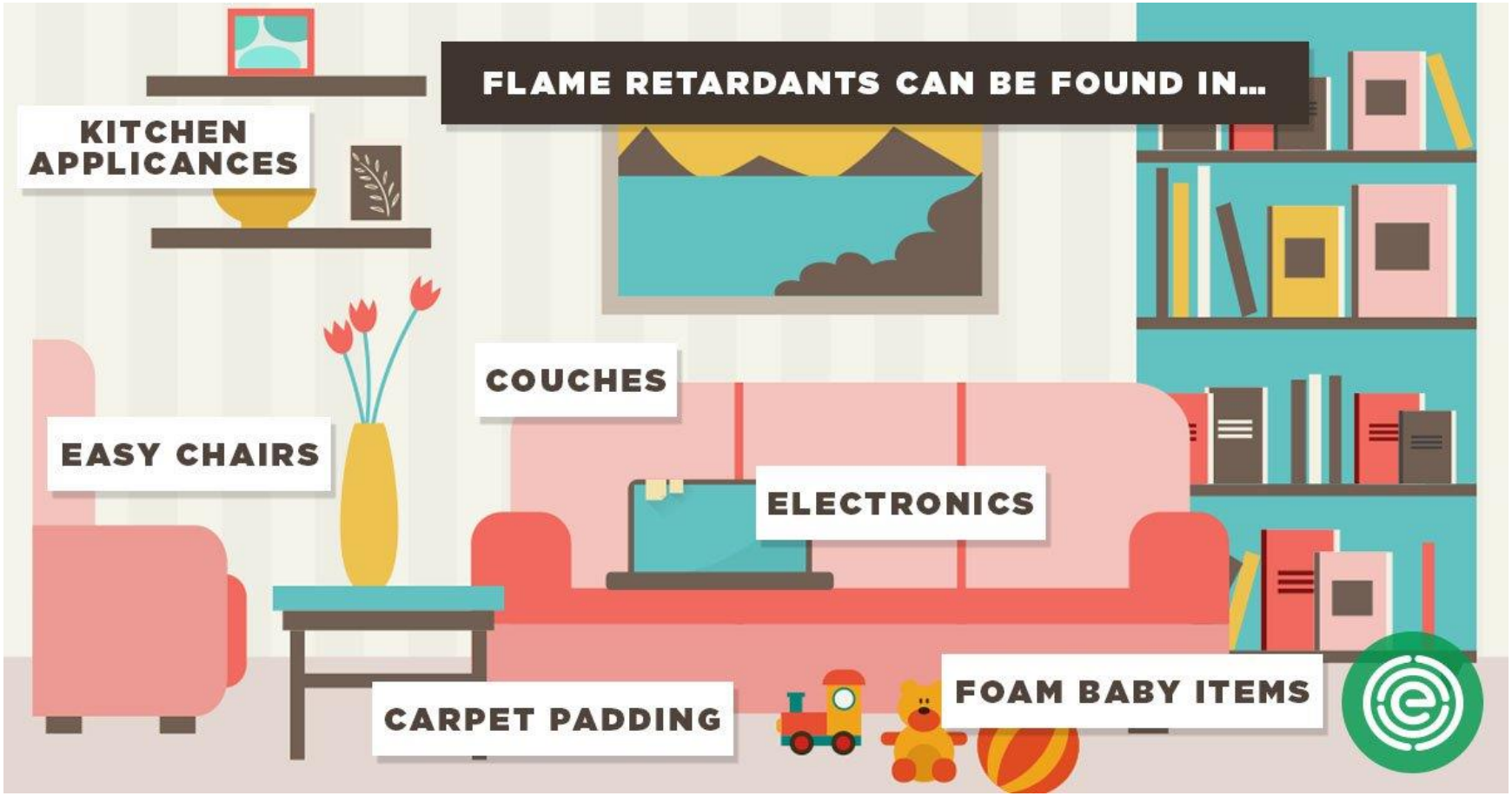
FLAREX

Mitigation of environmental impact caused by Flame retardant textile finishing chemicals

CENTEXBEL

Duratex/Flarex Workshop, Kortrijk, 14/3/2019

Ine De Vilder



www.alternet.org

Upholstery

Curtains

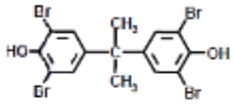
Mattress ticking

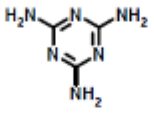
Bed linen

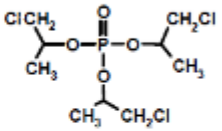
Focus Flarex: interior textiles for the contract market

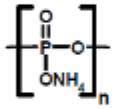
Huge variety of FRs!

^{35}Cl ^{31}P ^{27}Al





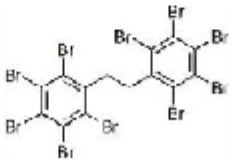




^{80}Br

^{14}N

$Al(OH)_3$ ^{11}B

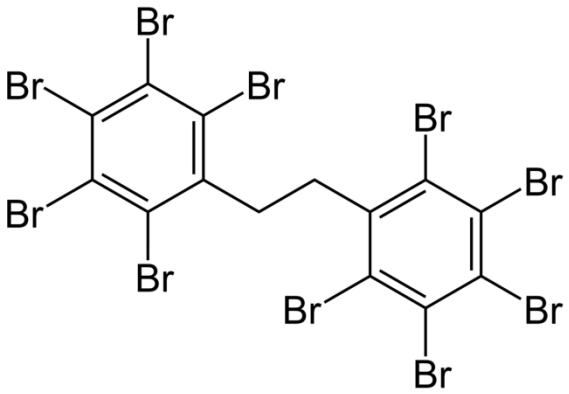


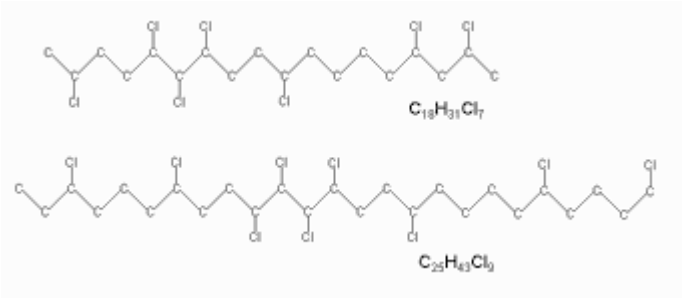
^{24}Mg ^{12}C

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





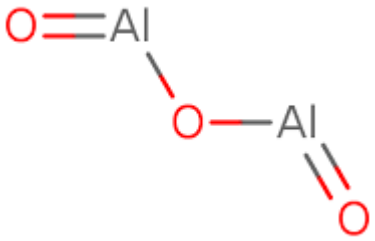
Classes

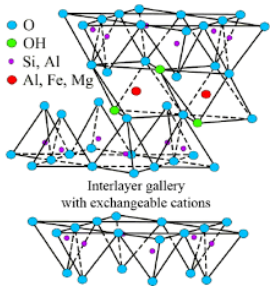
Minerals (Al, Mg,…)

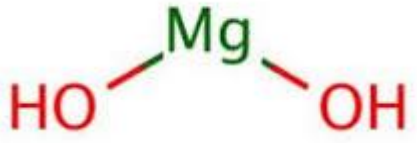
- Endothermic decomposition (energy capture)
- Dilution of combustion zone with inert gases (water)
- Non flammable layer material surface
- Low efficiency – high loadings (60%wt)

$Mg_3Ca(CO_3)_4$

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



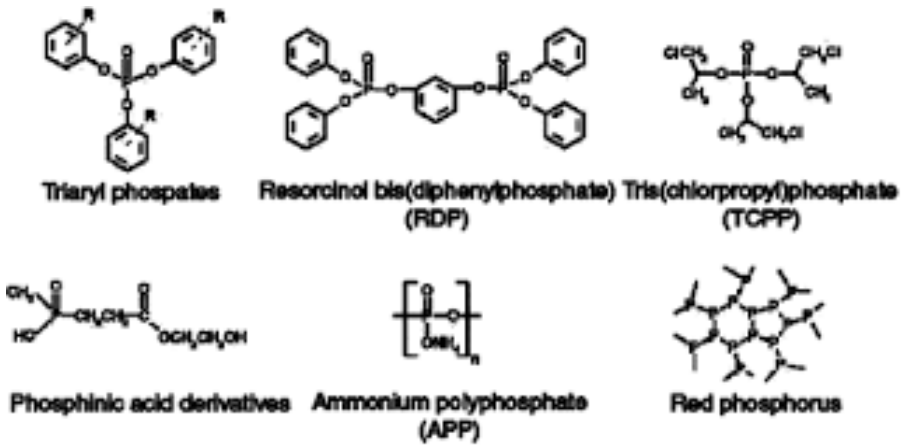




Classes

Phosphorus

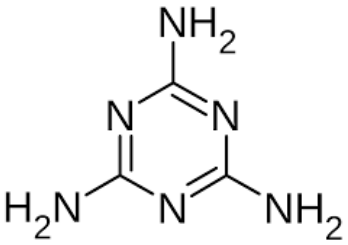
- Powerful char promoter
- Often intumescent systems
- Char hinders the passage of flammable gases to the flame
- Char shields polymer from energy (heat) supply
- Varying efficiency & loadings (10-30%wt)

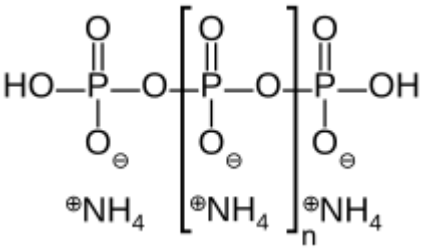


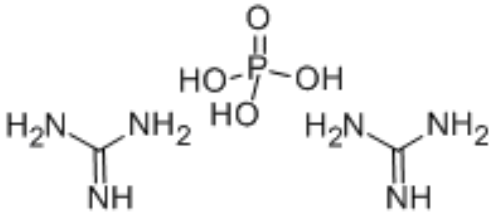
Classes

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



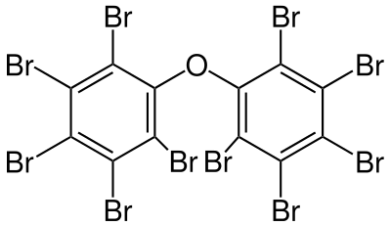


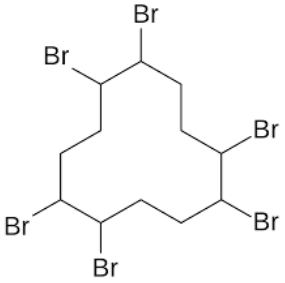


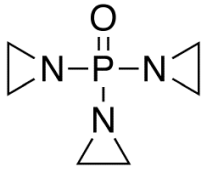
FLAREX

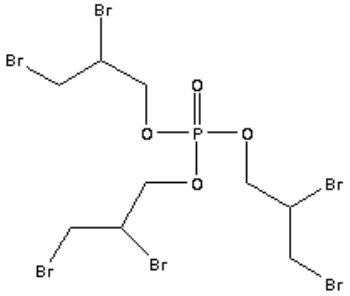
Some flame retardants are HARMFUL

→ Several have been phased out









Life

Others are still UNCLEAR

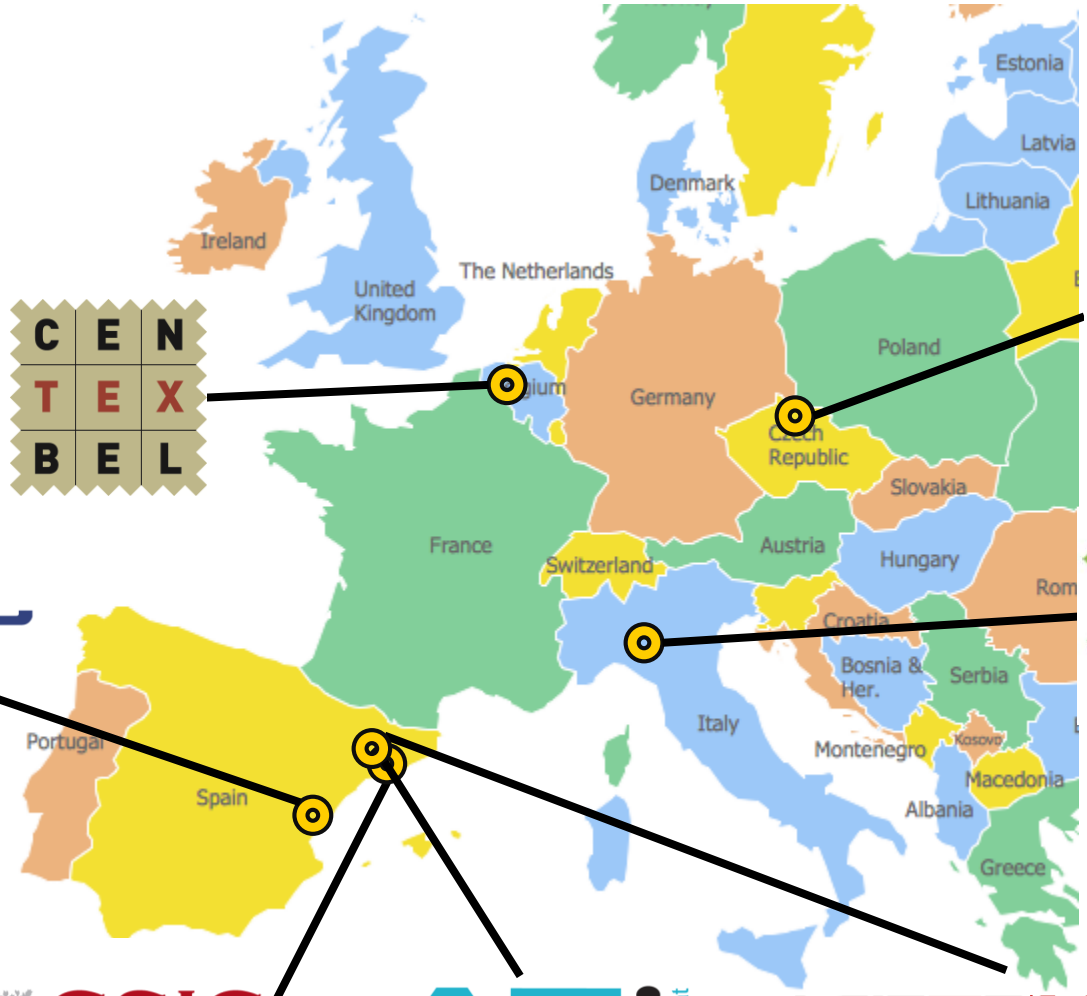
Project facts

- **European LIFE project**

  LIFE-FLAREX is a project co-funded by the European Union under the LIFE+ Financial Instrument within the axe Environment Policy and Governance and under the Grant Agreement n. LIFE16 ENV/ES/000374

- **Coordinated by AEI Textil, Spain**
- **3 years – started July 2017**
- **7 partners from 4 countries**
- **Grant: ~700.000 Euro**
- **www.life-flarex.eu**

Project consortium



CENTEXBEL

clutex
cluster technical textiles

ATEVAL

po.in.tex
Polo Innovazione Tessile

Città Studi
BIELLA

iQAC

CSIC
Consejo Superior de Investigaciones Científicas

AEI Textils.cat
Agrupació d'empreses innovadores

LEITAT
managing your technologies
Technological Center
member of TECNIO

PROJECT OBJECTIVES

- To apply the substitution principle to FR chemicals
- To demonstrate and evaluate suitable FR alternatives
- To encourage the substitution

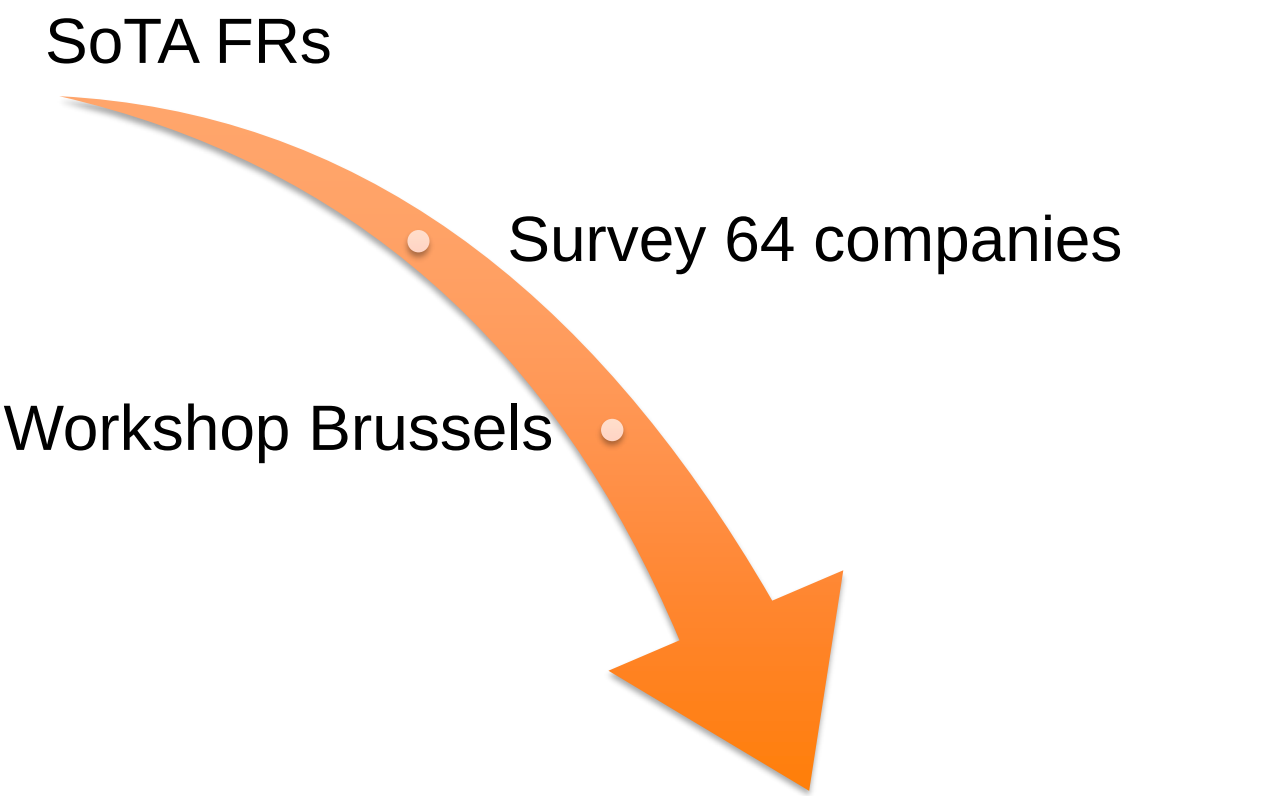
External advisory board

- ECHA
- Euratex
- Flame Retardant Europe (previously EFRA)
- Polytechnic University of Catalonia

Project steps

A. Preparatory actions → B.Implementation actions → C. Impact Monitoring

Preparatory actions



Preparatory actions

Application	Specific fabric composition	Conventional Flame Retardants	Intermediate Flame retardants	Alternative Flame Retardants
Curtains	100% PES	(1) Decabromodiphenyl ethane + melamine cyanurate (2) Decabromodiphenyl ethane + ATO	(1) Polymeric FR	(1) Cyclic phosphonate
Upholstery	100% PES	(1) Decabromodiphenyl ethane + melamine cyanurate (2) Decabromodiphenyl ethane + ATO	(1) Polymeric FR	(1) Ammonium polyphosphate (2) Expandable graphite
Mattress ticking	50/50 CO/PES 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

Application of FR onto textile via coating/padding

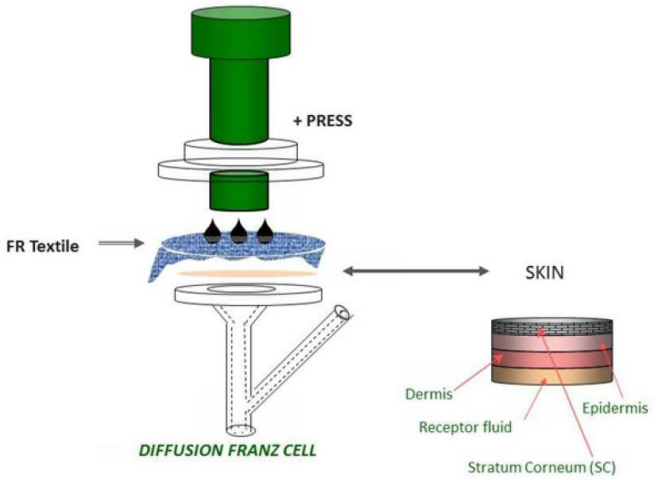
Technical performance

- Evaluation at lab scale

  → Burning behaviour & other textile properties
- Upscaling to industrial scale

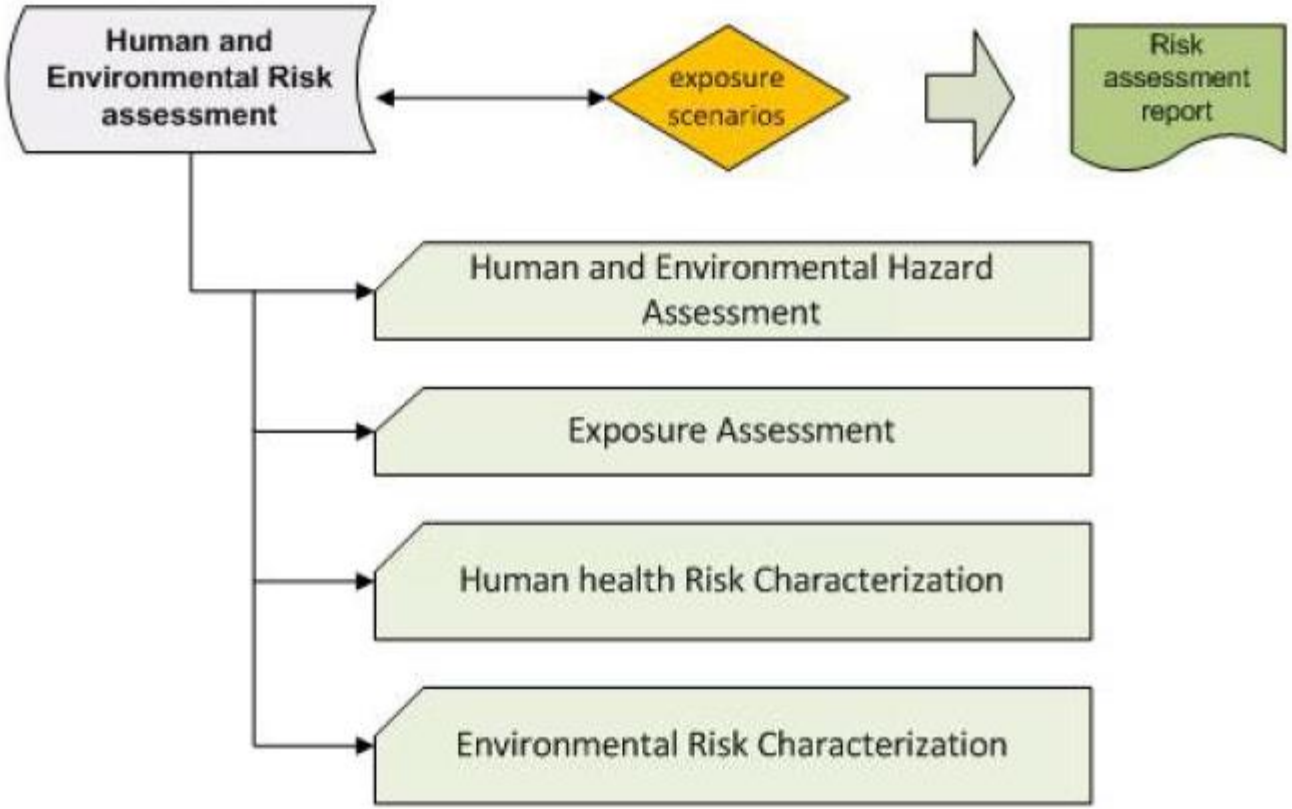
Toxicology

- Percutaneous absorption tests



Implementation actions

Risk assessment



Implementation actions

→ View on the overall impact of different FRs

Lab results mattress ticking

- Materials

  PES 3D spacer fabric

  PES/CO 50/50

- Tested by EN 597-1 and 2
  on 35 kg flame retardant foam

Lab results mattress ticking

Application	Conventional Flame Retardants	Intermediate Flame retardants	Alternative Flame Retardants
Mattress ticking	(1) Decabromodiphenyl ethane + melamine cyanurate (2) Decabromodiphenyl ethane + ATO	(1) Polymeric FR	(1) Ammonium polyphosphate (2) Guanidine phosphate (3) Ammonium sulfamate

Applied via coating/padding

Different concentrations

A4 scale

EN 597 mattress ticking – coating

Textile	Formulation Add-on	Flame ignition	Flame ignition Afterburn time (s)	Cigarette ignition
CO/PES	Untreated	yes	2 x >120	no
CO/PES	DBDPE + ATO 62%	no	0 - 0	no
CO/PES	DBDPE + ATO 74%	no	0 - 0	no
CO/PES	DBDPE + MC 57%	no	1 - 3	no
CO/PES	DBDPE + MC 72%	no	0 - 2	no
PES	Untreated	no	0 - 0	no
PES	DBDPE + ATO 90%	no	0 - 0	no
PES	DBDPE + ATO 100%	no	0 - 2	no
PES	DBDPE + MC 120%	no	0 - 0	no
PES	DBDPE + MC 128%	no	0 - 0	no

Conventional halogenated FR good results

EN 597 mattress ticking – padding

Textile	Formulation & Pick-up	Flame ignition	Flame ignition Afterburn time (s)	Cigarette ignition
CO/PES	Untreated	yes	2 x >120	no
CO/PES	Guanidine phosphate 11%	no	0 - 0	no
CO/PES	Guanidine phosphate 19%	no	0 - 0	no
CO/PES	Ammonium sulfamate 5%	no	0 - 0	no
CO/PES	Ammonium sulfamate 11%	no	0 - 0	no
CO/PES	APP 7%	no	0 - 2	no
CO/PES	APP 16%	no	0 - 0	no
PES	Untreated	no	0 - 0	no
PES	Guanidine phosphate 12%	no	0 - 0	no
PES	Guanidine phosphate 19%	no	0 - 0	no
PES	Ammonium sulfamate 7%	no	0 - 2	no
PES	Ammonium sulfamate 13%	no	0 - 0	no
PES	APP 16%	no	0 - 0	no
PES	APP 27%	no	0 - 0	no

All 3 alternatives pass the EN 597-1 and 2

But no differentiation

BS6807 mattress ticking – padding

Textile	Formulation & Pick-up	Preliminary Pass/fail	Burning time	Depth/width crater	Longest burning
CO/PES	Untreated	fail	escalating	-	-
CO/PES	Guanidine phosphate 11%	pass	3'22''	4 / 10	fabric
CO/PES	Guanidine phosphate 19%	pass	3'21''	4 / 9.5	fabric
CO/PES	Ammonium sulfamate 5%	pass	3'32''	3.5 / 11.5	fabric
CO/PES	Ammonium sulfamate 11%	pass	3'25''	4 / 13	fabric
CO/PES	APP 7%	pass	3'14''	3.5 / 12.5	fabric
CO/PES	APP 16%	pass	3'38''	3.5 / 10	crib
PES	Untreated	pass	4'33''	5 / 18	fabric
PES	Guanidine phosphate 12%	pass	2'33''	4 / 12	crib
PES	Guanidine phosphate 19%	pass	4'11''	5.5 / 18	fabric
PES	Ammonium sulfamate 7%	pass	3'13''	5 / 14.5	fabric
PES	Ammonium sulfamate 13%	pass	2'50''	5.5 / 12.5	crib
PES	APP 16%	pass	4'20''	6 / 16	fabric
PES	APP 27%	pass	2'39''	3 / 10.5	fabric

Differentiation possible:
Beter performing ones in green

EN 597 mattress ticking – coating

FR is mixed with waterborne polyurethane binder

Textile	Formulation & Pick-up	Flame ignition	Flame ignition Afterburn time (s)	Cigarette ignition
CO/PES	Untreated	yes	2 x >120	no
CO/PES	40 wt% APP 67% add-on	no	0 - 0	no
CO/PES	40 wt% APP 39% add-on	no	0 - 2	no
CO/PES	20 wt% APP 31% add-on	yes	2 x >120	no
CO/PES	20 wt% APP 66% add-on	no	36 - 41	no
CO/PES	Polymeric FR 45% add-on	no	0 - 0	no
PES	Untreated	no	0 - 0	no
PES	40 wt% APP 48% add-on	no	0 - 0	no
PES	20 wt% APP 39% add-on	no	0 - 0	no

Conclusion mattress ticking

- Well performing alternatives with different chemistries
- Padding proces no (or minor) influence on handle
- Often already applied in industry
- Oeko-tex® compliance possible

Lab results bed sheets

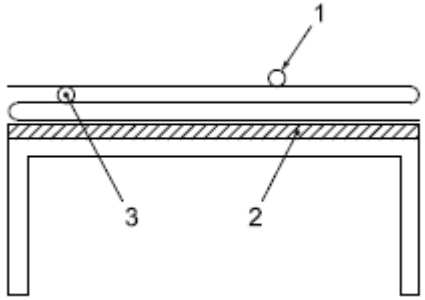
- Materials

Cotton – 112 g/m²

PES/CO 50/50 – 112 g/m²

- Tested by EN 12952-1 and 2

5 times washed at 60°C (ISO 6330)



deviation: 3 A4 samples stacked for cigarette test

Bed sheets

Application	Specific fabric composition	Conventional Flame Retardants	Intermediate 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

Applied via padding

A4 scale

ISO 12952-1 and 2 bed sheets

Textile	Formulation & Add-on	Flame ignition	Flame ignition Afterburn time (s)	Cigarette ignition
CO/PES	Untreated	yes	2 x >120	no
CO/PES	DBDPE + MC – 11%	yes	2 x >120	no
CO/PES	DBDPE + MC – 4%	yes	2 x >120	no
CO/PES	DBDPE + ATO – 11%	yes	2 x >120	no
CO/PES	DBDPE + ATO – 3%	yes	2 x >120	no
CO/PES	DPCAA – *6%*	no	15 - 10	no
CO	Untreated	no	39 - 75	no
CO	DBDPE + MC – 6%	yes	2 x >120	no
CO	DBDPE + MC – n.d.	yes	2 x >120	no
CO	DBDPE + ATO – 3%	yes	2 x >120	no
CO	DBDPE + ATO – n.d.	yes	2 x >120	no
CO	DPCAA – *0.4%*	yes	>120 - 31	no

- Halogenated FRs: bad results → not resistant to washings
- Pyrovatex: potential good results on both fabrics

ISO 12952-1 and 2 bed sheets

Textile	Formulation	Flame ignition	Flame ignition Afterburn time (s)	Cigarette ignition
CO/PES	Untreated	yes	2 x >120	no
CO/PES	AS + Urea + P-based	yes	2 x >120	no
CO/PES	Polymeric FR + ATO	no	0 - 0	no
CO	Untreated	no	39 - 75	no
CO	AS + Urea + P-based	no	0 - 0	no
CO	Polymeric FR + ATO	no	23 - 0	no
CO	P-based FR	no	6 - 1	no

- Polymeric FR: good FR results for both cotton and CO/PES but increasing stiffness
- Alternative FRs possible for cotton fabric

Conclusion bed sheets

- Well performing alternatives but only for cotton fabrics
- No alternative for PES/CO 50/50 blend detected
  → PES content too high (as PES does not react with FR)
- Bottle neck is the repeated washing cycles → permanent treatment necessary
- Oeko-tex® compliance with alternatives possible (cotton)
- Pyrovatex-like treatments which release less formaldehyde on the market

Lab results curtains

- Materials

PES 100 g/m²

PES 250 g/m²

- Tested by UNE EN 13773

after 1 x washing at 30°C:

Part 1: UNE EN 1101

Part 2:UNE EN 13772

Lab results curtains

Application	Specific fabric composition	Conventional Flame Retardants	Intermediate Flame retardants	Alternative Flame Retardants
Curtains	100% PES	(1) Decabromodiphenyl ethane + melamine cyanurate (2) Decabromodiphenyl ethane + ATO	(1) Polymeric FR	(1) Cyclic phosphonate

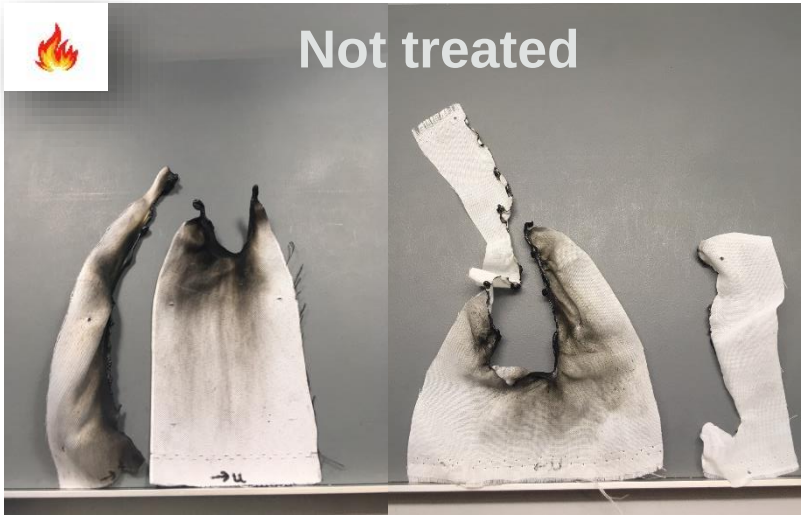
Applied via padding

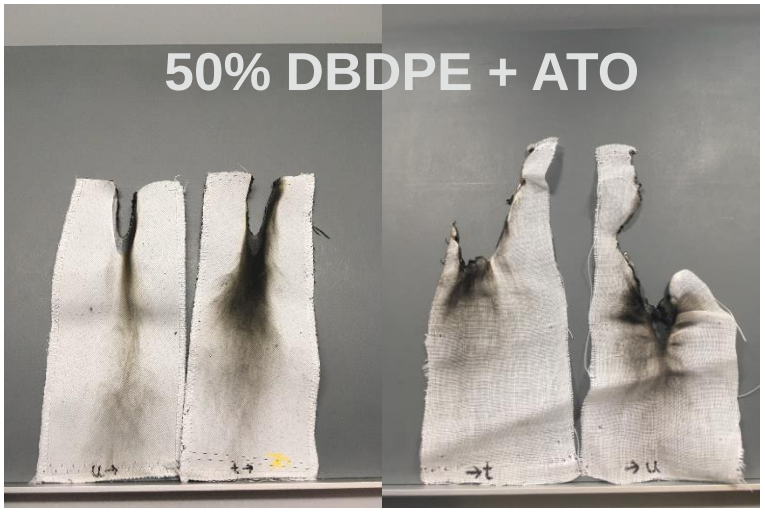
A4 scale

Lab results curtains

Textile	Formulation Add-on	Flame ignition pass
PES	DBDPE + MC 90%	yes
PES	DBDPE + ATO 50%	yes

Resistance to washing poor!

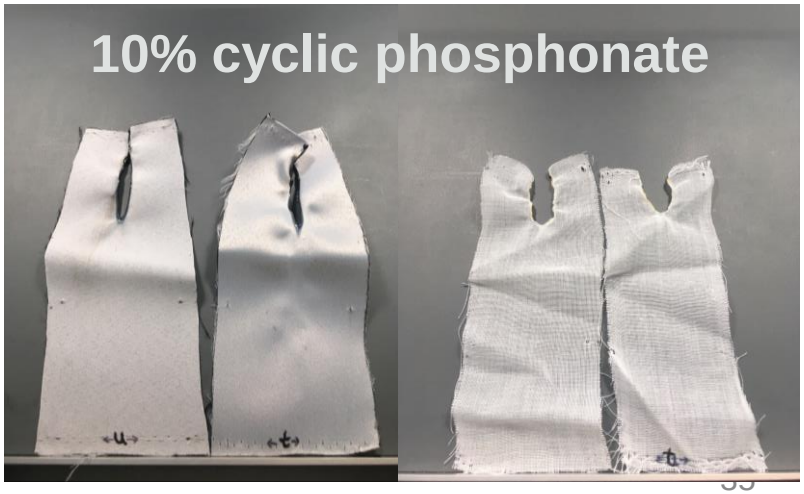




Lab results curtains

Textile	Formulation Add-on	Flame ignition pass textile B	
5 seconds ignition		warp	weft
PES	Cyclic phosphonate 10%	✓	✓
PES	Cyclic phosphonate 30%	✓	✓
PES	Cyclic phosphonate 50%	✓	✓
PES	Cyclic phosphonate 70%	✓	✓

Results on polymeric FR pending



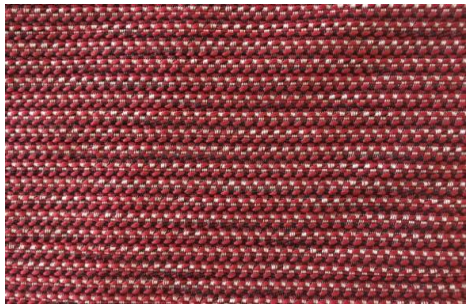
Conclusion curtains

- Wash resistance for conventional FR low
  -> high loadings needed
- Effective treatment with alternatives possible
- Results pending

Lab results upholstery

- Materials

  PES 320 g/m²



- Tested by UNE EN 1021:2015
  After 30 min of soaking at 40°C

Lab results upholstery

Application	Specific fabric composition	Conventional Flame Retardants	Intermediate Flame retardants	Alternative Flame Retardants
Upholstery	100% PES	(1) Decabromodiphenyl ethane + melamine cyanurate (2) Decabromodiphenyl ethane + ATO	(1) Polymeric FR	(1) Ammonium polyphosphate (2) Expandable graphite

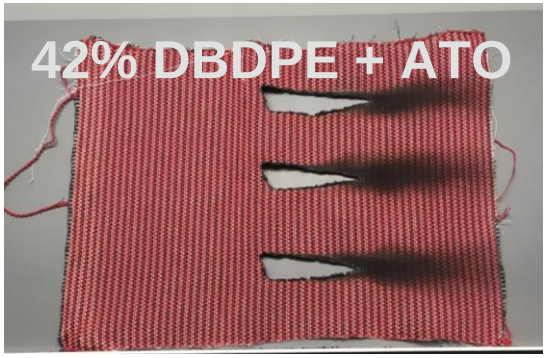
Applied as backcoating

On A4-scale

Lab results upholstery – backcoating

Textile	Formulation Add-on	Flame ignition pass
PES	DBDPE + MC 4%	no
PES	DBDPE + MC 6%	no
PES	DBDPE + MC 45%	yes
PES	DBDPE + MC 49%	yes
PES	DBDPE + ATO 2%	no
PES	DBDPE + ATO 5%	no
PES	DBDPE + ATO 16%	yes
PES	DBDPE + ATO 42%	yes

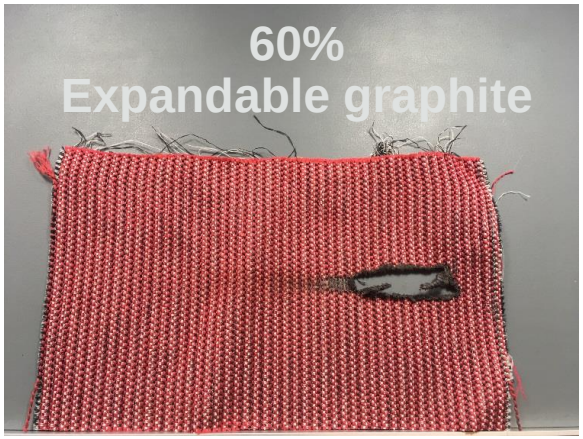
Conventional FR good working

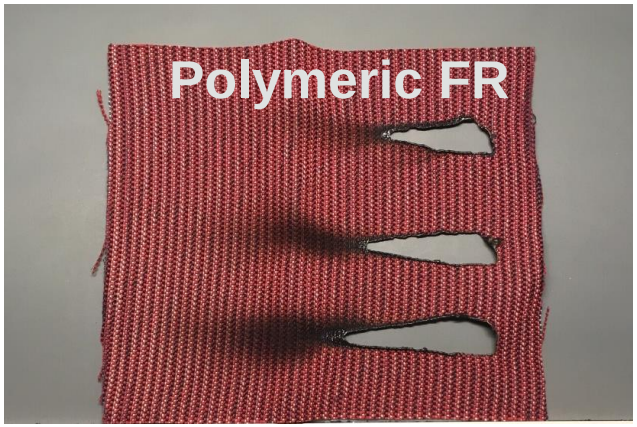


Lab results upholstery – backcoating

Textile	Formulation	Flame ignition pass
PES	Expandable Graphite 49%	no
PES	Expandable Graphite 60%	yes
PES	Expandable Graphite 70%	yes
PES	Polymeric FR 43%	yes
PES	Polymeric FR + ATO 38%	yes

Possibilities with expandable graphite and polymeric FR





Conclusion upholstery

- Halogenated FR well performing
  Still often used in industry
- Well performing alternatives with different chemistries
  Drawbacks? Colour (graphite), stiffness (polymeric FR)
- Evaluation APP pending

Implementation actions

Selection of FRs will demonstrated in industrial run

- **Companies in Italy, Spain and Czech Republic**
- **Monitoring of the process by Leitat → LCI**

  e.g. electricity comsumptions, emissions, …

  → Input for LCA and risk assessment

- **Re-assessing the technical performance**

Outcome

- Best practices
- Policy recommendations
- REACH annexes proposals
- Roadmap
- Distribution of layman's report

FLAREX

Lets **work together**

for a safer and greener future

ivi@centexbel.be
info@life-flarex.eu