Application of Flame Retardants in Home textiles (bed linen, mattress ticking curtains and upholstery)

Biella, 12th of July 2019

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Coordinating partner:

Beneficiary partners:

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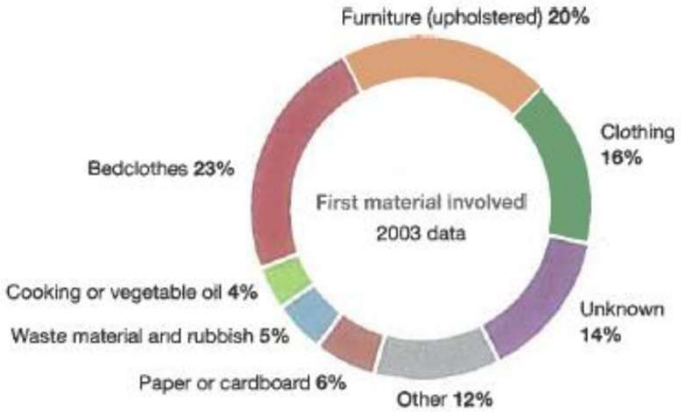
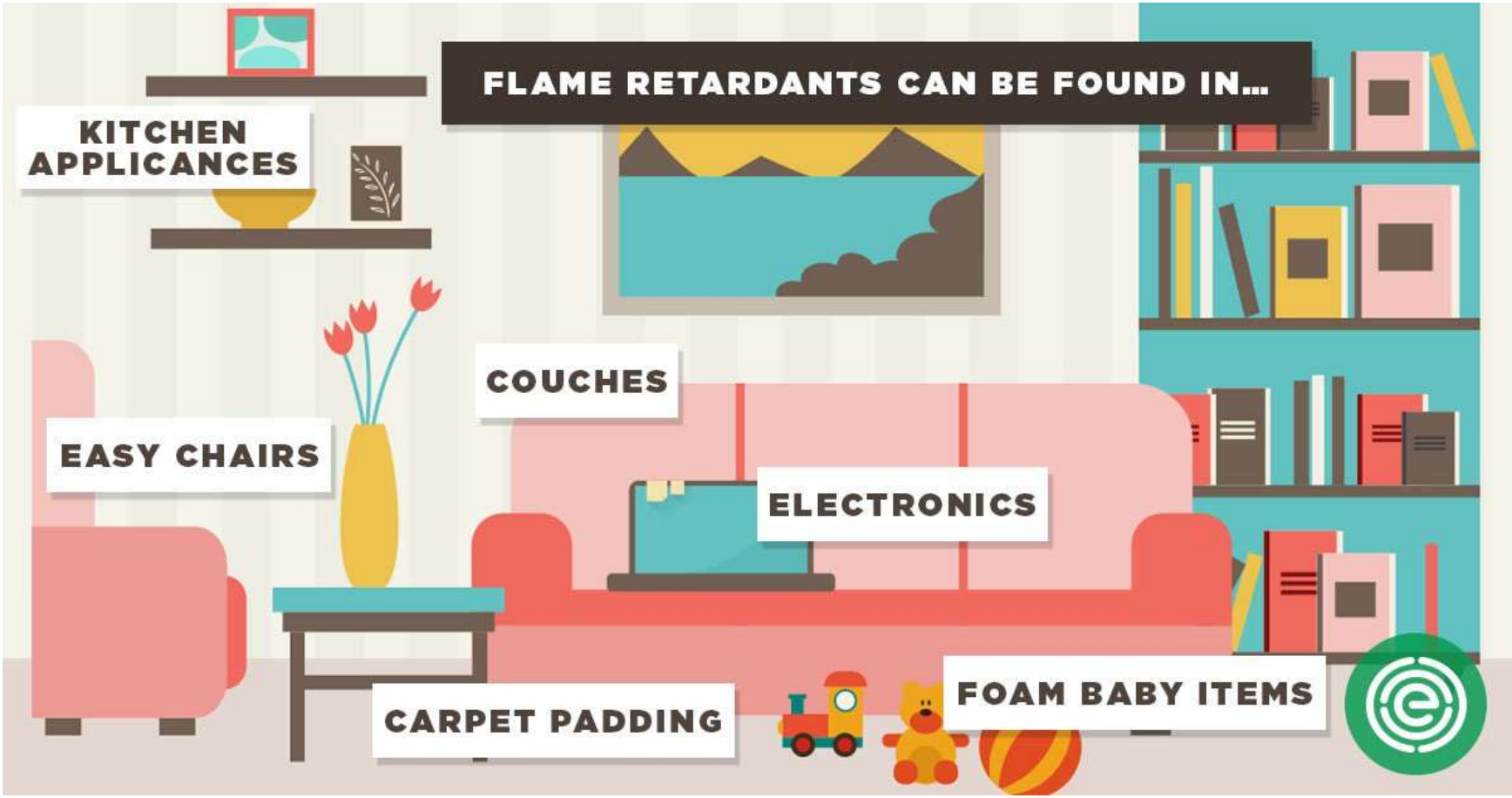
Introduction - Figures

- 2 to 2,5 millions fires each year in Europe
- 80% deadly victims → domestic fires
- 73% of fatal fires start in living or bedroom
- in 59% cases textile involved as first in fire



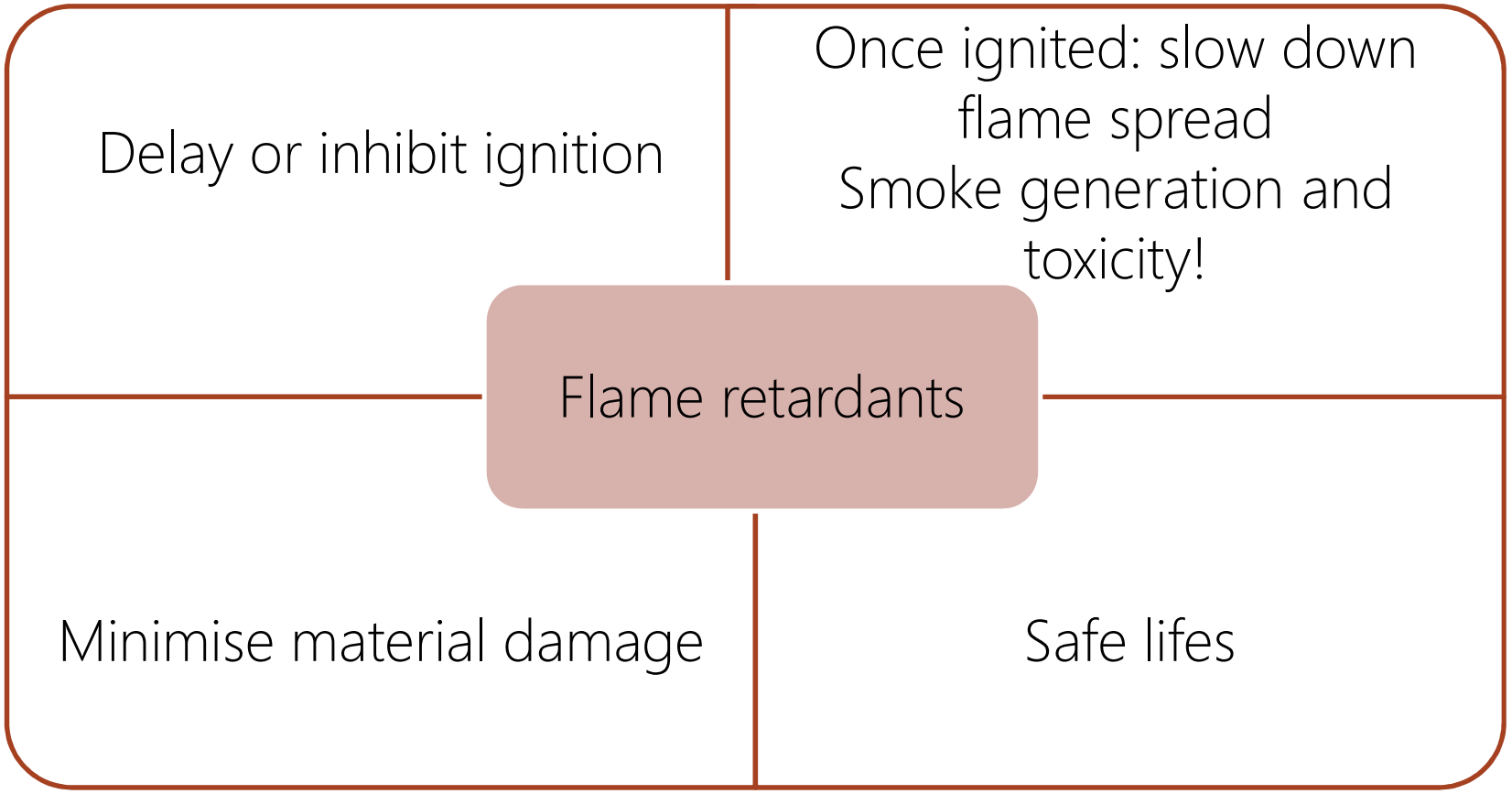
Source: M. Kobes, and K. Groenewegen - Ter Morsche, Consumer fire safety: European statistics and potential fire safety measures, Netherlands Institute for Safety Nibra, January 2009, p. 27.

Introduction – Where?

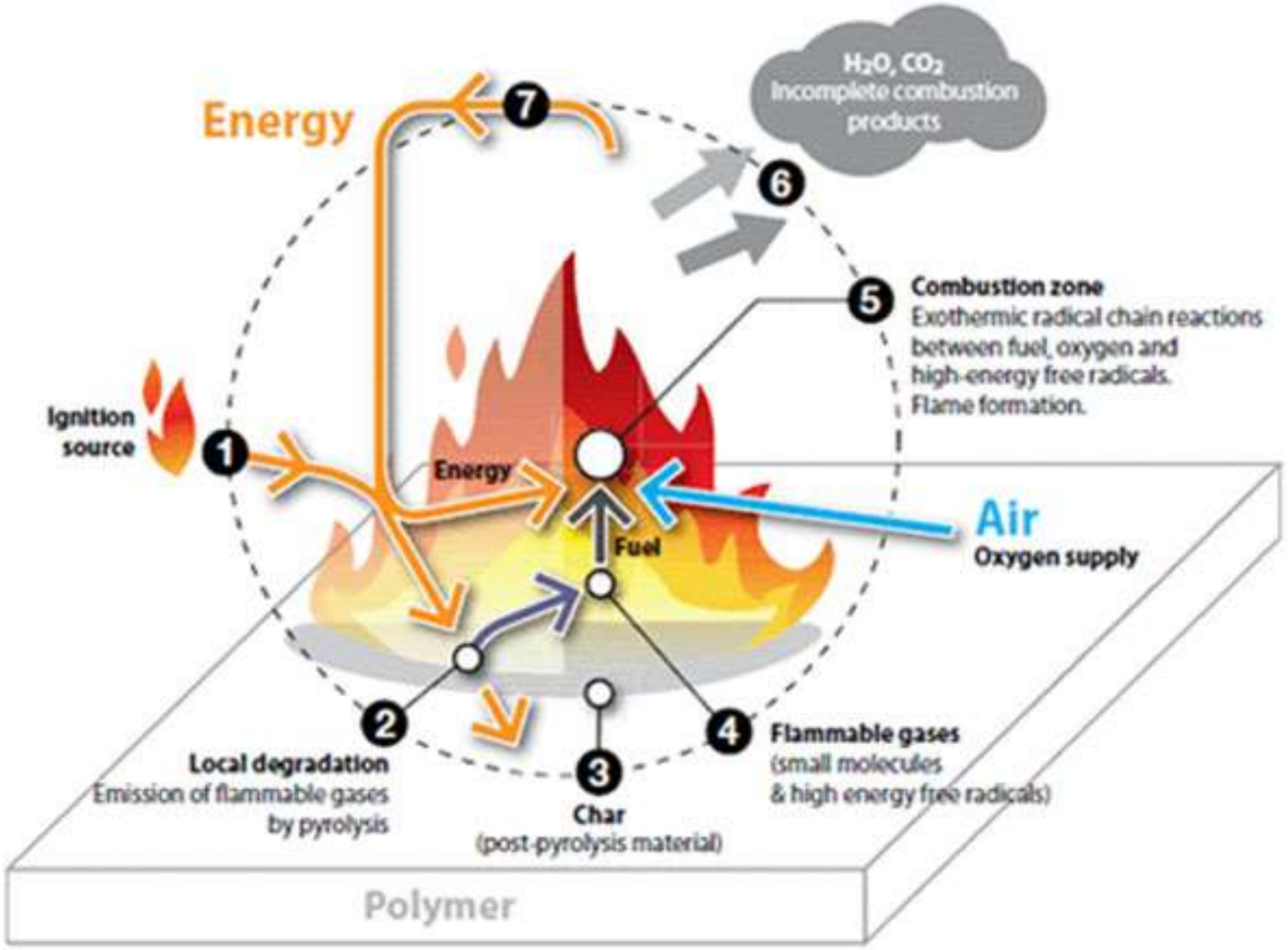


Public places, transport, Domestic (UK), …

Goal of flame retardants

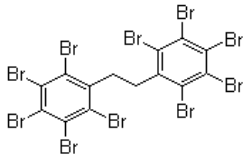


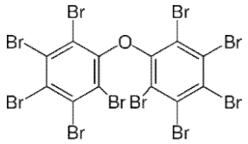
Combustion mechanism



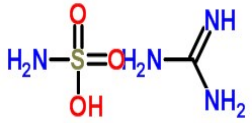
Flame retardant groups

Halogenated

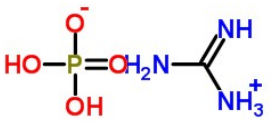




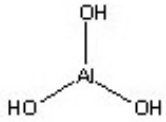
Nitrogen based



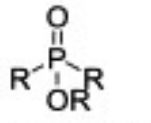
Phosphorous and Nitrogen



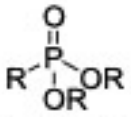
Minerales (AL, Mg)



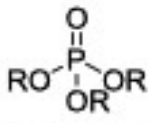
Phosphorous based



Phosphinate



Phosphonate

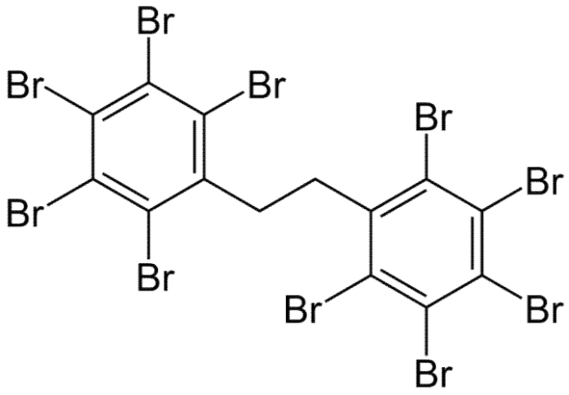


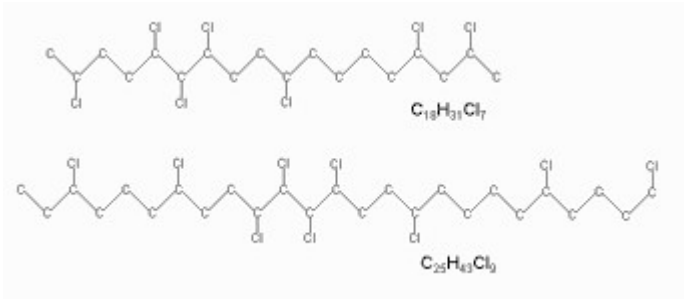
Phosphate

Classes

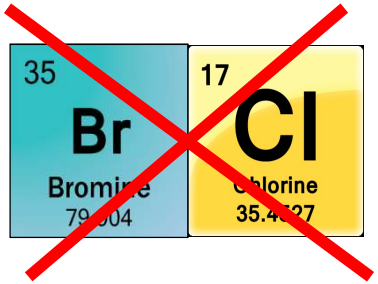
Halogenated (Br, Cl, F)

- Radical quenching in gas phase (substitution of high-energy free-radicals by low-energy free-radicals)
- Avoid the fire cycle to establish or to sustain itself
- High efficiency – low loadings (e.g. 12%wt)
- Bromine more efficient than chlorine
- Mostly used in combination with antimony trioxide as synergist





Halogenated flame retardants



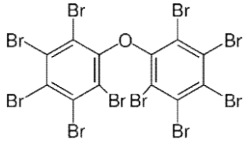
- Halogenated small molecules: often persistent, bioaccumulation and toxic to humans
- Regulation
- Continuous pressure from NGOs on OEMs

- Antimony trioxide (ATO) as synergist

Classification according to Regulation (EC) No.1272/2008(CLP):	Carcinogen Category2
Classification according to Directive 67/548/EEC:	Harmful;Xn; Carcinogen Category3;R40: Limited evidence of a carcinogenic effect.
Signal word:	Warning
Hazard pictogram:	
Hazard statement:	H351: Suspected of causing cancer by inhalation. H412: Harmful to aquatic life with long lasting effects.

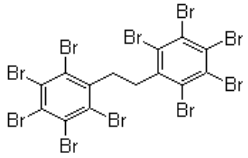
Halogenated flame retardants

Deca-BDE (decabromodiphenyl ether)

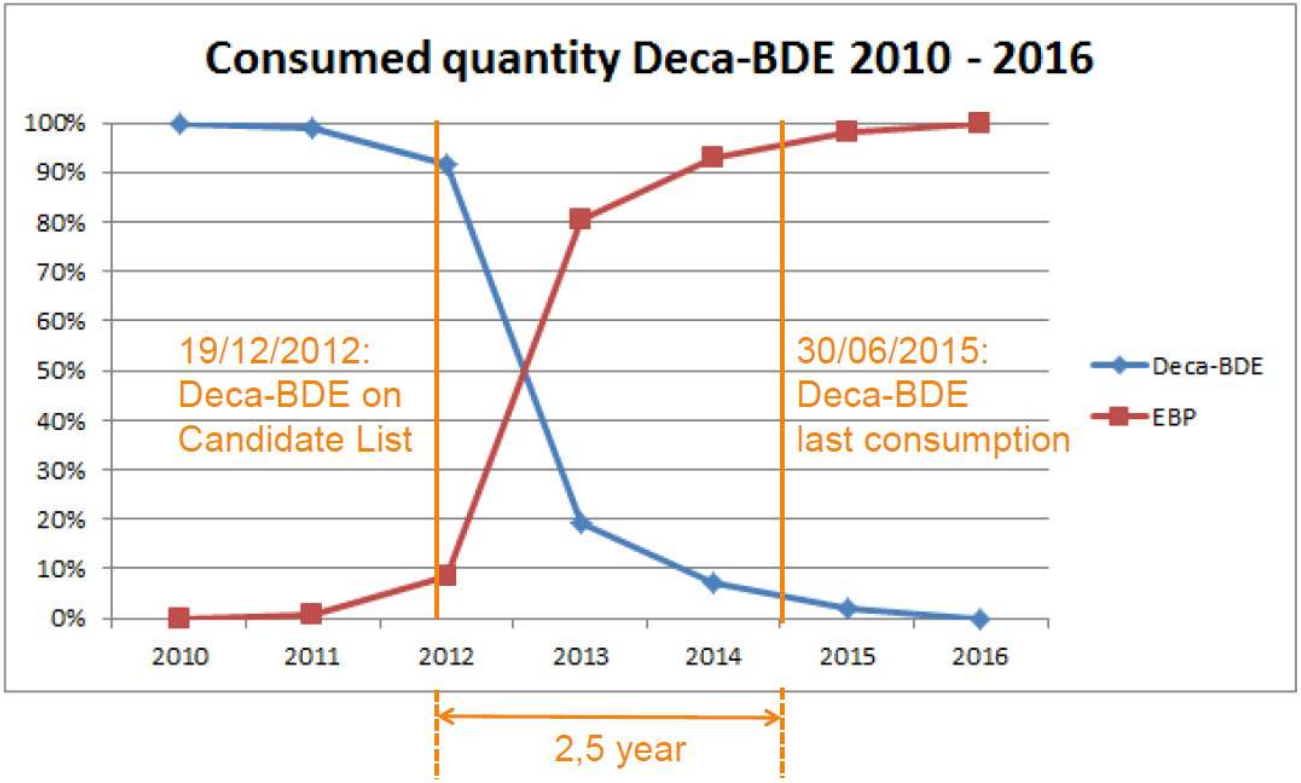


Deca-BDE
forbidden since March

EBP (decabromodiphenyl ethane)



→ Regrettable substitute???

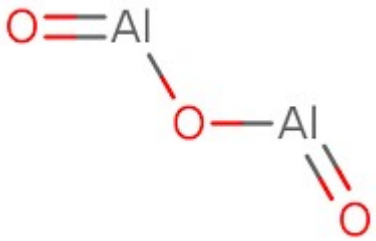


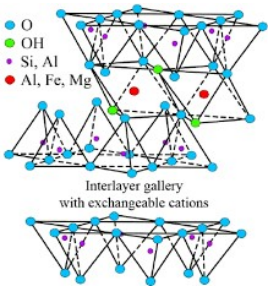
Classes

Minerals (Al, Mg,…)

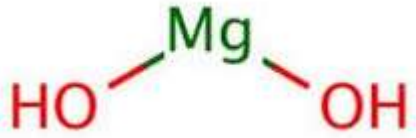
- Endothermic decomposition (energy capture)
- Dilution of combustion zone with inert gases (water)
- Non flammable layer material surface
- Low efficiency – high loadings (60%wt)

$Mg_3Ca(CO_3)_4$





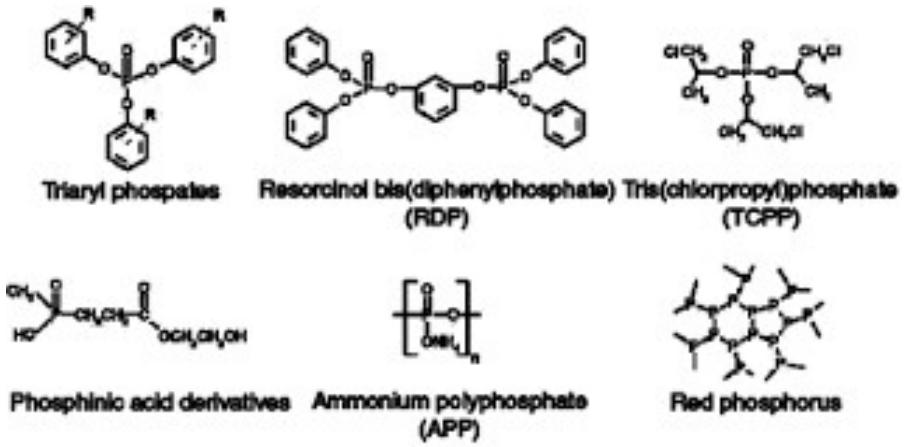
$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$



Classes

Phosphorus

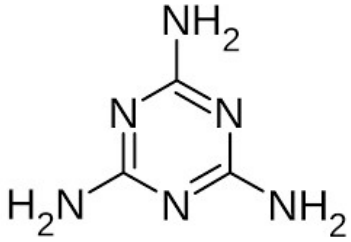
- Powerful char promoter
- Often intumescent systems
- Char hinders the passage of flammable gases to the flame
- Char shields polymer from energy (heat) supply
- Varying efficiency & loadings (10-30%wt)

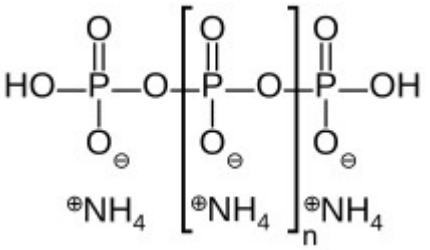


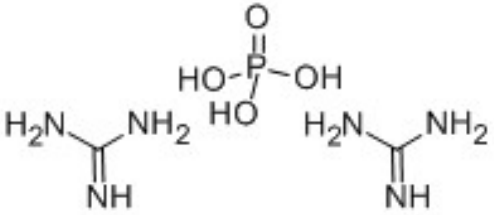
Classes

Nitrogen

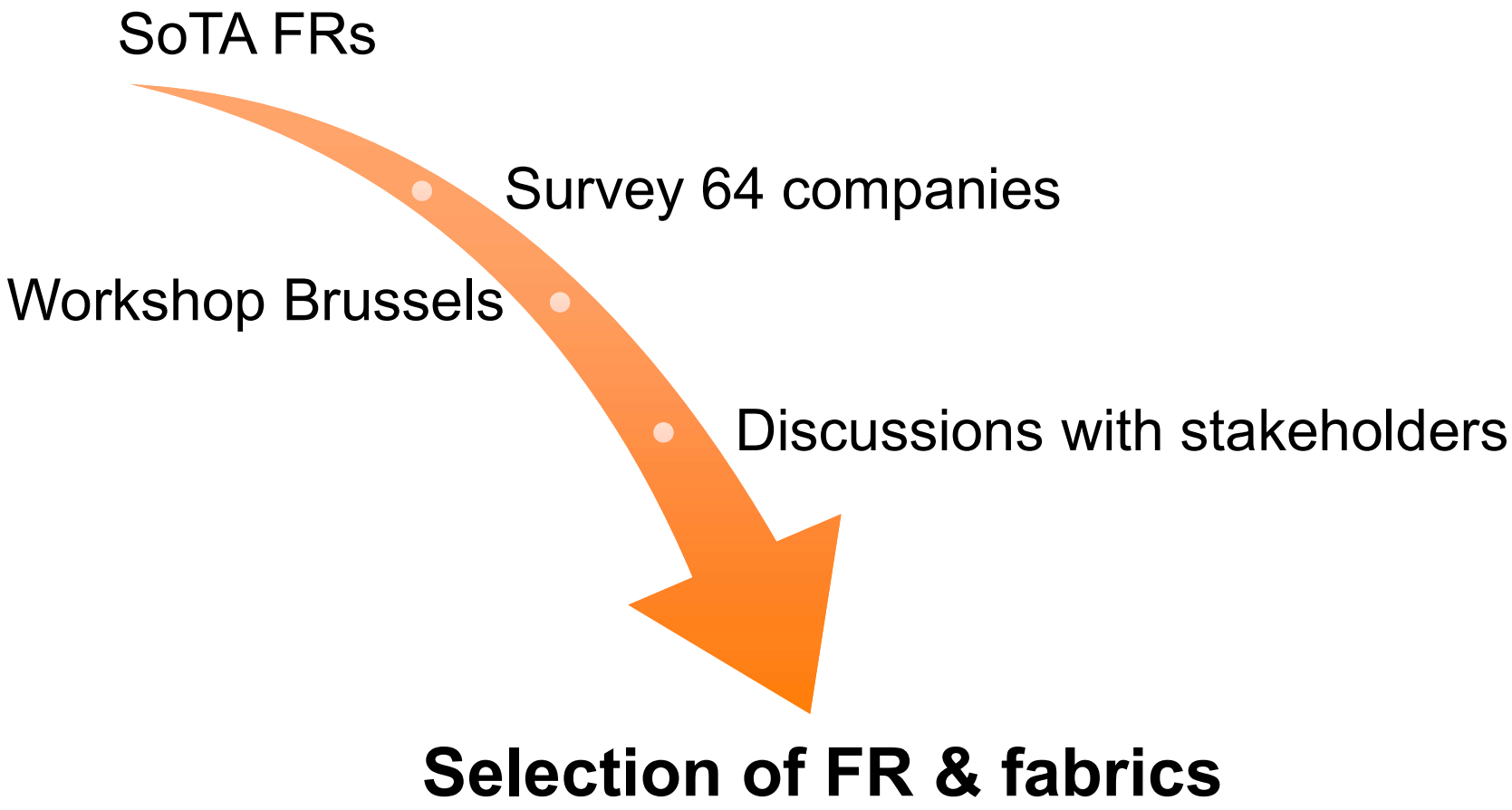
- Enhancing formation of cross-linked stable compounds at high temperatures, which inhibits pyrolysis
- Dilution of combustion zone with inert gas (nitrogen)
- Used as blowing agent in intumescent systems
- Low efficiency alone, good synergist
- Often used in combination with P-based FRs







Preparatory actions



FR selection Life-FLAREX

Application	Specific fabric composition	Conventional Flame Retardants	Transitional Flame retardants	Alternative Flame Retardants
Curtains	100% PES	(1) Decabromodiphenyl ethane + melamine cyanurate (2) Decabromodiphenyl ethane + ATO	(1) Polymeric FR	(1) Cyclic phosphonate (2) Organophosphonate
Upholstery	100% PES	(1) Decabromodiphenyl ethane + melamine cyanurate (2) Decabromodiphenyl ethane + ATO	(1) Polymeric FR	(1) Organophosphorus salt (2) Expandable graphite
Mattress ticking	50/50 CO/PES and 100% PES	(1) Decabromodiphenyl ethane + melamine cyanurate (2) Decabromodiphenyl ethane + ATO	(1) Polymeric FR	(1) Ammonium polyphosphate (2) Guanidine phosphate (3) Ammonium sulfamate
Bed sheets	50/50 CO/PES and 100% CO	(1) Dialkyl phosphono carboxylic acid amide (2) Decabromo diphenyl ethane + melamine cyanurate (3) Decabromo diphenyl ethane + ATO	(1) Polymeric FR	(1) Ammonium sulfamate + Urea + $PO(OH)_2$-R-$PO(OH)_2$ (2) Phosphorous based (3) Tetrakis(hydroxymethyl)phosphonium sulphate

Transitional Flame retardants

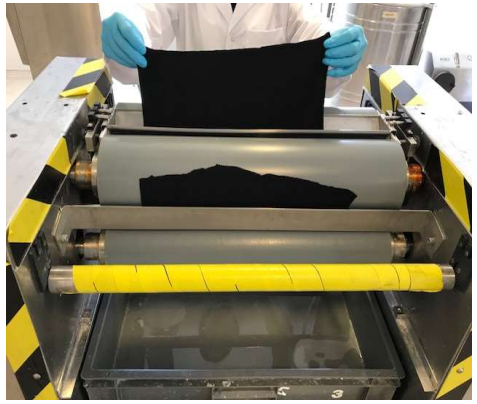
- Polymeric FR = Brominated Polymer
  Why included?

  - Claimed to be environmental friendly
  - Non-migrating / low fogging
  - Considered as safer FR approach by end users and regulatory bodies
  - Both halogen containing as halogen-free polymeric FR
  - Lot of interest from industry

Action B1- Methodology

The application of the flame reatrdants is performed as impregnation or coating

Impregnation



Back-knife coating

Stenter for drying and curing

Action B1- Mattress ticking

Materials

PES - 266 g/m²

PES/CO 50/50 - 148 g/m²

Testing

EN 597-1 & 2

Pass:

part 1: no flaming or smouldering (< 15 min)

part 2: afterflame < 2min

Action B1- Mattress ticking

Application	Specific fabric composition	Conventional Flame Retardants	Transitional Flame retardants	Alternative Flame Retardants
Mattress ticking	50/50 CO/PES and 100% PES	(1) Decabromodiphenyl ethane + melamine cyanurate (2) Decabromodiphenyl ethane + ATO	(1) Polymeric FR	(1) Ammonium polyphosphate (2) Guanidine phosphate (3) Ammonium sulfamate

Conventional FR: as finish or foamed back coating

→ Stiffening and coating visible

→ Good FR behaviour

Polymeric FR: as back coating

→ Stiffening

→ Good FR behaviour

Action B1- Mattress ticking

Application	Specific fabric composition	Conventional Flame Retardants	Transitional Flame retardants	Alternative Flame Retardants
Mattress ticking	50/50 CO/PES and 100% PES	(1) Decabromodiphenyl ethane + melamine cyanurate (2) Decabromodiphenyl ethane + ATO	(1) Polymeric FR	(1) Ammonium polyphosphate (2) Guanidine phosphate (3) Ammonium sulfamate

APP: as foamed back coating

→ Stiffening

→ Good FR behaviour possible with higher loadings (40 wt% in binder, >40 wt% dry add-on)

Alternatives: as finish

→ all 3 good FR behaviour

EN 597-1 and 2: no ignition

crib 5: all passed but differentiation

Mattress ticking	Guanidine phosphate	Ammonium sulfamate	Ammonium polyphosphate
PES/CO	11% - 19%	5% - 11%	7% - 16%
PES	12% - 19%	7% - 13%	16% - 27%

Higher loadings guanidine phosphate: worse FR result

Higher add-on APP: slight stiffening

Action B1- Bed linen

Materials

CO - 112 g/m²

PES/CO 50/50 - 112 g/m²

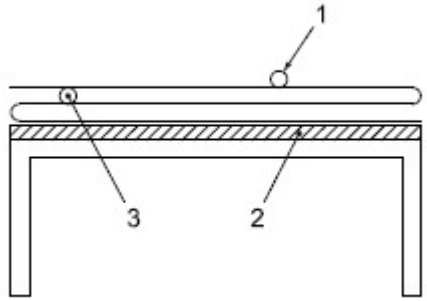
Testing

EN 12952-1 & 2 (after 5x washing at 60°C):

Pass

part 2: afterflame < 2min

part 1: no flaming or smouldering (< 15 min)



Action B1- Bed linen

Application	Specific fabric composition	Conventional Flame Retardants	Transitional Flame retardants	Alternative Flame Retardants
Bed sheets	50/50 CO/PES and 100% CO	(1) Dialkyl phosphono carboxylic acid amide (2) Decabromo diphenyl ethane + melamine cyanurate (3) Decabromo diphenyl ethane + ATO	(1) Polymeric FR	(1) Ammonium sulfamate + Urea + $PO(OH)_2$-R-$PO(OH)_2$ (2) Phosphorous based (3) Tetrakis(hydroxymethyl)phosphonium sulphate

Conventional FRs: as finish

EBP

→ Influence on appearance and handle

→ Not wash resistant: bad FR

DPCAA

→ No influence on appearance and handle

→ Wash resistant: good FR behaviour

Action B1- Bed linen

Application	Specific fabric composition	Conventional Flame Retardants	Transitional Flame retardants	Alternative Flame Retardants
Bed sheets	50/50 CO/PES and 100% CO	(1) Dialkyl phosphono carboxylic acid amide (2) Decabromo diphenyl ethane + melamine cyanurate (3) Decabromo diphenyl ethane + ATO	(1) Polymeric FR	(1) Ammonium sulfamate + Urea + $PO(OH)_2$-R-$PO(OH)_2$ (2) Phosphorous based (3) Tetrakis(hydroxymethyl)phosphonium sulphate

Polymeric FR: as finish

→ Stiffening, Co: colour change

→ Wash resistant: good FR behaviour

Action B1- Bed linen

Application	Specific fabric composition	Conventional Flame Retardants	Transitional Flame retardants	Alternative Flame Retardants
Bed sheets	50/50 CO/PES and 100% CO	(1) Dialkyl phosphono carboxylic acid amide (2) Decabromo diphenyl ethane + melamine cyanurate (3) Decabromo diphenyl ethane + ATO	(1) Polymeric FR	(1) Ammonium sulfamate + Urea + $PO(OH)_2$-R-$PO(OH)_2$ (2) Phosphorous based (3) Tetrakis(hydroxymethyl)phosphonium sulphate

Alternative FRs: as finish

→ No influence on handling

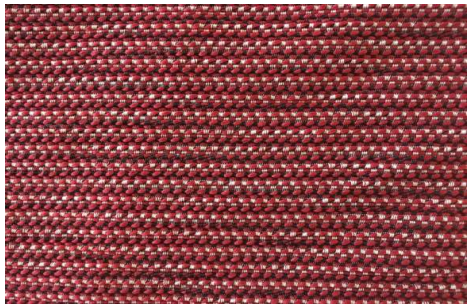
→ EN 12952-1 & 2:

Bed linen	Ammonium sulfamate + Urea + $PO(OH)_2$-R-$PO(OH)_2$	P-based	Tetrakis(hydroxymethyl) phosphonium sulphate
CO	√	√	√
PES/CO	√	/	√

Action B1- Upholstery

Materials

PES- 320 g/m²



Face

Reverse

Testing

UNE EN 1021:2015,

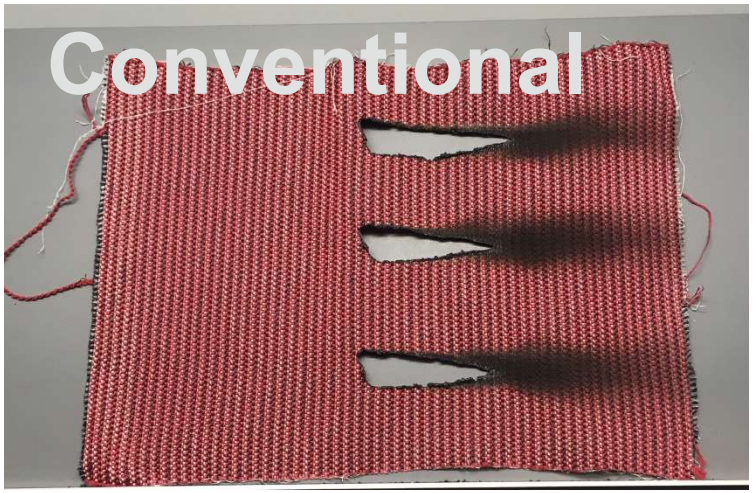
Pass (after 30 min soaking at 40°C):

- part 2: afterflame < 2min , 3 test areas
- part 1: no flaming or smouldering (< 15 min)

Action B1- Upholstery

PES textile untreated

Action B1- Upholstery



DBDPE +ATO 50% – pass

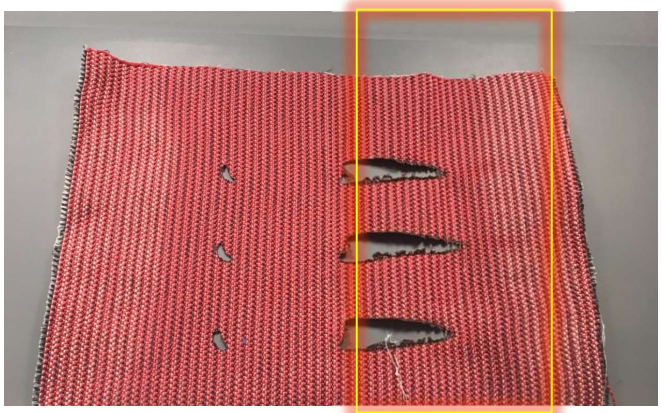
Expandible graphite 50% – pass

Brominated polymer 50% – pass

Action B1- Upholstery

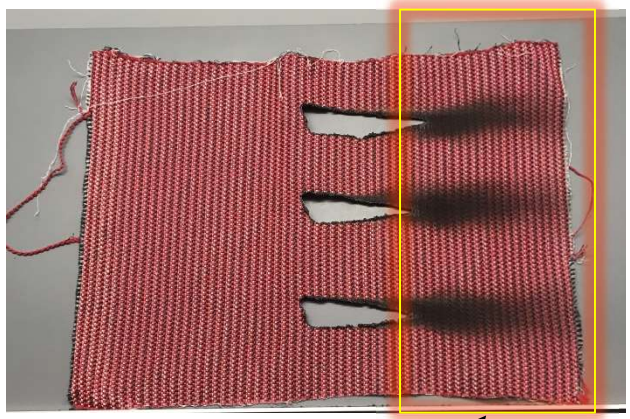
Conventional:

PES treated with 50% DBDPE + MC



No black smoke liberation

PES treated with 50% DBDPE + ATO



Black smoke liberation

Action B1- Upholstery

First application 50% EG

Second application 50% EG

Action B1- Upholstery

20% Dispersion of a styrene acrylic copolymer with organophosphorus salt

50% Dispersion of a styrene acrylic copolymer with organophosphorus salt

Action B1- Curtains

Materials

PES A) - 100 g/m²

PES B) - 250 g/m²

Testing (pre-screening)

UNE EN 13773,

Pass (after 1 x washing at 30°C):

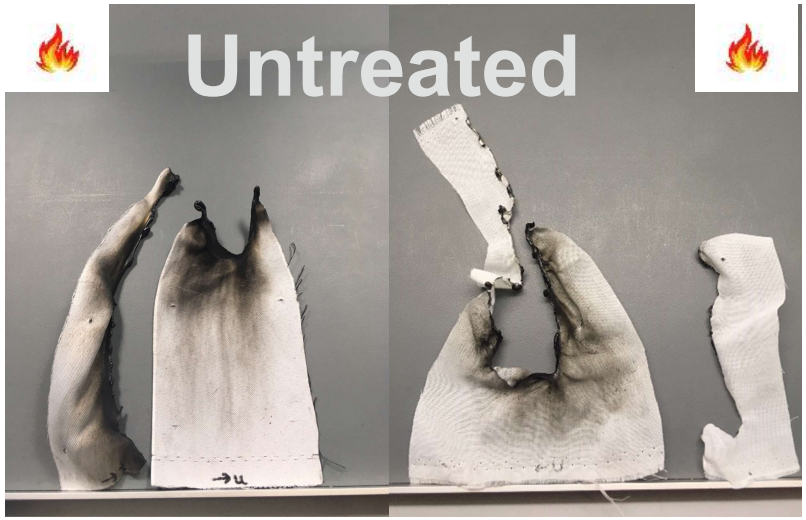
Part 1: UNE EN 1101

- 4 samples of 20 sec. ok

Part 2:UNE EN 13772

- 1st yarn not affected
- No burned residue

Action B1- Curtains



DBDPE + ATO 50% – pass

Cyclic Phosphonate 30% – B no pass , A passes

DBDPE + MC 70% – no pass

Action B1- Curtains

Cyclic phosphonate - Alternative difficulties:

Sample	Weight before washing (g)	Weight after washing (g)	Dry Pick-up (%)	Weight loss (%)
BS70	3	2	38	27

Action B1- Curtains

Alternative Cyclic phosphonate is trialed:

-> Thermosol process

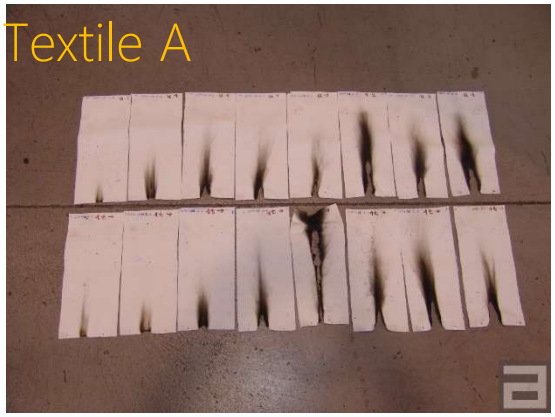
+Higher temperature (190º approx) and less curing time (1 min approx)

+Continuous process

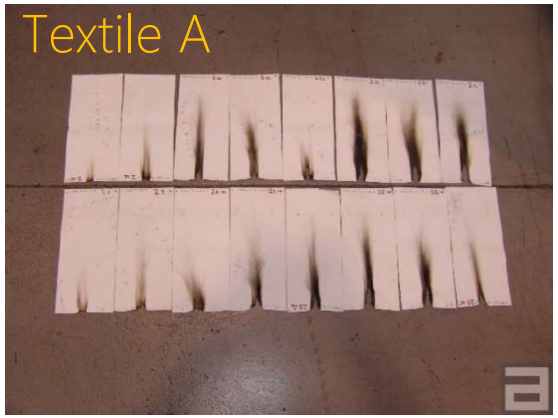
+Better penetration and fixation into the substrate

Action B1- Curtains

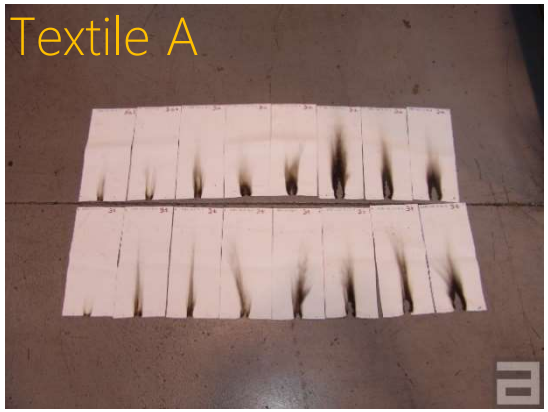
1.Polimeric FR

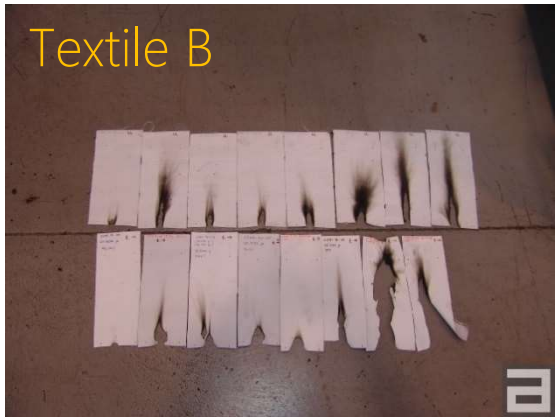


2. Polymeric FR -ATO



3. Polymeric FR -ATO





Action B1- summary

- Mattress ticking: all tested alternatives well performing
- Upholstery: polymeric halogenated FR and expandable graphite possible solutions
- Bed sheets: alternatives detected for cotton, PES/CO 50/50 more difficult → washability, handle!
- Curtains: possible alternatives with thermosol process for cyclic phosphonate (assessment not complete yet)

Alternative FR

Use of alternatives has limitations because of e.g.

- Higher loadings needed
- More prone to hydrolysis (washability!)
- Some FRs are coloured (e.g. red phosphor, graphite, …)
- More difficult to disperse in formulation
- Migration/leaching
- Impact on handle
- Corrosion during extrusion

→ Intensive technical screening needed

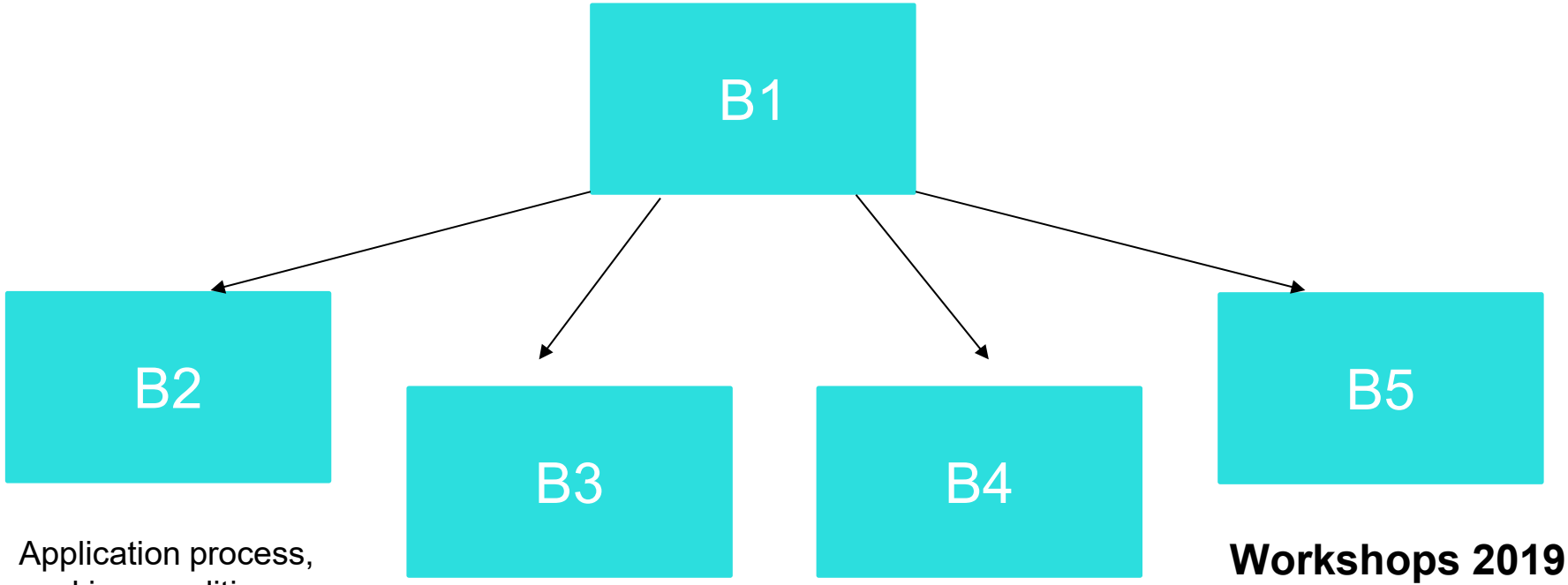
Conclusion

Nevertheless results show that conventional flame retardants can be replaced by alternatives

BUT has to be evaluated case by case

No simple one to one replacement of halogen based FR by an alternative → different working principle

Interaction with other project parts



Application process, working conditions have been studied

- Relevant exposure identifid

LCA – Life cycle assessment

In-vitro tests
Chemicals, farbics and treated fabrics sent for toxicological tests (CSIC)

Workshops 2019

- Barcelona, 20th February
- CIE workshop 12th March
- Duratex-Centexbel 14th March
- Biella 12th July

- It is planned to hold another workshop in a European framework) but pending of data confirmation.

Next steps

Upscaling of the treatments (industrial scale)

- Collecting data for risk assessment and LCA
- Sample production for elaborate testing (fire, physical, …)

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Grazie mille per la tua attenzione!

ci sono domande