GC3 Webinar Series

Innovation Spotlight: Greener Flame Retardants

Thursday March 2, 2017

GC3 GREEN CHEMISTRY & COMMERCE COUNCIL
Business Mainstreaming Green Chemistry

What is the GC3?

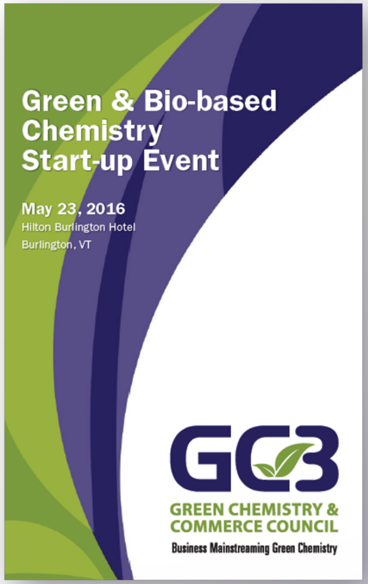
- Cross-sectoral, B2B network of over 100 companies and other organizations
- Formed in 2005
- Collaboratively advances green chemistry across sectors and supply chains

Over 100 members across sectors and value chain

Johnson & Johnson
BEHR
bioamber
SC Johnson A Family Company
LEVI STRAUSS & CO.
BASF The Chemical Company
Chemours
Beiersdorf
AMYRIS
Unilever
BEST BUY
P&G
STAPLES
hp
DELL
ACS Green Chemistry Institute
TARGET
Walmart
CVSHealth
EASTMAN
DOW
L'ORÉAL
Timberland
NB
Steelcase
THE HOME DEPOT
GC3

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

TURI
TOXICS USE REDUCTION INSTITUTE
UMASS LOWELL

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

FRX polymers ®

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

Source: FEPS DR. TROITZSCH ®
Fire and Environment Protection Service

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

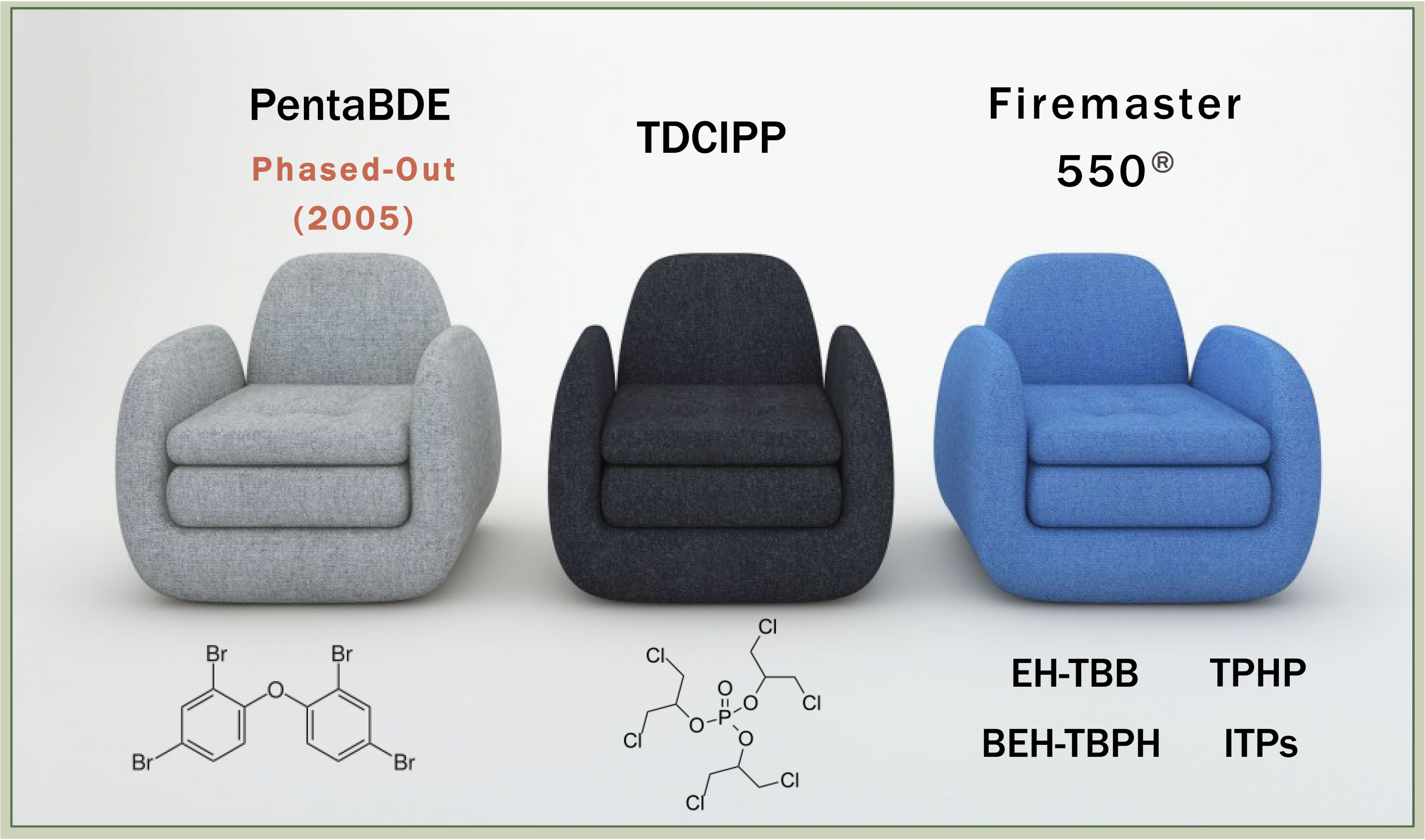
Halogenated Organic Flame Retardants

- 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



Courtney Carignan - 2015

Thank-you

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University of Massachusetts Lowell
600 Suffolk St. Suite 501
Lowell, MA 01854

Paxymer

The flame retardant

GC3 Webinar, March 2, 2017

Amit Paul
Managing Director

Greener flame retardants: An overview

What are green flame retardants?

- legislation is governed by the "precautionary principle"

Green according to the EU and Stockholm convention
- Not PBT - Persistent, Bio-accummulating, 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)

Flame retardant
vs
Fire resistant

Where are we today?

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

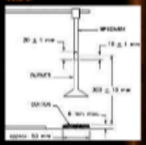
Safety
vs
Environment

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

The push for fire safety

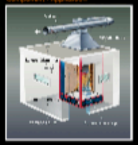
Material



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

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vs
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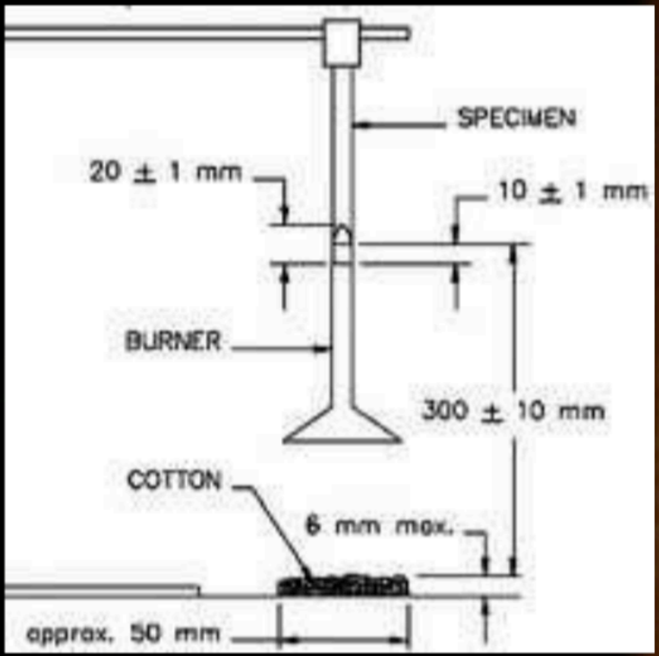
Flame retardant
vs
Fire resistant

Paxymer vs Brominated V0 material

Paxymer (PP-Co, 1.6 mm) Brominated (PP-Co, 1.6 mm)

The push for fire safety

Material



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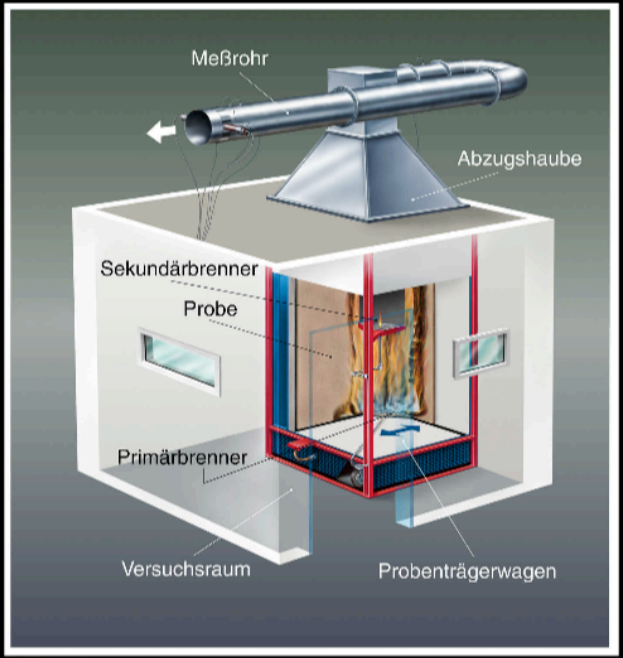

Euroclass (SBI-test)
- FIGRA, Peak-HRR
- Smoke (composition and temp)
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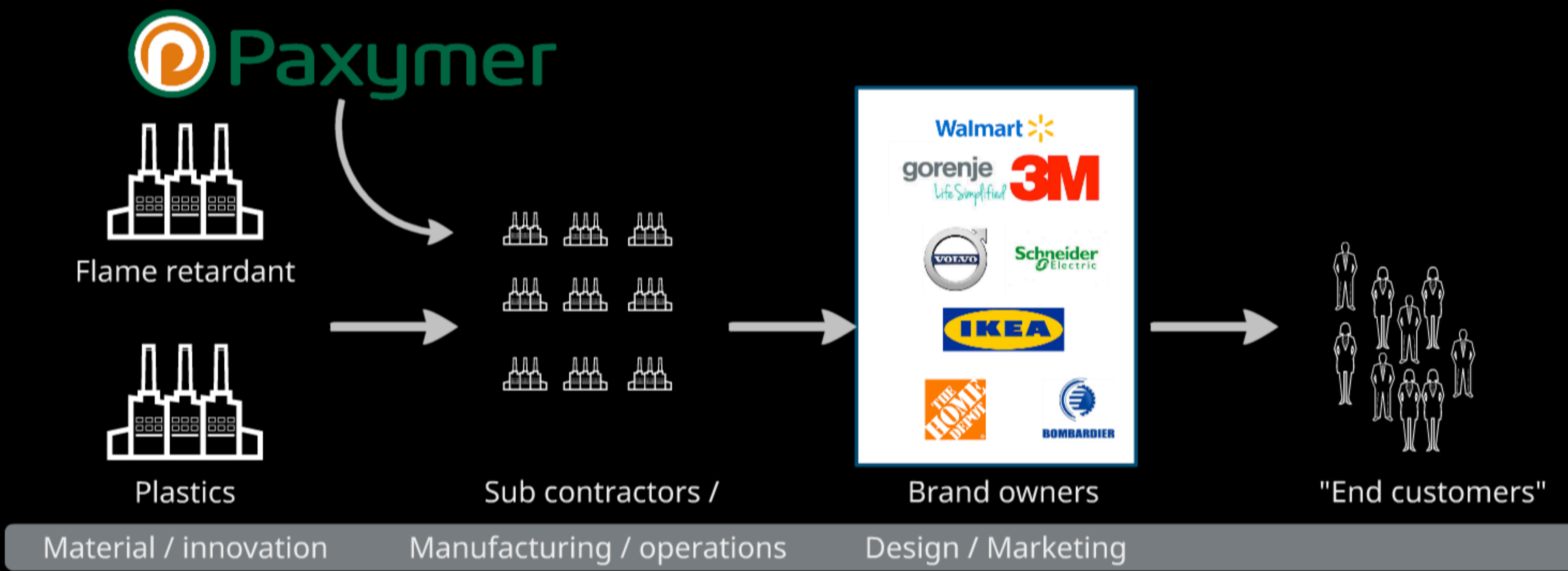
20 min of burning 30-90 kW flame, modeled fire scenario

Incentives in the supplychain are scewed - 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

Paxymer

The flame retardant

"In the 1950s you had approximately 15 minutes to get out of a burning building. In 1990s you had approximately 2 minutes."

- Swedish Civil Contingencies Agency & US Fire marshals (2000)

The innovation:
Boosting the performance of halogen free flame retardants

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

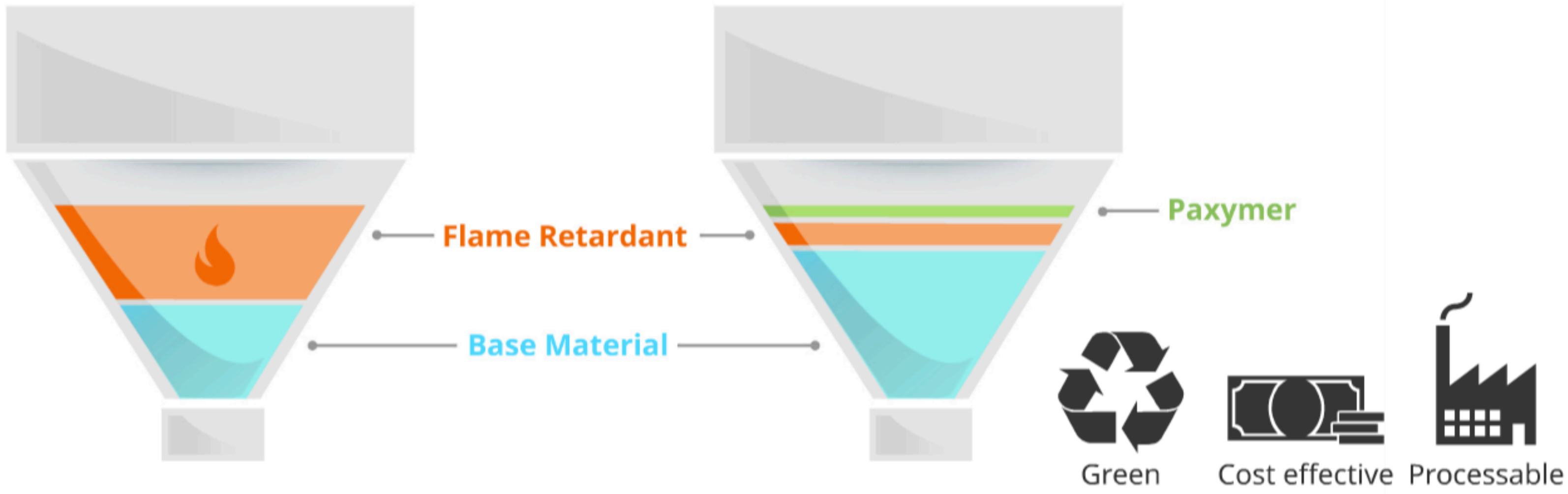
Prevents flame spread by controlling heat release

Eliminates burning drops and thereby re-ignition of surrounding materials

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

... free from persistent and endocrine disrupting chemicals

Paxymer is a novel technology that address the industrial problem with halogen free flame retardants



Cases

Application	Company	Description
Polypropylene welding mask	3M	Cost and weight savings. Substitution of PA for PP with retained performance.
Wash-machine ventilation	Confidential	Blow mouldable HDPE formulation that meet US fire requirements.
Designer office furniture	Confidential	Green solution that meet IMO and CalTB fire standards & performance criteria
Conduits (electrical)	Confidential	Meets cold impact requirements and FR requirements for corrugated conduits (PP)
Optical cable ducts	GM plast	Working solution for HDPE optical cable ducts. Mechanical and processing perf.

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

Paxymer

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+46 8 44 55 302

Novel Polyphosphonates 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

- **P**hosphorous, **I**norganic and **N**itrogen containing **F**lame retardants
- Information on applications and regulatory information is available (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

$$2\ Al(OH)_3 \xrightarrow[+1050\ kJ\ /\ kg]{200°C} 3\ H_2O + Al_2O_3$$

$$Mg(OH)_2 \xrightarrow[+1300\ kJ\ /\ kg]{300°C} H_2O + MgO$$

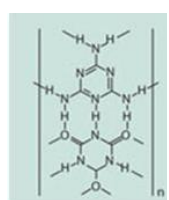
Nitrogen Based

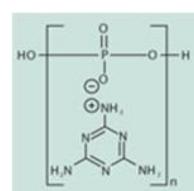
- Melamine Cyanurate (MC)
- Melamine Polyphosphate (MPP)
- Melam, Melem, Melon

- 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

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Flame Retardant Types

← Market Preference

Market Preference ↑

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

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Nofia Phosphonates - Sustainable FRs

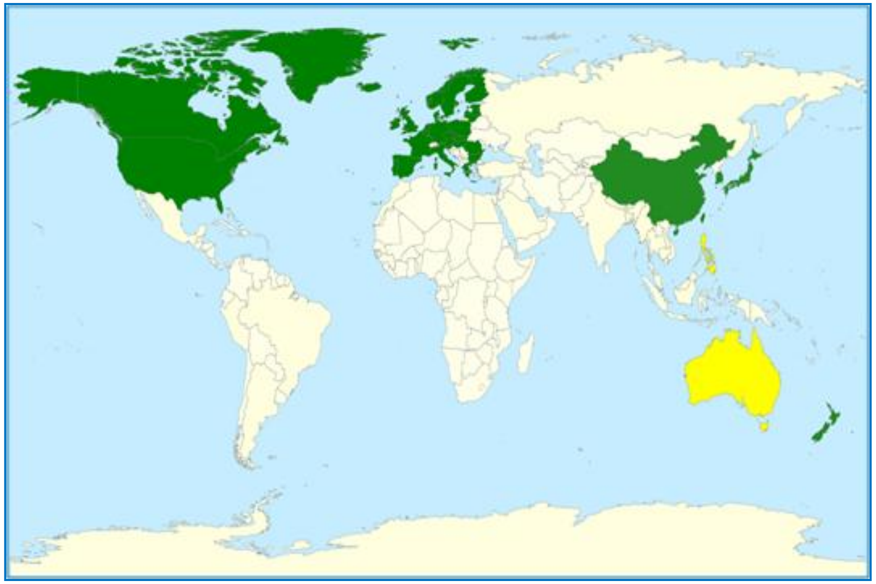
- NOFIA polyphosphonates have favorable health profile and obtained a Benchmark Score of 3 in the GreenScreen assessment.
- Recognized by the EPA as one of the FR alternatives for DecaBDE.
- NOFIA polyphosphonates are registered in almost all countries that have a polymer exemption process (Australia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

Polyphosphonate was assigned a <u>Benchmark Score of 3</u> based on very high persistence. Data gaps (DG) exist for single dose systemic toxicity (ST-single), single dose neurotoxicity (N-single), and respiratory sensitization (SnR). Polyphosphonate meets requirements for a GreenScreen® Benchmark Score of 3 despite the hazard data gaps. In a worst-case scenario, if Polyphosphonate were assigned a high score for respiratory sensitization or a very high score for either single dose systemic toxicity or single dose neurotoxicity it would be categorized as a Benchmark 1 Chemical.

Green Screen Hazard Ratings: [*Polyphosphonate*]																			
Group I Human					Group II and II* Human									Ecotox		Fate		Physical	
C	M	R	D	E	AT	ST		N		SnS*	SnR*	IrS	IrE	AA	CA	P	B	Rx	F
						single	repeated	single	repeated										
L	*L*	*L*	*L*	*L*	L	DG	*L**	DG	*L*	*L*	DG	*L*	*L*	*L*	*L*	*vH*	*vL*	*L*	L

Note: Hazard levels (Very High (vH), High (H), Moderate (M), Low (L), Very Low (vL)) in *italics* reflect estimated values, authoritative B lists, screening lists, weak analogues, and lower confidence. Hazard levels in **BOLD** font are used with good quality data, authoritative A lists, or strong analogues. Group II Human Health endpoints differ from Group II* Human Health endpoints in that they have four hazard scores (i.e., vH, H, M and L) instead of three (i.e., H, M and L), and are based on single exposures instead of repeated exposures.

*While DfE assigned a moderate score for repeat dose toxicity due to possibility of lung overloading as a result of dust forming operations, it has been concluded that this is not a likely exposure scenario based on identified uses and therefore has not been included in the GreenScreen assessment.



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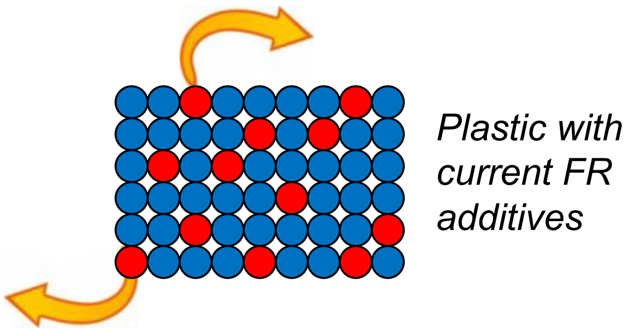
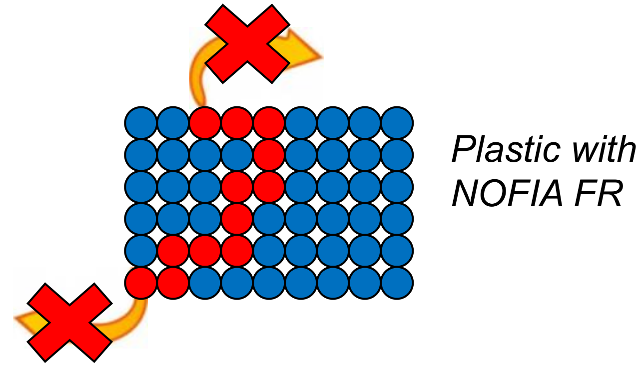
NOFIA Polyphosphonates, A Unique FR Solution



Small molecules end up in environment

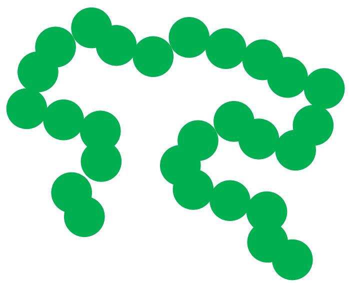


Large molecules trapped in plastic

- 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

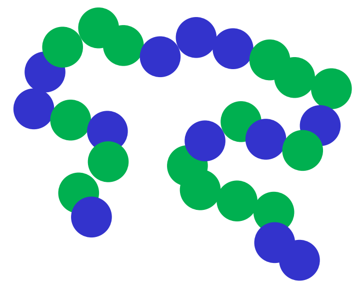
FRX POLYMERS' Products - Characteristics

Nofia Homopolymer



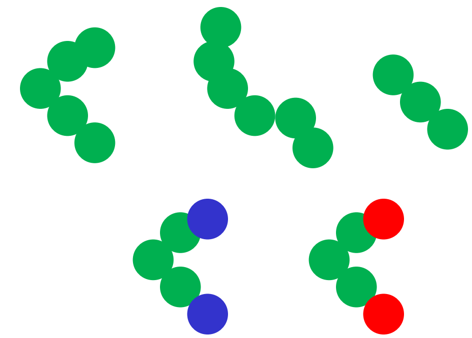
- Polyphosphonate (P ~ 11wt%)
- High molecular weight (40-100,000 g/mole, PS)
- Tg ~ 100-105°C
- Plastic pellets
- Typically used as blend component in plastics

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

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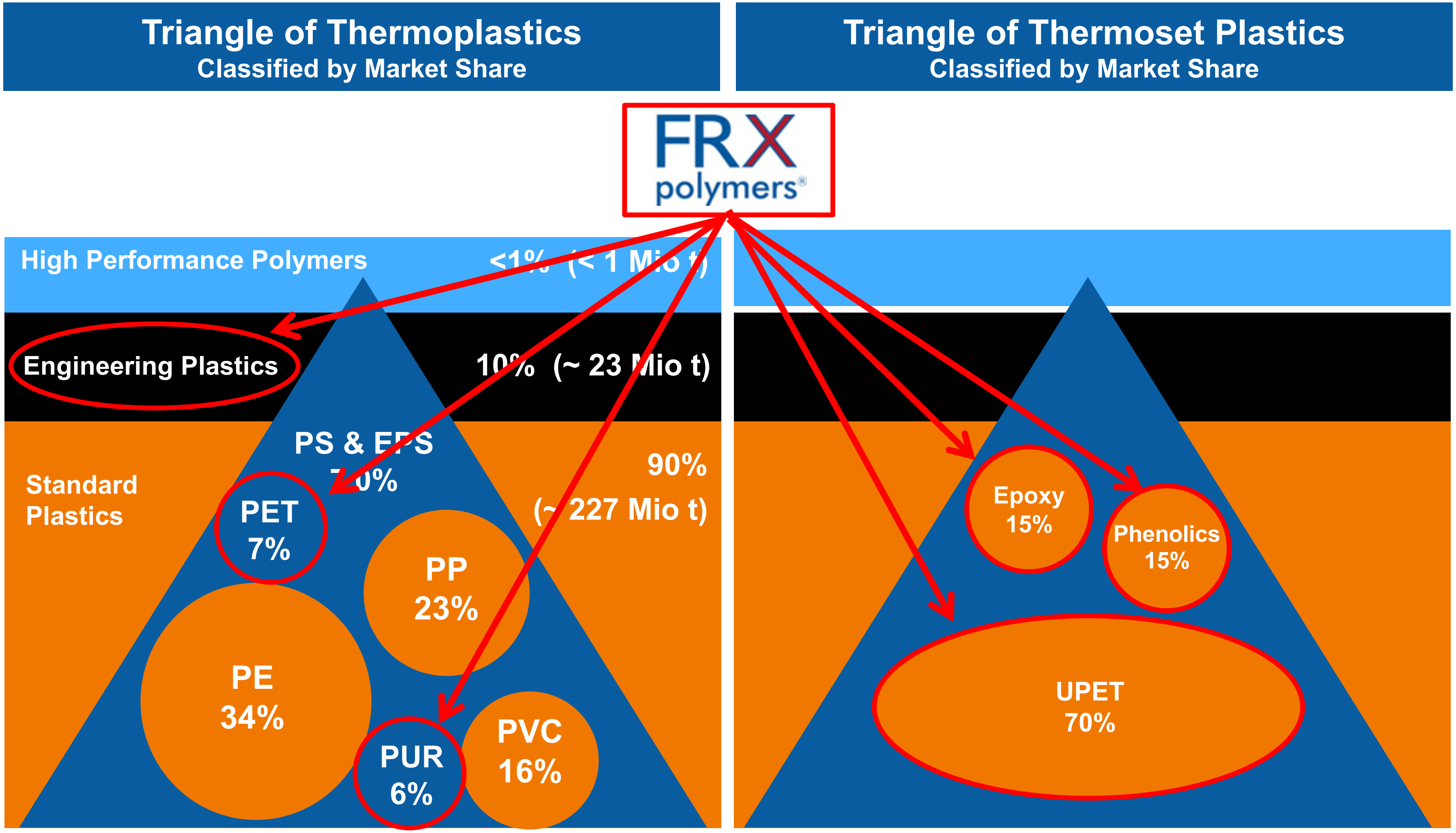
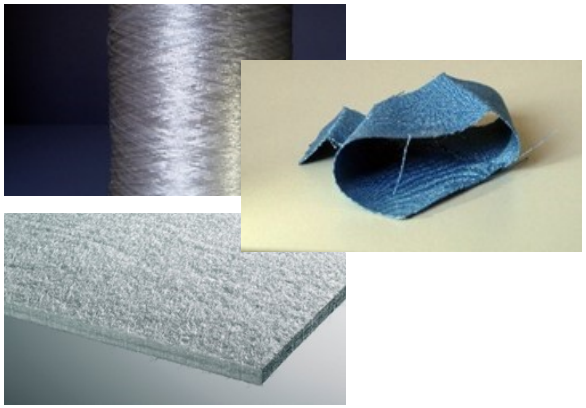
FRX Polymers' Fit with the Plastic Market

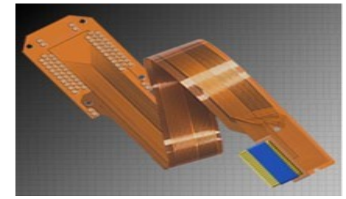
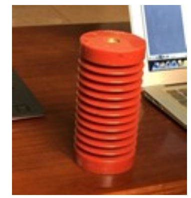
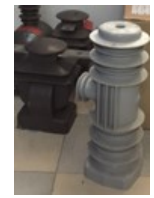


Source: PlasticsEurope Market Research Group (PEMRG)/Consultic Marketing & Industrieberatung GmbH

Applications with Nofia Phosphonates

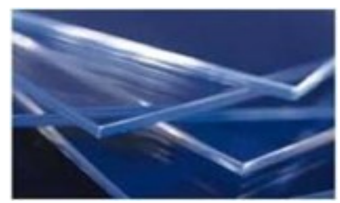



PET monofilament, multifilament, staple, and bulk continuous fibers for FR textiles, non-wovens, carpets, and synthetic hair

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


BOPET films and FR PET shrink tubes



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:

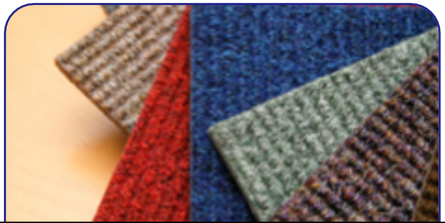
- Melt processability → dry blending with the base fiber-polymer at the hopper
- Flexibility of base polymer (e.g. use recycle PET, PTT)
- FR performance at relatively low loadings
- Flexibility of addition level of FR (higher than 6,000ppm P)
- No limitation in fiber diameter
- Enhancement of spinning 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



Radial Panel Test ASTM E648 Class A

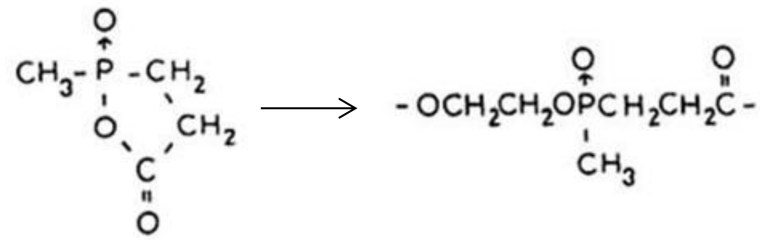
NF P 92-507 M1

FRX polymers ®

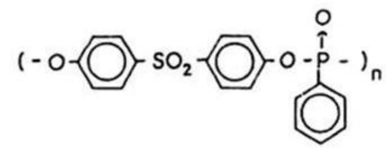
nofia ®

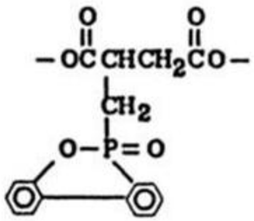
Commercial Inherent FR PET Options

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

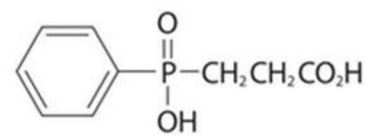


- Toyoba Heim I and Heim II
  - Phosphonate or phosphinate based
  - Heim II has pendant P-based groups





- 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)

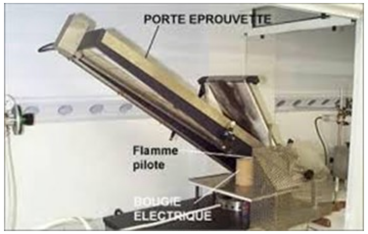
FRX polymers®

nofia®

NF P 92-507 – “M1”

"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



melting materials

- **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	Classes				
NF P 92 - 505	-	No ignition of the wool	No ignition of the wool	Ignition of the wool	Ignition of the wool
NF P 92 - 503	No droplets	Not-burning droplets	Burning droplets	Not-burning droplets	Burning droplets
Ignition time =< 5s	M1	M1	M2	M4	M4
Ignition time > 5s; damaged length < 350mm	M2	M2	M3	M4	M4
Ignition time > 5s; damaged length between 450mm and 600mm; damaged width < 90mm	M3	M3	M4	M4	M4
NF P 92 - 504	-	-	M4	M4	M4

NP P 92-504 (1995) - "Flame Persistence" (for melting materials)

Classification	M1	M2	M3 a	M3 b	M4
Duration of Combustion	none	<5s	<5s	>5s	>5s
Droplets	None or non burning	None or non burning	Burning	None or non burning	Burning

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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.

√ NF P 92-503 (1995) - "Electric Burner"

	Length		Width	
	Face A	Face B	Face A	Face B
Hole formation	yes	yes	yes	yes
Max. afterflame time (s)	0	0	0	0
Afterglow	no	no	no	no
Afterglow with propagation in area > 25 cm	no	no	no	no
Damaged length (cm)	16.5	15.0	16.5	19.0
Damaged width (cm) in area >45 cm	0	0	0	0
Flaming molten droplets	no	no	no	no
Non-flaming molten droplets	no	no	yes	yes
Flaming debris	no	no	no	no
Non-flaming debris	yes	no	no	no
Average damaged length (cm)	17.0			
Average damaged width (cm) in area > 45 cm	0			

M1: <= 5

M1: None

NF P 92-507 – “M1”

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

hest

	Specimen			
	1	2	3	4
#1	*	*	*	*
#2	*	*	*	*
#3	*	*	*	*
#4	*	*	*	*
#5	*	*	*	*
#6	*	*	*	*
#7	*	*	*	*
#8	*	*	*	*
#9	*	*	*	*
#10	*	*	*	*

*: 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

•

•

ng droplets observed during electric burner test

NF P 92-507 – “M1”

√ NF P 92-505 (1995) - “Dripping Test”

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

		First ignition (s)	Non-flaming debris	Flaming debris	Ignition cotton wool
#1	face A	*	yes	no	no
#2	face B	*	yes	no	no
#3	face A	*	yes	no	no
#4	face B	*	yes	no	no

* no ignition

M1: None **M1: None**

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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**

First Commercial Plant in Antwerp

2015 Inauguration

2013 Plant Commissioned

2012 Groundbreaking

"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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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!

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