Pushing the Boundaries of Flame Retardancy

Rome, 10th October 2019

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2. BPPO Derivatives as novel Flame Retardants
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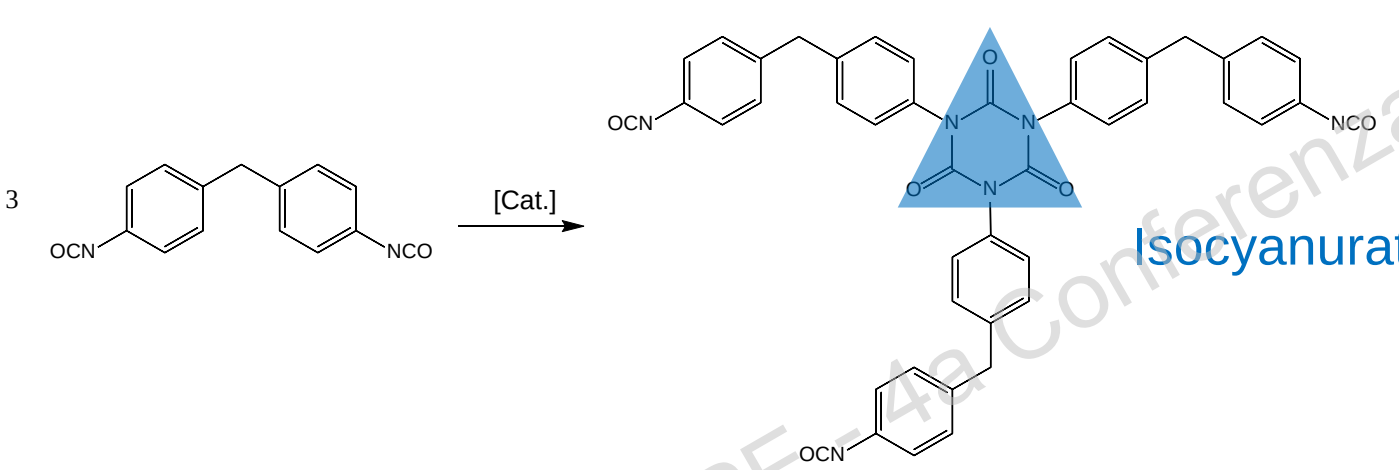
Common Flame Retardants in ISB and MP

Polyisocyanurate Foams (PIR)
Thermally more robust than PUR foams



→ Increase of cross-linkages

→ Improved fire resistance

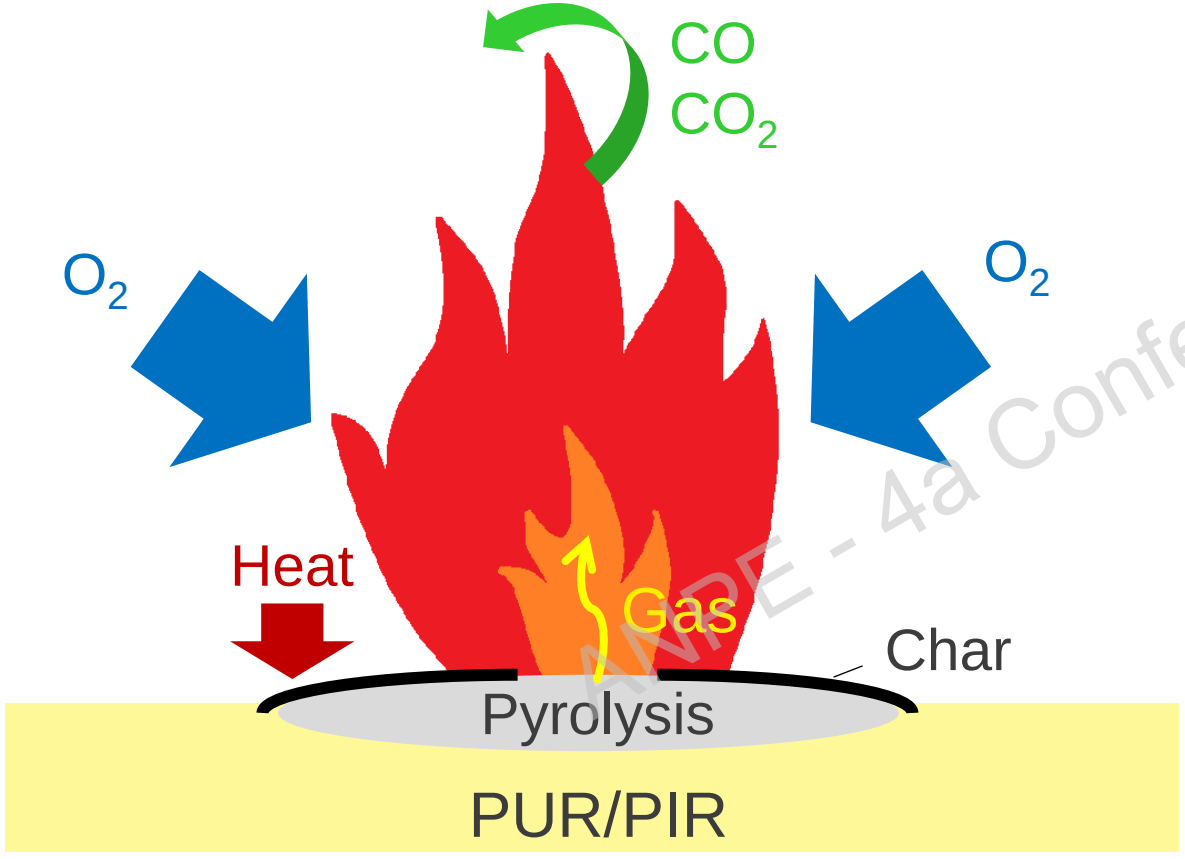
Flame Retardants

- Delay or even prevent ignition
- Reduce smoke
- Deter or hinder flame propagation

→ Needs to be combined with other technical safety measures of buildings

→ Increases time to escape in the event of a fire

Phophorus-based Flame Retardants



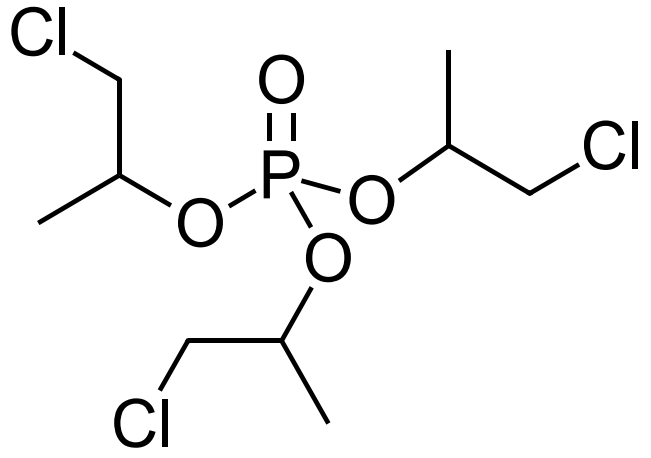
Phosphorus-based Flame Retardants

- Mainly condensed phase mode
- Support the development of char

→ Char as a barrier for O_2 and heat transfer

Tris(2-chloroethyl) phosphate (TCPP)

- Low reactivity towards water and bases
- 9.5 wt% P
- Viscosity$_{20\ °C}$ 68.5 mPas
- Reduces friability in PIR foams
- Preferred additive in rigid PU foams
- Believed to be the largest commercial phosphorus flame retardant (2015)[1]



[1] Kirk-Othmer Encyclopedia of Chemical Technology, 2017 John Wiley & Sons, DOI:10.1002/0471238961.1608151923050912.a01.pub3

EU TCPP Regulation
– Estimated time-schedule–

Regulations

This process starts if substance is proven to be CMR

REACH dossier update (Lanxess, 2015)

REACH dossier update (7/2018)

RAC: harmonized classification (≥2020)

TCPP on SVHC cand. (≥ 2021)

NTP Results public (≥2019)

TCPP ECHA decision (2020)

Valid new classification (≥2021)

CoRAP will start in 2020

Triethyl phosphate (TEP)

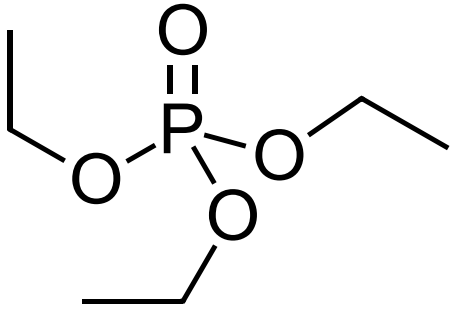
- 17 wt% P

→ Lower amount of FR necessary in formulations

- Reduces friability in PIR foams
- Viscosity$_{20\ °C}$ 1.7 mPas

→ Viscosity depressant

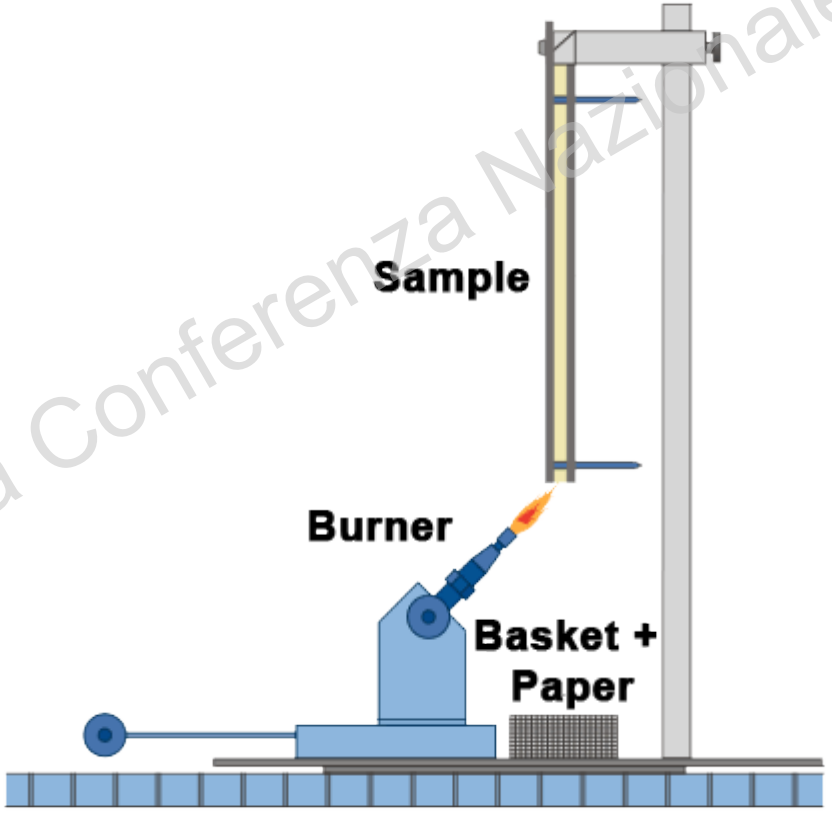
- No critical classification with regard to REACH



Flammability testing standards in EU
Small Burner Test (DIN EN ISO 11925-2)

Ignitability when exposed to small flame

- Sample size
  - 250 x 90 x d mm³ (d ≤ 60 mm)
- Test conditions
  - 30 s flame treatment
  - 60 s Test
- Requirement for E-Class
  - Max Flame height ≤ 150 mm



Comparison TCPP vs. TEP

Insulation Boards based on same formulation with variation of FR

Thickness [mm]		80	80	120	120
FR		TCPP	TEP	TCPP	TEP
P content (wt%)		0,43	0,47	0,43	0,48
Small Burner Test (11925-2)	Ø Flame Height [mm]	130	130	130	130
	Class	E	E	E	E

→ Same classification in small burner test

Demands

Regulations

Sustainability

- Reactive FR
- Polymeric FR
- Alternative FR

BPPO Derivatives as novel Flame Retardants

A fundamental Study

BPPO Derivatives as novel Flame Retardants
A fundamental Study between Covestro and IPF Dresden

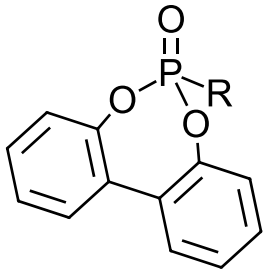
Influence of the phosphorus oxidation state

Gas phase action

Solid phase action

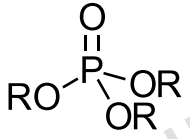
Phosphorus oxidation state:

+ III



BPPO
Acrylate Addition
Products

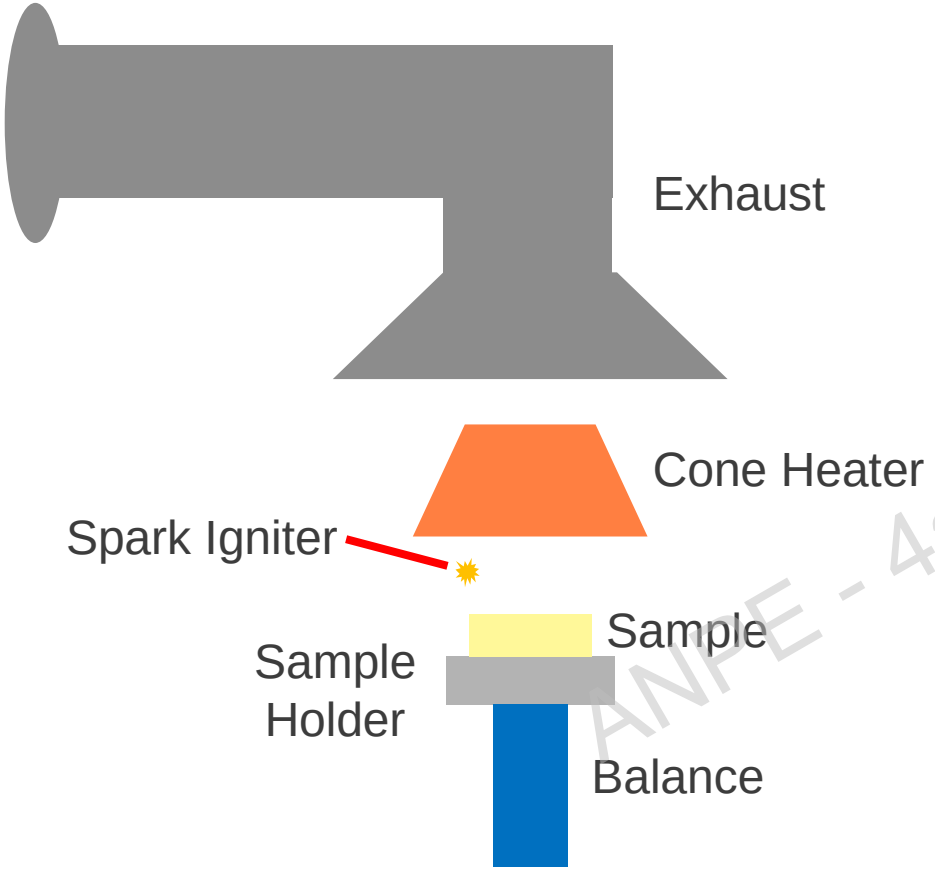
+ V



- Investigation of FR properties of BPPO derivatives
- Acrylate addition products not commercially available

J. Lenz, D. Pospiech, M. Paven, R. W. Albach, M. Günther, B. Schartel and B. Voit, *Polymers* **2019**, 11, 1242.

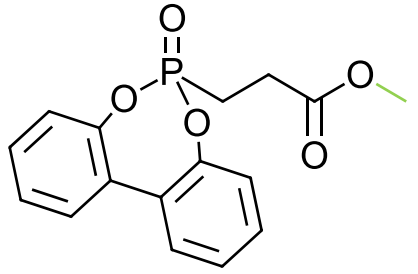
Cone Calorimeter Test
ISO 5660-1



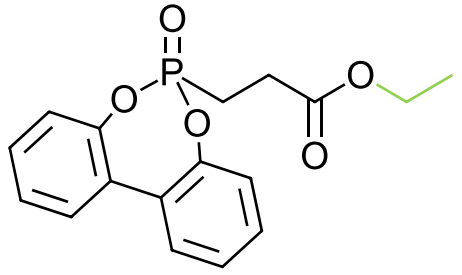
- Samples
  - 100 x 100 x d (≤50) mm³
  - In this study: 100 x 100 x 30 mm³
- Radiation Heat Flux: 50 kW/m²
- Measurement of the Average Rate of Heat Emission

BPPO Derivatives

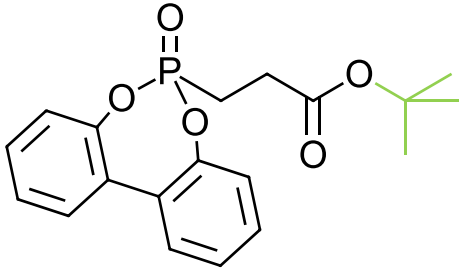
FR	Small Burner Test DIN 4102	Cone Calorimeter Test DIN ISO 5660-1		
	Ø Flame Height [mm]	MARHE [kW/m²]	THR [MJ/m²]	TSR [m²/m²]
-	200	172	24	551
TEP (0.3 wt% P)	180	128	26	392
MA-BPPO/TEP (0.7/0.3 wt% P)	150	132	28	527
EA-BPPO/TEP (0.7/0.3 wt% P)	150	121	23	433
^{t}BuA-BPPO/TEP (0.7/0.3 wt% P)	150	114	26	380



MA-BPPO



EA-BPPO



^{t}BuA-BPPO

→ Tendency: MARHE↓ and TSR↓ with bigger side chain

J. Lenz, D. Pospiech, M. Paven, R. W. Albach, M. Günther, B. Schartel and B. Voit, *Polymers* **2019**, 11, 1242.

Summary

- The decision on whether the use of TCPP will be regulated is postponed to 2020
- For the moment TEP is a potential substitution for TCPP in the applications Insulation Board and Metal Panel
- Fundamental studies show that BPPO derivatives can be used as flame retardants

THANK YOU
FOR YOUR ATTENTION

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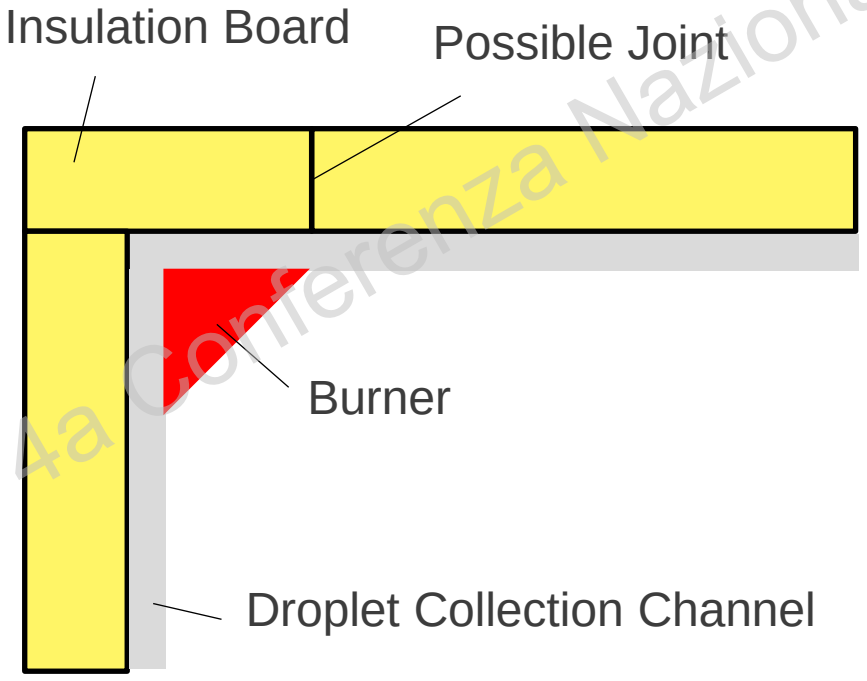
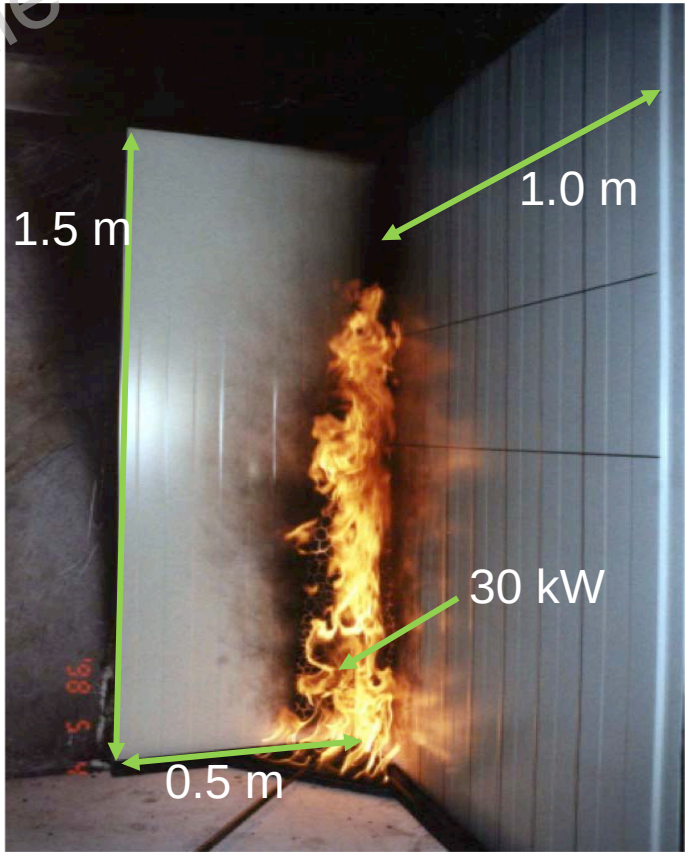
Flammability testing standards in EU
Thermal attack by a single burning item (SBI) – DIN EN 13823

- Sample size
  - 2 wings
  - Short Wing: 0.5 x 1,5 m²
  - Long Wing: 1 x 1,5 m²
- Test conditions
  - 21 min flame treatment
  - 26 min Test





Flammability testing standards in EU
Classification of construction products EN 13501-1

Measured Parameters:

- FIGRA – *Fi*re *G*rowth *Ra*te
- THR – *T*otal *H*eat *R*elease
- LFS- *L*ateral *F*lame *S*pread
- SMOGRA – *Smo*ke *G*rowth *Ra*te
- TSP – *T*otal *S*moke *P*roduction
- Burning Droplets

Flammability Class			
B	$FIGRA_{0,2\ MJ}$	[W/s]	≤ 120
	THR_{600}	[MJ]	≤ 7,5
	LFS		< Edge of Specimen
C	$FIGRA_{0,2\ MJ}$	[W/s]	≤ 250
	THR_{600}	[MJ]	≤ 15
	LFS		< Edge of Specimen
D	$FIGRA_{0,4\ MJ}$	[W/s]	≤ 750

Smoke Development Class		
s_1	SMOGRA	30 m²/s²
	TSP_{600}	50 m²
s_2	SMOGRA	180 m²/s²
	TSP_{600}	200 m²
s_3	Not s_1 or s_2	

Droplet Formation Class	
d_0	No burning droplets/particles within the first 600 s
d_1	No burning droplets/particles with an afterflame time > 10 s within the first 600 s
d_2	Not d_0 or d_1