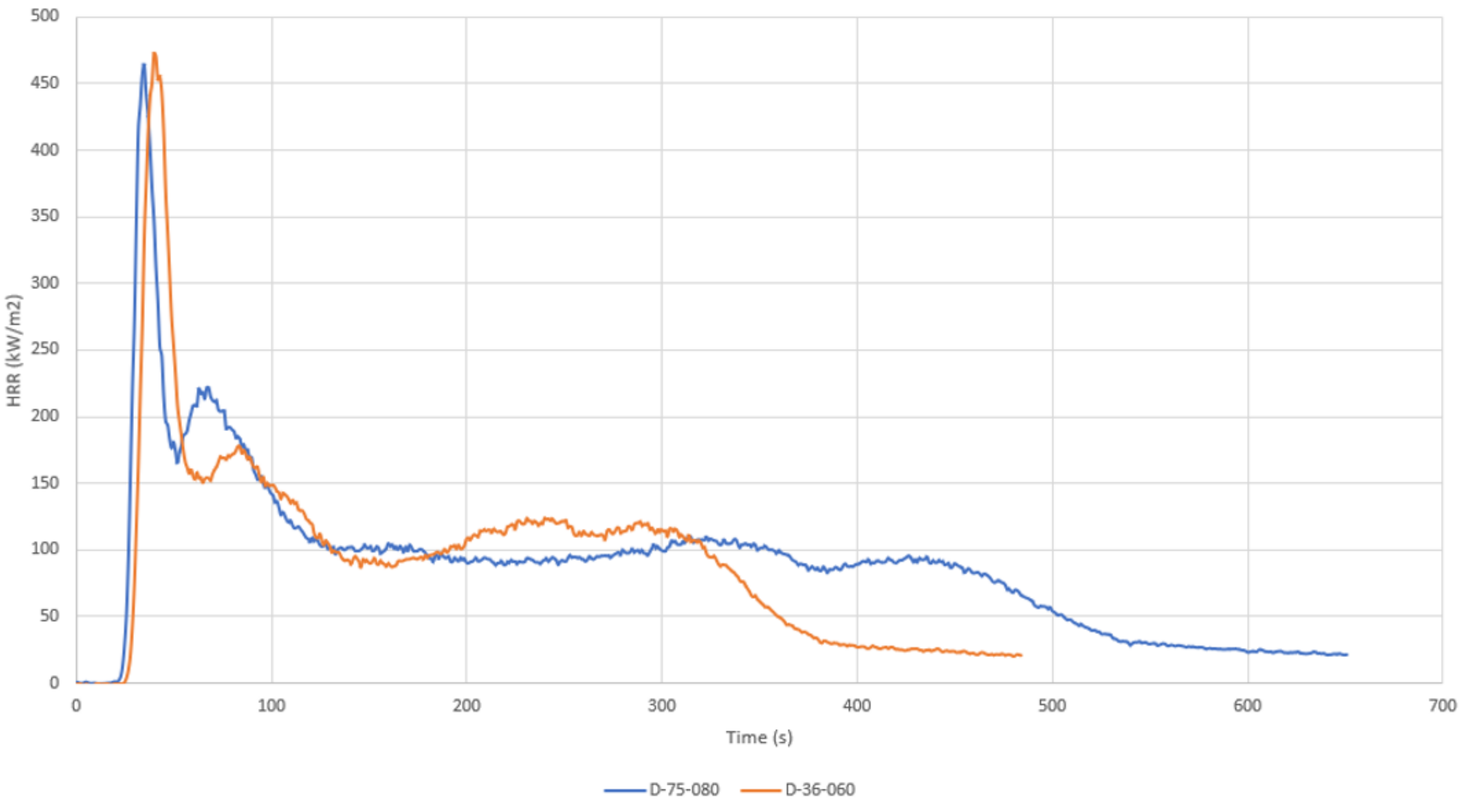
June 22, 2020

Cone Calorimeter Data – Production Panels

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

D-75-080 – Thick Panel

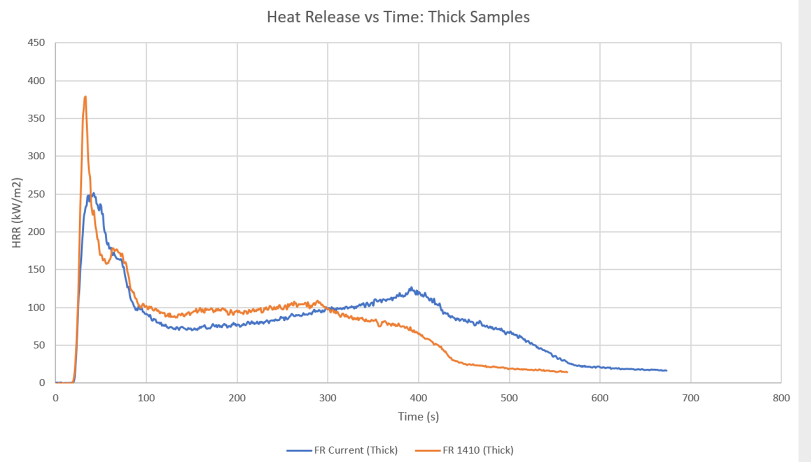
D-36-060 – Thin Panel

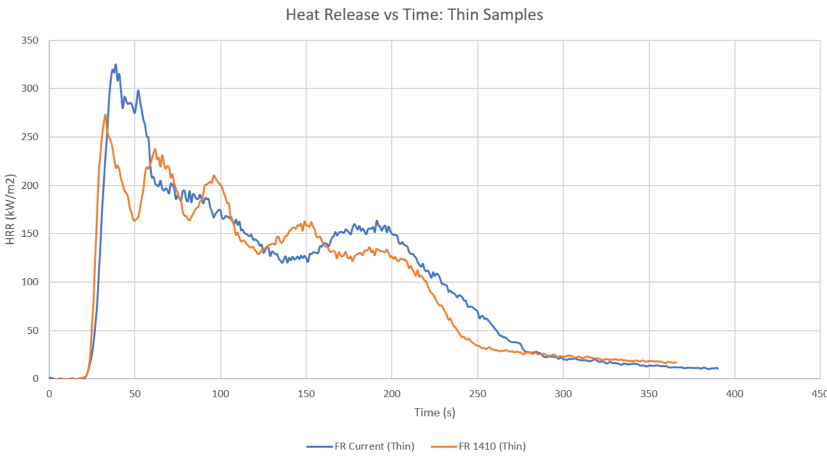


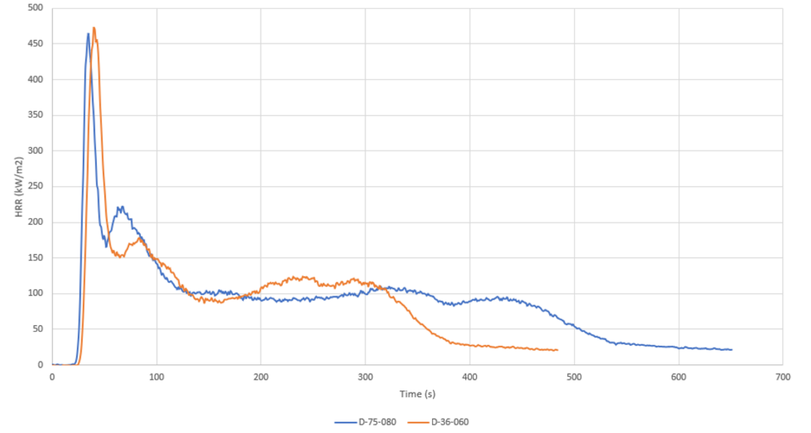
Heat Release Rate Comparisons

- 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.

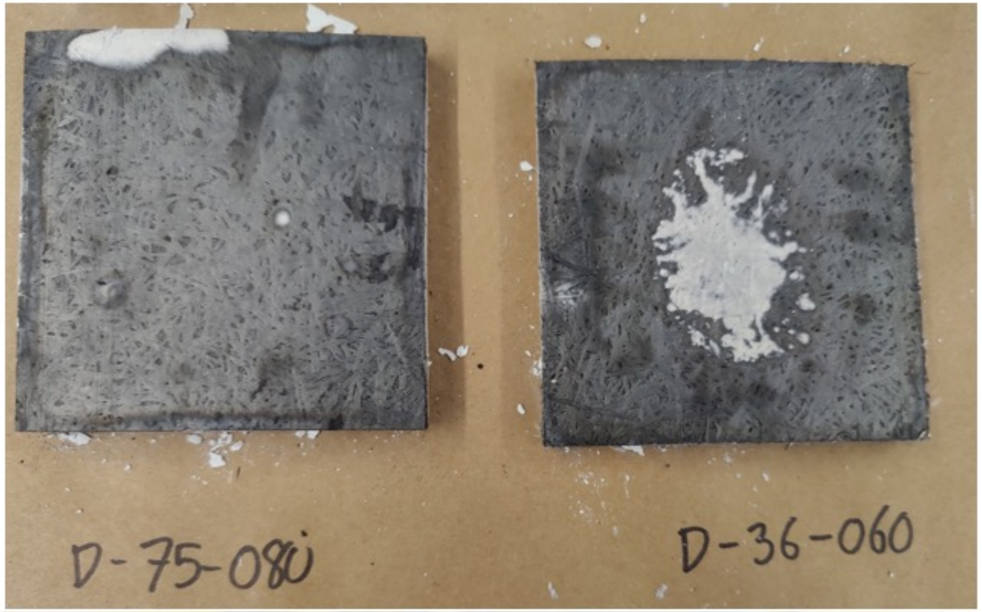
- Heat release behavior between the two samples was remarkably similar. Sample D-36-060 exhibited slightly higher peak and average heat release rates, by a nearly negligible margin. The significant difference in thickness between the two samples resulted in sample D-36-060, the thinner of the two, showing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

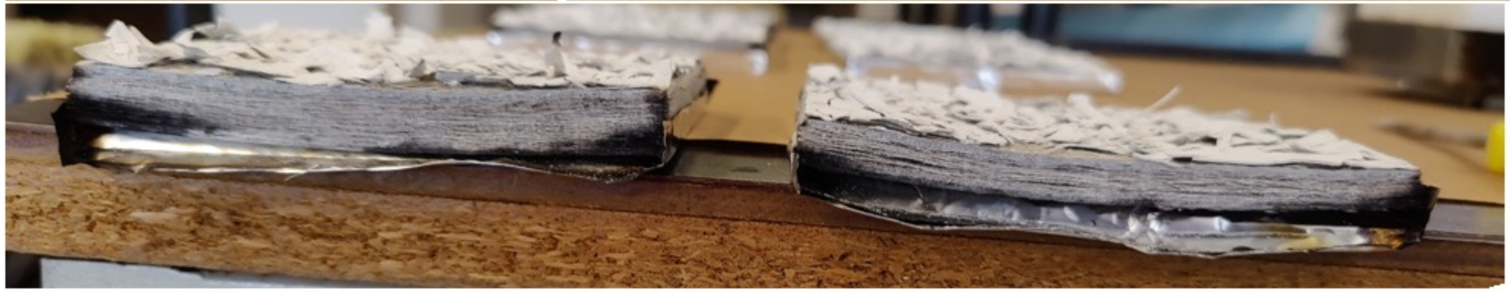






Samples After Burn Test





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.