What is the GC3?

• Cross-sectoral, B2B network of over 100 companies and other organizations
• Formed in 2005
• Collaboratively advances green chemistry across sectors and supply chains
Over 100 members across sectors and value chain
GC3 Green & Bio-based Chemistry Startup Network

• Support the growth of green and bio-based chemistry start-ups

• Provide visibility for innovative startups and small companies with great technologies

• Help connect startups with established chemical suppliers, brands, retailers and investors who can serve as strategic development and commercialization partners

• Advance the discussion on how best to accelerate green chemistry innovation and the growth of innovative startups
Today’s Speakers

Liz Harriman  
Deputy Director, Massachusetts Toxics Use Reduction Institute

Amit Paul  
Managing Director, Paxymer

Jan-Pleun Lens  
VP Research and Applications, FRX Polymers
Ground Rules

• Due to the number of participants in the webinar, all lines will be muted

• If you have a question or comment, please type it in the “Questions” box located in the control panel

• Questions will be answered at the end of the presentation
Flame Retardants and Fire Safety

GC3 Webinar
Mar 2, 2017

Liz Harriman - TURI
Why do we use Flame Retardants?

• We use polymerized fuels (hydrocarbons) as materials of construction
• Flame Retardants are an attempt to delay ignition of flammable materials

Fire safety and flammability standards, building codes, insurance co. standards
FR Plastics Markets - $18B Global Industry

- **Consumer Electronics and Electrical Equipment (50%)**
  - Audio/video, IT
  - Printed circuit boards
  - Appliances
  - Lighting
  - Wire and cable

- **Transportation: (Railways, ships, aircraft, automotive, 25%)**:
  - Linings
  - Seating
  - Coverings

- **Building & Construction (12.5%)**:
  - Foams
  - Films
  - Linings
  - Floorings
  - Piping

- **Furniture & furnishings (12.5%)**:
  - Upholstered furniture
  - Mattresses
  - Textiles

Average Annual Growth Rate of Flame Retardants ~6-7%

Source: FR Plastics Markets
Flame Retardant (FR) Substances

• Halogens
  – Bromine (BFRs), Chlorine (e.g., PBDEs, HBCD, polymeric BFRs)

• Phosphorous, phosphorus + halogens (e.g., triphenyl phosphate, chlorinated tris)

• Antimony (e.g., antimony trioxide ATO)

• Metal salts and hydroxides (e.g., aluminum or magnesium hydroxide)

• Nitrogen (e.g., melamine)

• Nano-clays
Halogenated Organic Flame Retardants

- PBDEs – deca-BDE, penta-BDE
- TBBPA
- TBPP
- Firemaster 550
  - TBPH (brominated DEHP)
  - Triphenyl phosphate

- Endocrine disruptors
- Developmental and reproductive toxins
- Persistent and bioaccumulative

- Increasing concern, regulatory actions, supply chain restrictions
Regrettable Substitutions

PentaBDE
Phased-Out (2005)

TDCIPP

Firemaster 550®

EH-TBB
BEH-TBPH
ITPs

Courtney Carignan - 2015
Thank-you

Liz Harriman
harriman@turi.org
www.turi.org

Massachusetts Toxics Use Reduction Institute
University of Massachusetts Lowell
600 Suffolk St. Suite 501
Lowell, MA 01854
Greener flame retardants: An overview

What are green flame retardants?
- Legislation is governed by the "precautionary principle"
- According to the EU and Stockholm Convention
  - Not PBT - Persistent, Bio-accumulating, Toxic
  - Not POPs - Persistent Organic Pollutants
  - (REACH/CLP): Novel Hazard (H) or Risk (R) phrases
  - Not CMR - Carcinogenic, Mutagenic, Toxic to Reproduction
  - Not EDC - Endocrine Disrupting

Industry nomenclature: "Eco-friendly" "Halogen free" "Non-brominated"

Where are we today?

Macro trends
- Cheaper materials
- Greener materials
- Increased producer responsibility
- More regulation

Safety vs Environment

Key drivers:
- Revision of ER standards
- OEMs / Brand owners / Producer responsibility
- Legislation

In a nutshell:
Focus on the holistic balanced product performance - meeting performance, fire and commercial requirements

The push for fire safety
Where are we today?

Macro trends
- Cheaper materials
- Greener materials
- Increased producer responsibility
- More regulation (?)

Key drivers:
- Revision of FR standards
- OEMs / Brand owners / Producer responsibility
- Legislation

In a nutshell:
Focus on the holistic balanced product performance - meeting performance, fire and commercial requirements
What are green flame retardants?

- legislation is governed by the "precautionary principle"

Green according to the EU and Stockholm convention
- Not PBT - Persistent, Bio-accumulating, Toxic
- Not POPs- Persistent Organic pollutant
- (REACH/CLP: No/few Hazard (H) or Risk (R) phrases)
- Not CMR - Carcinogenic, mutagenic, toxic to reproduction
- Not EDC - Endocrine disrupting

Industry nomenclature: "Eco-friendly" "Halogen free" "Non-brominated"

It is "safe" (Fire marshalls definition)
- Reducing fire spread (Low PeakHRR, FIGRA) including non-dripping
- Low Smoke - smoke opacity
- Low smoke toxicity - mainly -NOX, SOX, HCl, HBr (CO/CO2)
Paxymer vs Brominated V0 material

Paxymer (PP-Co, 1.6 mm)  Brominated (PP-Co, 1.6 mm)
The push for fire safety

Material

UL94-V0 Pass criteria:
- Self extinguishing
- No burning drops

2 x 10 s of burning, 50W flame

Component / Application

Euroclass (SBI-test)
- FIGRA, Peak-HRR
- Smoke (composition and temp)
- Dripping/Pool fire

20 min of burning 30-90 kW flame, modeled fire scenario
Incentives in the supply chain are screwed - innovation benefits material suppliers and brand owners.

Elimination of hazardous chemicals is a substantial supply chain challenge. Initiatives such as the GC3 that connect parties from different segments is critical for its success.
Summary: Green flame retardants

- Green flame retardants are defined as non-persistent, non-toxic and non-bio accumulating
- The main driver on the market are changing fire standards, the OEMs/brand owners and legislation
- The challenge is to find a competitive solution and meet: commercial, processing and performance requirements
- There are several options available in the sustainable segment but there is no "one size fits all".

Responsible procurement, product specification and supply chain management is key to successful implementation.
"In the 1950s you had approximately 15 minutes to get out of a burning building. In 1990s you had approximately 2 minutes."

The innovation:
Boosting the performance of halogen free flame retardants

Reduces amount of smoke and smoke toxicity, free from corrosive gasses

Eliminates burning drops and thereby re-ignition of surrounding materials

Prevents flame spread by controlling heat release

Stabilizes the material and controls the degradation into hazardous bi-products

New Generation Flame Retardants

... free from persistent and endocrine disrupting chemicals
Paxymer is a novel technology that address the industrial problem with halogen free flame retardants
<table>
<thead>
<tr>
<th>Application</th>
<th>Company</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wash-machine ventilation</td>
<td>Confidential</td>
<td>Blow mouldable HDPE formulation that meet US fire requirements.</td>
</tr>
<tr>
<td>Designer office furniture</td>
<td>Confidential</td>
<td>Green solution that meet IMO and CAITB fire standards &amp; performance criteria</td>
</tr>
<tr>
<td>Conduits (electrical)</td>
<td>Confidential</td>
<td>Meets cold impact requirements and FR requirements for corrugated conduits (PP)</td>
</tr>
<tr>
<td>Optical cable ducts</td>
<td>GM plast</td>
<td>Working solution for HDPE optical cable ducts. Mechanical and processing perf.</td>
</tr>
</tbody>
</table>
Cost and weight savings. Substitution of PA for PP with retained performance.

Success factors

- Project coordinated by 3M
- Clear idea of target performance
- Openness to try new ideas:
  Welding masks are traditionally done in PA - PP could however meet the performance and commercial spec.
- Few "fixed variables" - focus on the final product
- Close 3 party collaboration between 3M, Paxymer and injection molding subcontractor until product approval.
Potential applications: flame retardant polyolefins in DIY – an educated guess

Compatible materials
- PP - polypropylene
- PE - polyethylene
- TPE - thermoplastic elastomer
- EVA - ethylene vinyl acetate
- WPC (PP + wood fiber)
- TPO

Example applications
- Electrical power tools
- Power cords / conduits
- Cables
- Lamp plugs / electrical
- Furniture (some markets)
- Wall cladding
- Insulation (wall / pipe)
- Housings (?)

Paxymer is an enabling technology that helps you achieve functional, halogen-free performance
Novel Polyphosphononates for Multiple Flame Retardant Applications

GC3 Webinar, March 02, 2017
Mega Trends

✓ Halogen Free
  • Persistent
  • Bio Accumulation
  • Toxic in to humans
  • Continuous pressure from NGOs on OEMs

✓ Polymeric FR Solutions
  • Non-migrating / low fogging
  • Widely perceived as safest FR approach (customers & regulatory bodies)
  • Bromine FR suppliers now offering polymeric forms of Bromine
  • Due to Polymeric nature – more than just an FR additive
  • Nofia is the only halogen-free Polymeric FR additive available today
Non-Halogenated Flame Retardants

- Phosphorous, Inorganic and Nitrogen containing Flame retardants
- Information on applications and regulatory information is available ([www.pinfa.eu](http://www.pinfa.eu))
- Applications range from Thermoplastics, Foams, Textiles, Paints/Coatings, Adhesives, Thermosets, and Wire and Cables

### Inorganic
- Aluminum Trihydroxide (ATH)
- Magnesium Hydroxide (MDH)
- Aluminum oxide hydroxide (AOH)
- LDPE, PP, EVA
- Wire & Cable
- Not volatile
- Requires high amounts

\[
2 \text{Al(OH)}_3 \xrightarrow{200^\circ \text{C} + 1050 \text{kJ/kg}} 3 \text{H}_2\text{O} + \text{Al}_2\text{O}_3 \\
\text{Mg(OH)}_2 \xrightarrow{300^\circ \text{C} + 1300 \text{kJ/kg}} \text{H}_2\text{O} + \text{MgO}
\]

### Nitrogen Based
- Melamine Cyanurate (MC)
- Melamine Polyphosphate (MPP)
- Melam, Melem, Melon
- Polyamides, Polypropylene
- Electrical Equipment
- Generally used as synergist with phosphor based FRs

### Phosphor Based
- Red Phosphorus
- Aryl Phosphates (BDP and RDP)
- Metal and Inorganic Phosphinates
  - Polyphosphonates
- PE, EVA
- Polyamides, Polyesters
- PC (blends)
- PPO, (HI)PS
- Epoxies
- EE&CE, B&C, Transportation
- Used as additives or mixed with polymer systems as reactive ingredients

FRX polymers®
## Flame Retardant Types

<table>
<thead>
<tr>
<th>Polymeric</th>
<th>Phosphor Based FRs</th>
<th>Halogenated FRs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polyphosphonates</strong></td>
<td>+ Halogen free + Do not migrate + Favorable toxicity profile. + Do not bioaccumulate + Melt processable and transparent + Deliver more properties than only FR</td>
<td><strong>Brominated polymers</strong> + Do not migrate from host plastic – Use antimony trioxide as synergist – Formation of dioxins and furans possible at incomplete incineration</td>
</tr>
<tr>
<td>Small Molecules</td>
<td><strong>Phosphates, phosphinate salts, DOPO</strong> + Halogen free – Can migrate from host plastic – Can negatively affect thermal and mechanical properties of host plastic (act as plasticizer) – Environmental concerns</td>
<td><strong>PBEs, PBDEs, TBBPA, decaBDE, HBCD</strong> – Persistent, Bioaccumulate, Toxic – Use antimony trioxide as synergist – Migrate from host plastic – Formations of dioxins and furans at incomplete incineration</td>
</tr>
</tbody>
</table>
Nofia Phosphonates - Sustainable FRs

- NOFIA polyphosphonates have favorable health profile and obtained a Benchmark Score of 3 in the GreenScreen assessment.
- Recognized by the EPA as one of the FR alternatives for DecaBDE.
- NOFIA polyphosphonates are registered in almost all countries that have a polymer exemption process (Australia pending).
- All monomers are registered under REACh (production facility is in Europe).
NOFIA Polyphosphononates, A Unique FR Solution

- Polymer:
  - Permanent and will not migrate out
  - Minimal impact on host plastic properties
  - Possible to use plastic processing methods
- Non-halogen flame retardant
- Extreme FR properties
- High melt flow
- Transparent
- Range of toughness
## FRX POLYMERS’ Products - Characteristics

### Nofia Homopolymer
- Polyphosphonate (P ~ 11wt%)
- High molecular weight (40-100,000 g/mole, PS)
- Tg ~ 100-105°C
- Plastic pellets
- Typically used as blend component in plastics

### Nofia Copolymers
- Polyphosphonate-co-carbonate (P ~ 3-7 wt%)
- High molecular weight (40-100,000 g/mole, PS)
- Tg ~ 120-135°C
- Plastic pellets
- Used as stand alone polymer or blend component in plastics

### Nofia Oligomers
- Phosphonate oligomers
- Tailored end groups
- Low molecular weight (1,000 – 6,000 g/mole)
- 35 - 70 mg KOH/g
- Solid white material
- Used as reactive ingredient in thermoset applications
FRX Polymers’ Fit with the Plastic Market

Triangle of Thermoplastics
Classified by Market Share

High Performance Polymers
<1% (~ 1 Mio t)

Engineering Plastics
10% (~ 23 Mio t)

Standard Plastics

- PS & EPS 70%
- PET 7%
- PP 23%
- PE 34%
- PUR 6%
- PVC 16%

90% (~ 227 Mio t)

Source: PlasticsEurope Market Research Group (PEMRG)/Consultic Marketing & Industrieberatung GmbH
Applications with Nofia Phosphonates

PET monofilament, multifilament, staple, and bulk continuous fibers for FR textiles, non-wovens, carpets, and synthetic hair

BOPET films and FR PET shrink tubes

Epoxy applications like copper clad laminates for rigid and flexible PCB and coatings for insulators, motors

Structural panels for transportation (aviation, railway)

PET and PUR foam for structural and automotive applications

FR TPU for coatings and wire and cable
Fibers (Carpets, Textiles, Synthetic Hair)

**NOFIA FR delivers:**
- Melt processability → dry blending with the base fiber-polymer at the hopper
- Flexibility of base polymer (e.g. use recycle PET, PTT)
- FR performance at relatively low loadings
- Flexibility of addition level of FR (higher than 6,000ppm P)
- No limitation in fiber diameter
- Enhancement of spinning process and eliminates need for filter packs,
- No deterioration of fiber properties
- No secondary operations to add FR compound necessary
- No migration

**Target Polymer System**
- Polyesters

**FRX POLYMERS’ Solution**
- NOFIA HM1100
Commercial Inherent FR PET Options

- **Trevira CS**
  - Phosphinate built into PET chain
  - Later moved to CEPPA
  - Work cloths, Furniture

- **Toyoba Heim I and Heim II**
  - Phosphonate or phosphinate based
  - Heim II has pendant P-based groups

- **CEPPA containing PET**
  - Phosphinate built into the chain
  - Many Asian producers

- **Disadvantages for all options**
  - FR PET producer: Dedicated equipment or special production campaigns
  - FR PET user: Limited choice in P content (~6,000ppm max)
Nofia Provides Flexibility Choice of Raw Materials

- Improved quality versus current products
  → color, mechanicals (tenacity)

- No need for special FR PET

- Can use multiple PET sources
  - Regular PET
  - Recycled PET

- Options to add FR to biobased polyesters
  - PLA containing polyester blends
    (Natureworks)
  - PTT (Sorona®, DuPont)
  - Polyethylene furanoate (Avantium)
"Interior materials - Classification according to their reaction to fire"

- **NF P 92-503 (1995) - “Electric Burner”**
  - Classification M1 to M4; M1 is the highest
  - Specimen is placed in a specimen holder at 30° above a radiator which gives out heat
  - Duration of the flame; Burning droplets; Dimensions of damaged specimen

- **NP P 92-504 (1995) - “Flame Persistence & Rate of Flame Spread”**
  - Complimentary to electric burner test
  - Helps classify unusual behaving samples in NF P 92-503 “Electric Burner”

- **NF P 92-505 (1995) - “Dripping Test”**
  - Complimentary to electric burner test
  - Investigates potential hazard of burning droplets observed during electric burner test
### NF P 92-507 – “M1”

**Method**

<table>
<thead>
<tr>
<th>NF P 92 - 505</th>
<th>NF P 92 - 503</th>
<th>NF P 92 - 504</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>No ignition of the wool</td>
<td>Not-burning droplets</td>
<td>-</td>
</tr>
<tr>
<td>No ignition of the wool</td>
<td>Burning droplets</td>
<td>M4</td>
</tr>
<tr>
<td>Ignition of the wool</td>
<td>Not-burning droplets</td>
<td>M4</td>
</tr>
<tr>
<td>Ignition of the wool</td>
<td>Burning droplets</td>
<td>M4</td>
</tr>
</tbody>
</table>

**Ignition time =< 5s**
- M1
- M1

**Ignition time > 5s; damaged length < 350mm**
- M2
- M2

**Ignition time > 5s; damaged length between 450mm and 600mm; damaged width < 90mm**
- M3
- M3

---

### NF P 92-504 (1995) - “Flame Persistence” (for melting materials)

<table>
<thead>
<tr>
<th>Classification</th>
<th>M1</th>
<th>M2</th>
<th>M3 a</th>
<th>M3 b</th>
<th>M4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration of Combustion</td>
<td>none</td>
<td>&lt;5s</td>
<td>&lt;5s</td>
<td>&gt;5s</td>
<td>&gt;5s</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Droplets</th>
<th>None or non burning</th>
<th>None or non burning</th>
<th>Burning</th>
<th>None or non burning</th>
<th>Burning</th>
</tr>
</thead>
</table>
NF P 92-507 – “M1”

- Knitted fabric specimens were made from a false-twisted PET yarn (130, dtex (225), f 38 bright-3.5 dtex/filament).
- Washing, drying and conditioning of all specimens was conducted according to ISO 6330 (2000-2008), using washing procedure 5A.


<table>
<thead>
<tr>
<th></th>
<th>Length</th>
<th>Width</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Face A</td>
<td>Face B</td>
</tr>
<tr>
<td>Hole formation</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Max. afterflame time (s)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Afterglow</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Afterglow with propagation in area &gt; 25 cm</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Damaged length (cm)</td>
<td>16.5</td>
<td>15.0</td>
</tr>
<tr>
<td>Damaged width (cm) in area &gt;45 cm</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Flaming molten droplets</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Non-flaming molten droplets</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Flaming debris</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Non-flaming debris</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Average damaged length (cm)</td>
<td>17.0</td>
<td></td>
</tr>
<tr>
<td>Average damaged width (cm) in area &gt; 45 cm</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

M1: <= 5

M1: None
NF P 92-507 – “M1”

NP P 92-504 (1995) - “Rate of Flame Spread”

<table>
<thead>
<tr>
<th>Specimen</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>*</td>
<td>*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>#2</td>
<td>*</td>
<td>*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>#3</td>
<td></td>
<td>*</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>#4</td>
<td></td>
<td></td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>#5</td>
<td></td>
<td></td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>#6</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>#7</td>
<td>*</td>
<td>*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>#8</td>
<td>*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>#9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>#10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*: afterflame time $\leq 2$ s
$> 2$ s: afterflame time $> 2$ s and $\leq 5$ s
$> 5$ s: afterflame time $> 5$ s

- M1: None
- Flaming debris: no
- Non-flaming debris: yes

M1: None or non burning
NF P 92-507 – “M1”

NF P 92-505 (1995) - “Dripping Test”

Four specimens, two on both sides, have been tested.

<table>
<thead>
<tr>
<th></th>
<th>First ignition (s)</th>
<th>Non-flaming debris</th>
<th>Flaming debris</th>
<th>Ignition cotton wool</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>face A</td>
<td>*</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>#2</td>
<td>face B</td>
<td>*</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>#3</td>
<td>face A</td>
<td>*</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>#4</td>
<td>face B</td>
<td>*</td>
<td>yes</td>
<td>no</td>
</tr>
</tbody>
</table>

* no ignition

M1: None
Additional FR Tests

● **ISO 15025: Method for limited flame spread**
  - Procedure A: Ignition on the surface – **No after flame / glow time, no flaming drops**
  - Procedure B: Ignition at the edges – **No after flame / glow time, no flaming drops**

● **EN 597: Assessment of the ignitability of mattresses and upholstered bed bases**
  - Part 1: Ignition source: Smoldering cigarette: **No ignition**
  - Part 2: Ignition source: Match flame equivalent: **No ignition**

● **EN 13773: FR fabric test curtains and drapes – Class 1**
  - EN 1101 + A1 Textiles – Burning behavior – Curtains and drapes - Textile fabrics-
    Determination of the ignitability of vertically oriented specimens. **No ignition**
  - EN 13772 - Textiles and textile products – Burning behavior – Curtains and drapes.
    Measurement of flame spread of vertically oriented specimens with large ignition source
    **1st marker not reached**
“As a new, innovative company, with a sound focus on sustainability, FRX Polymers has its right place here in Flanders.” - Kris Peeters, minister-president of the Government of Flanders
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NOFIA is a registered trademark of FRX POLYMERS, INC
Question & Answer

• If you have a question or comment, please type it in the “Questions” box located in the control panel

• Questions will be answered in order as they are received.
Upcoming Events

12th Annual GC3 Innovators Roundtable
April 25-27, 2017
Hosted by Steelcase in Grand Rapids, MI

Green & Bio-Based Chemistry Technology Showcase & Networking Event
April 24, 2017, 1:00 - 6:30 pm
Amway Grand Plaza Hotel, Grand Rapids, MI
Thanks for joining us!

For more information about the GC3:
www.greenchemistryandcommerce.org