Phosphorus based Flame Retardants

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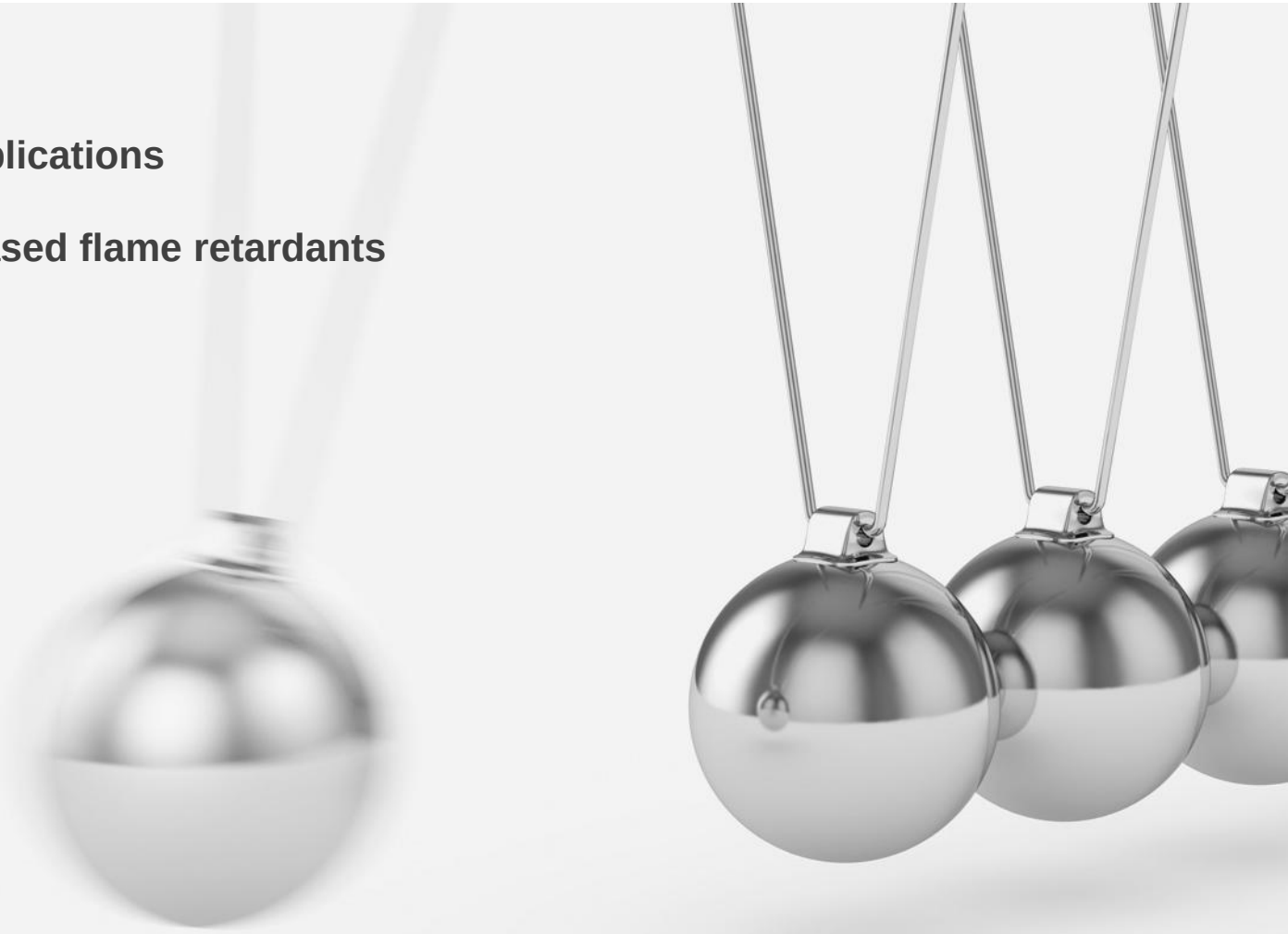
ADD Flame Retardants Day | Leverkusen, December 7, 2018

Phosphorus based flame retardants
Agenda

1. Flame retardants – Introduction
2. Phosphorus based flame retardants and their applications
3. New sustainable developments in phosphorus based flame retardants
4. Conclusions



Flame retardants
Introduction

Flame retardants are crucial components of fire safety

Flame retardants

- Prevent or delay the ignition of materials
- Reduce flame spread
- Reduce smoke density
- Increase the escape time » help to save lives

Fire safety

- Flame retardants are one solution to improve the fire safety
- Combination with other solutions are necessary
- Fire alarms, sprinkler systems, …

Triangle of fire
How does a fire arise?

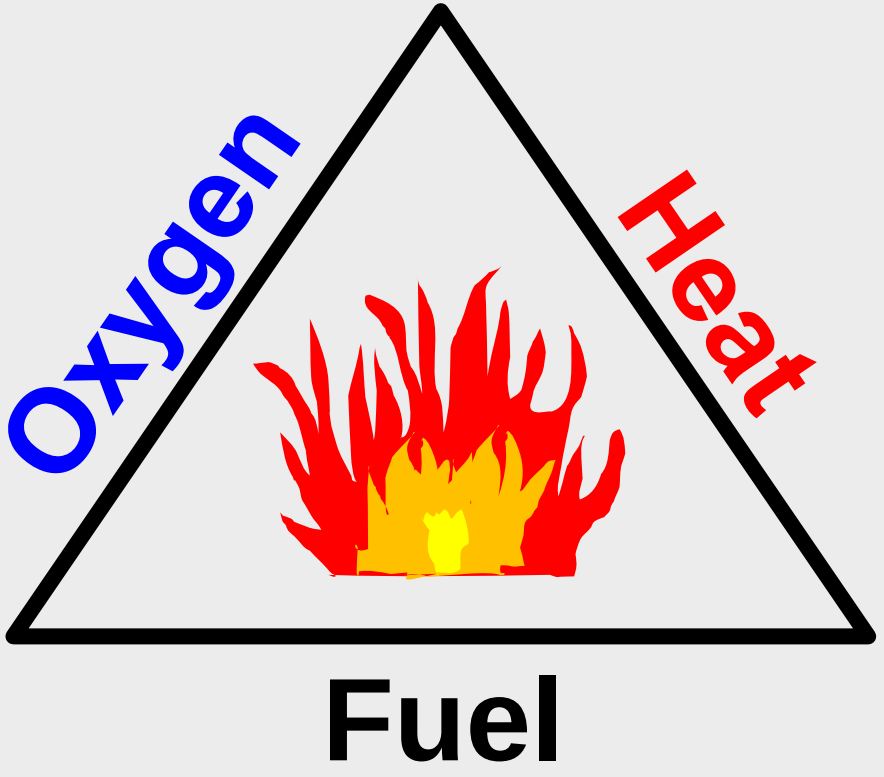
Conditions for a fire

1. **Fuel** provides energy for the fire
2. **Heat** pyrolizes / evaporates fuel and ignites
3. **O_2** from the air is the common oxidizing agent

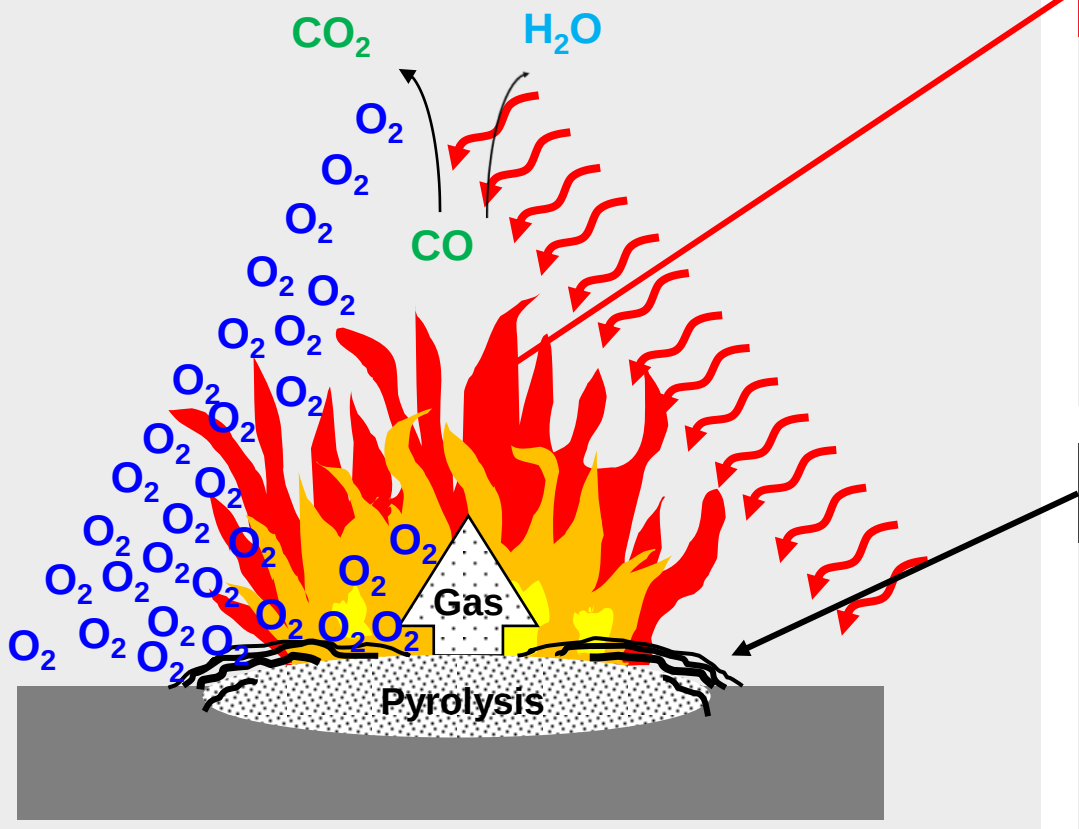
Fire = visible chemical reactions driven by radicals

Prevention or extinction of a fire

- **Fuel** remove or cover
- **Heat** decrease by energy absorption or cooling
- **O_2** displace or dilute
- **Fire** interrupt energy-releasing radical reactions



Flame retardants interfere with the triangle of fire



Bromine based flame retardants

- Act in the gas phase:
- Br radicals neutralize high energy radicals in the flame

➢ Energy / heat in the flame is reduced

Phosphorus based flame retardants

- Act mostly in the condensed phase:
- Phosphorus compounds help to create a char layer

➢ Prevents the polymer below from oxygen and heat

Flame retardants
Factors affecting the selection

Fire regulations

Fire standards, building code, insurances,…

Technical aspects

Processing, mechanical properties,…

Regulatory

Environmental laws, recycling,…

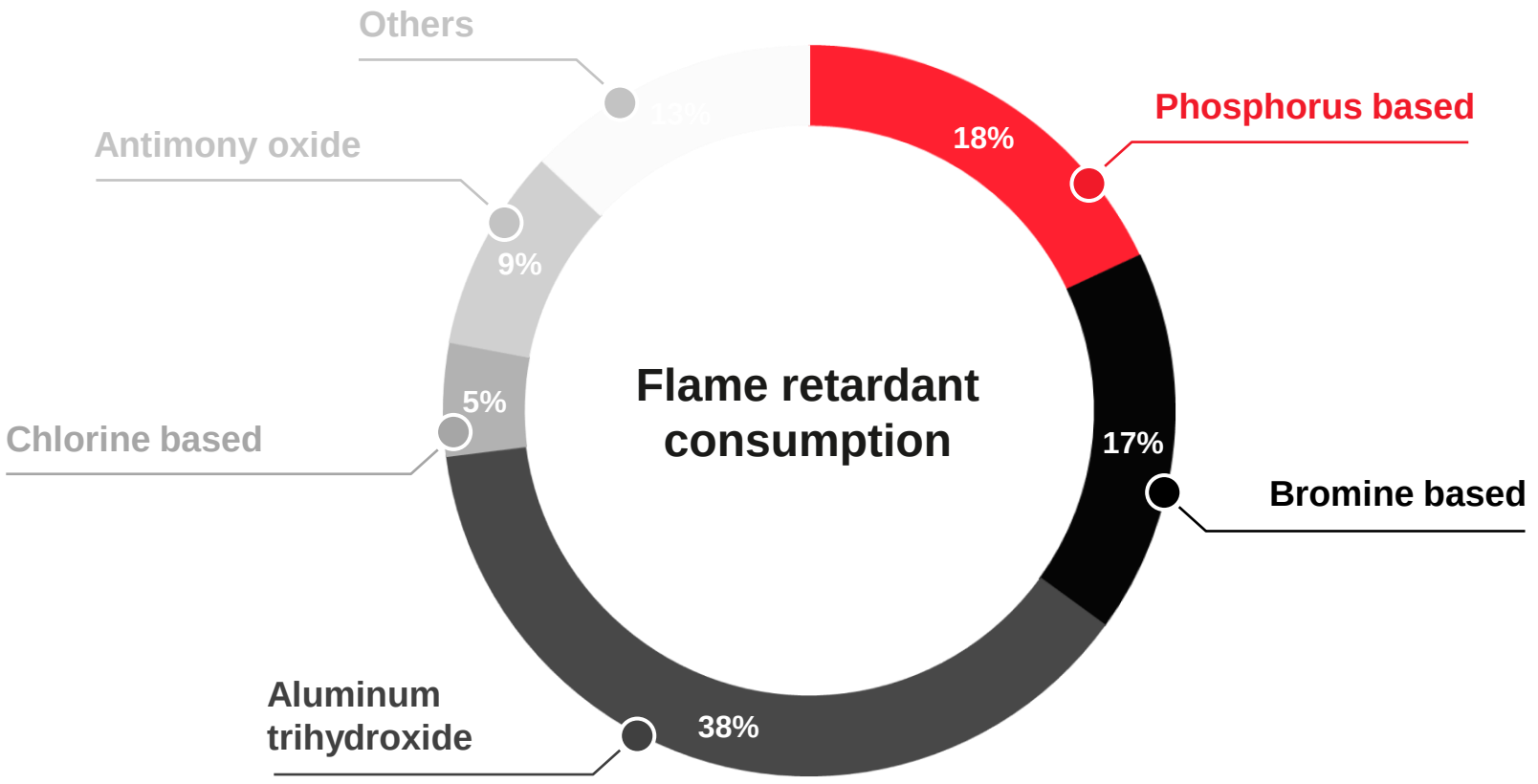
Economics

Cost efficiency, supply chain,…

Phosphorus based flame retardants and their applications

Flame retardants market by type

World consumption of flame retardants in 2016: 2,250 ktons



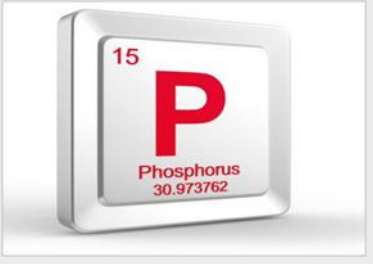
Flame retardants market

- Aluminum trihydroxide (ATH) has the highest consumption by volume
- Organophosphorus flame retardants account for 18% of the consumption: approx. 406 ktons

Source: LXS estimation

Value chain of phosphorus based flame retardants

Phosphate rock → Yellow phosphorus (P4) → Phosphorus intermediates → Water treatment / Phosphorus specialties / Flame retardants

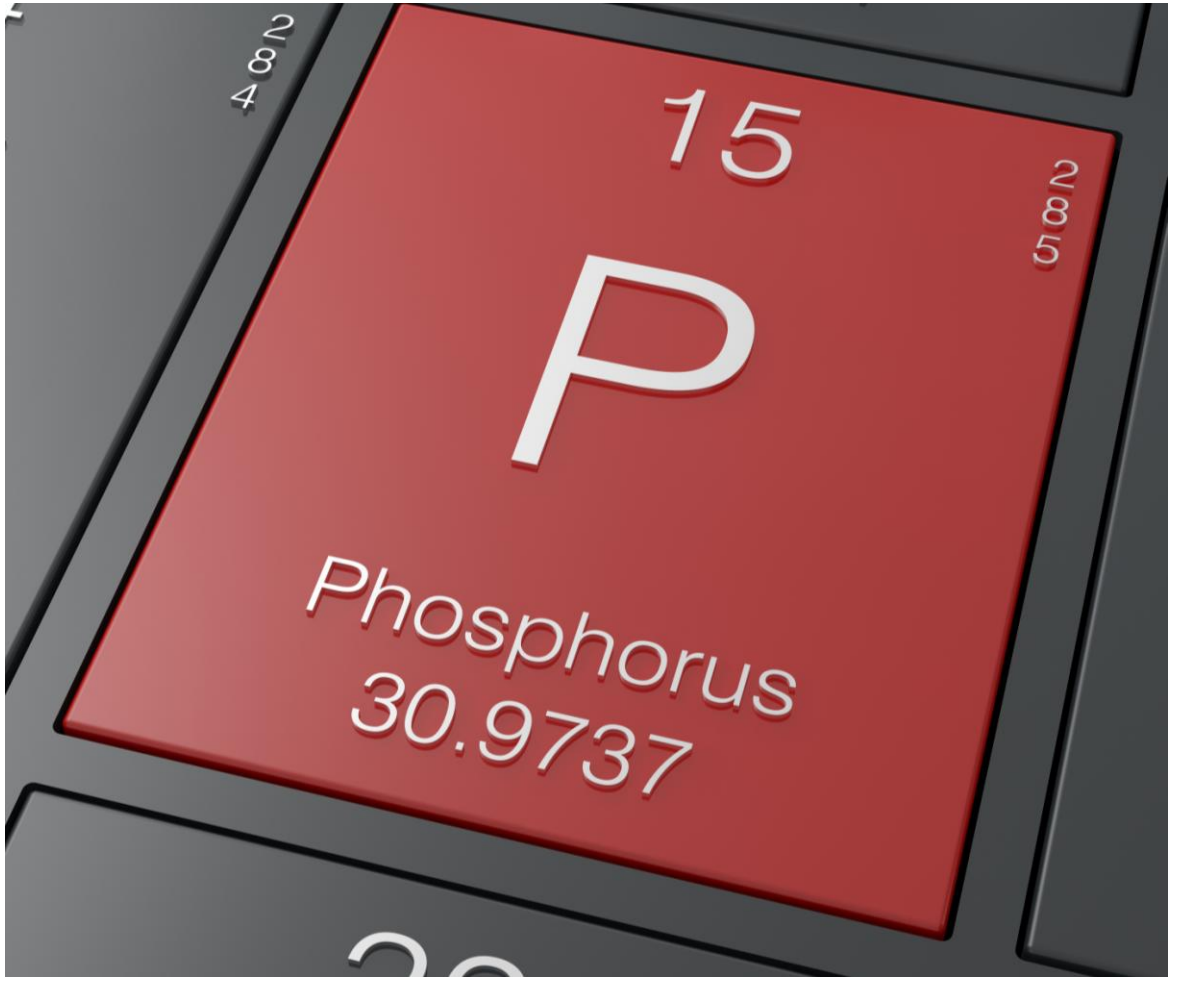


ADD has a strong position in the value chain

Phosphorus based flame retardants
Product portfolio

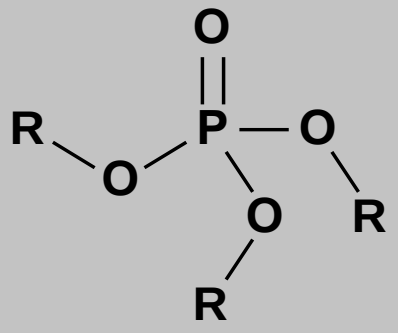
Brand names

- Amgard®
- Disflamoll®
- Emerald Innovation® NH-1
- Kronitex®
- Levagard®
- Reofos®
- Uniplex



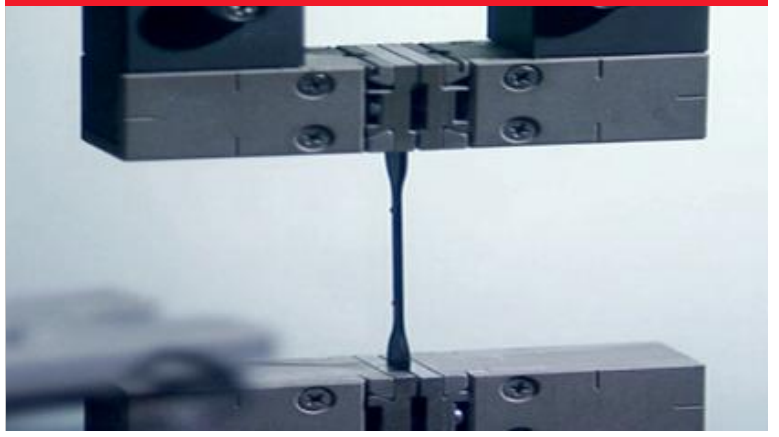
ADD offers a variety of phosphorus based flame retardants

Chemistry



Appearance

Performance

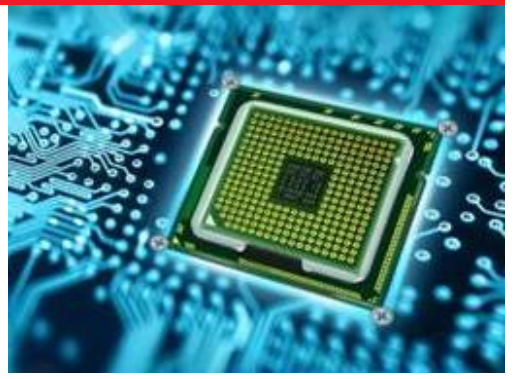


ADD phosphorus based flame retardants are mainly organic phosphate esters

ADD phosphorus based flame retardants are typically clear low viscous liquids

ADD flame retardants offer additional performance benefits besides flame retardancy

Phosphorus based flame retardants
In which polymers are they used?

TPU	Rigid PU foam	PF resin
		
		
Flexible PU foam	**NBR rubber**	**PVC (flexible)**

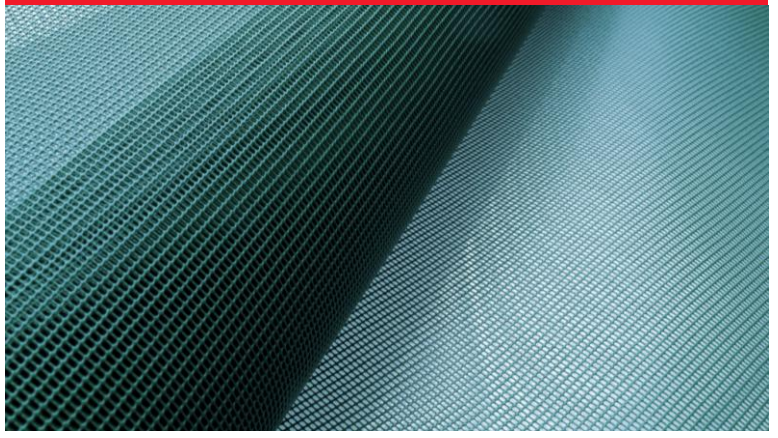
Polymers

- ADD phosphorus based flame retardants are used in a variety of polymers including thermoplastics, thermosets and elastomers.
- They are mainly used in polar polymers due to their compatibility

Phosphorus based flame retardants in flexible PVC

Flooring

Coated fabrics



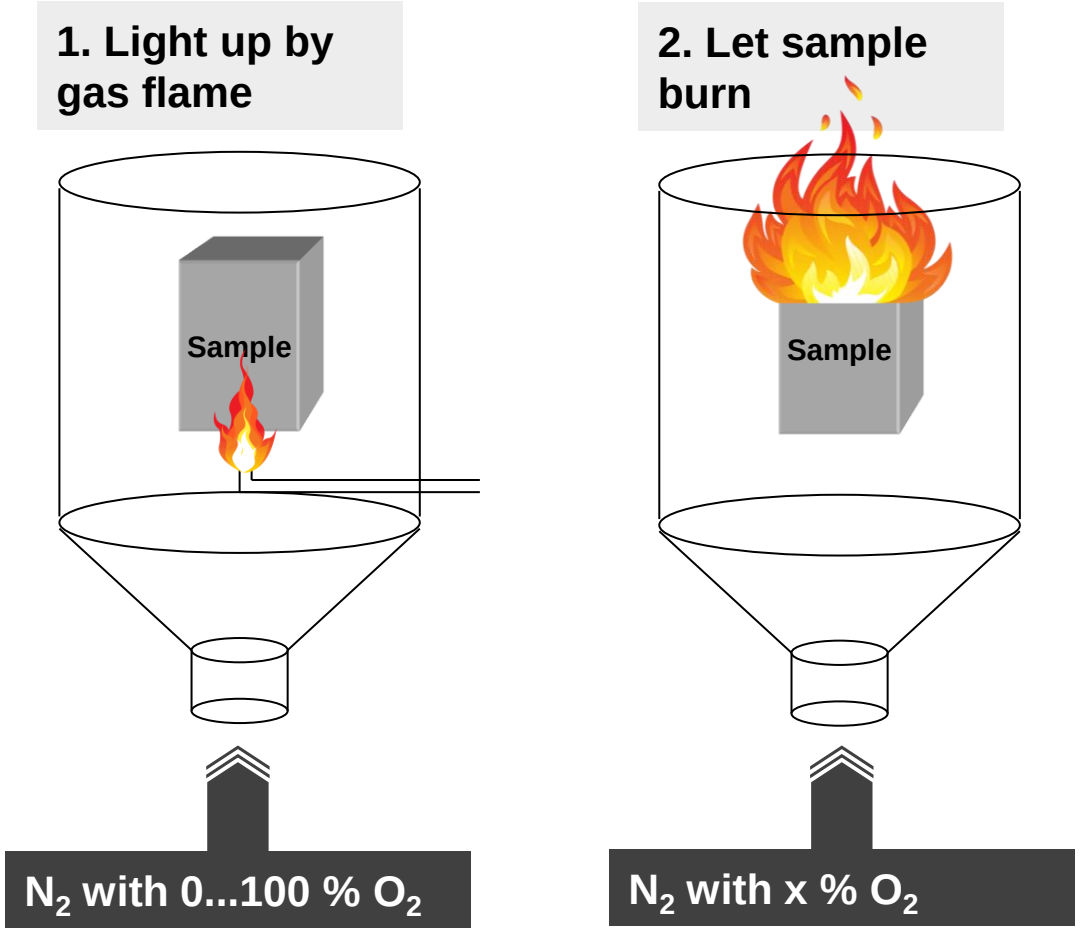
Cables

ADD phosphate esters are used as flame retardants in flexible PVC (PVC-P)

ADD phosphate esters act as plasticizer in PVC-P at the same time

ADD phosphate esters improve low temperature stability and smoke density in PVC-P

Fire standard
LOI method (ISO 4589)



LOI value

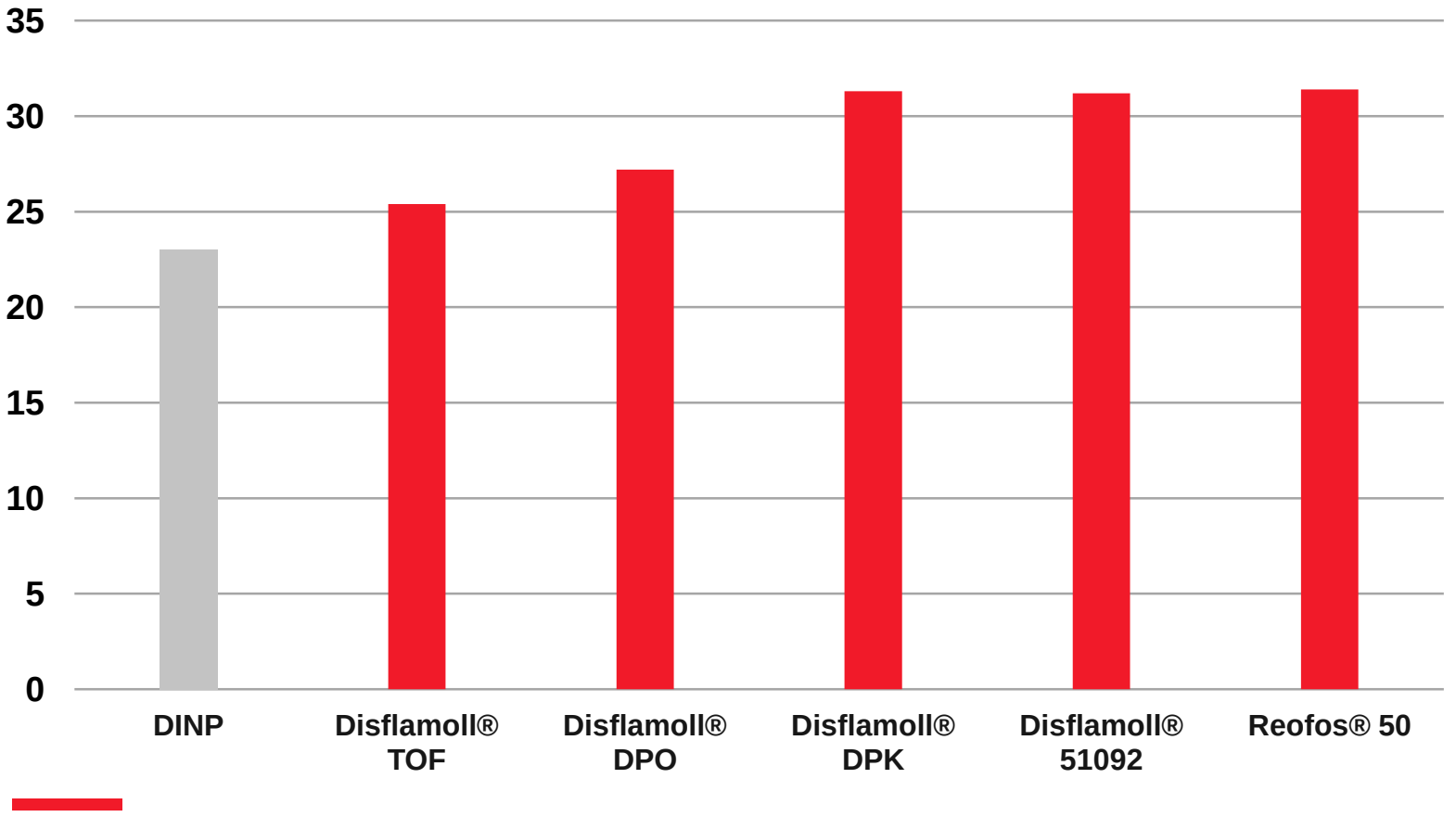
- The limiting oxygen index (LOI) is the lowest concentration of O_2 which allows the burning of the sample after removing the ignition flame
- The higher the index the more flame retardant is the material

> 27: Self-extinguishing

> 22: slowly burning

Phosphorus based flame retardants increase the LOI value of PVC formulations

LOI value [%] of a PVC-P formulation containing 54 phr plasticizer



PVC-P

- The LOI indicates the flammability of a material
- Aryl phosphates such as Disflamoll® DPK, Disflamoll® 51092 and Reofos® 50 show the highest LOI values / flame retardancy

Phosphorus based flame retardants in flexible polyurethane (PU) foam

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Automotive

Furniture

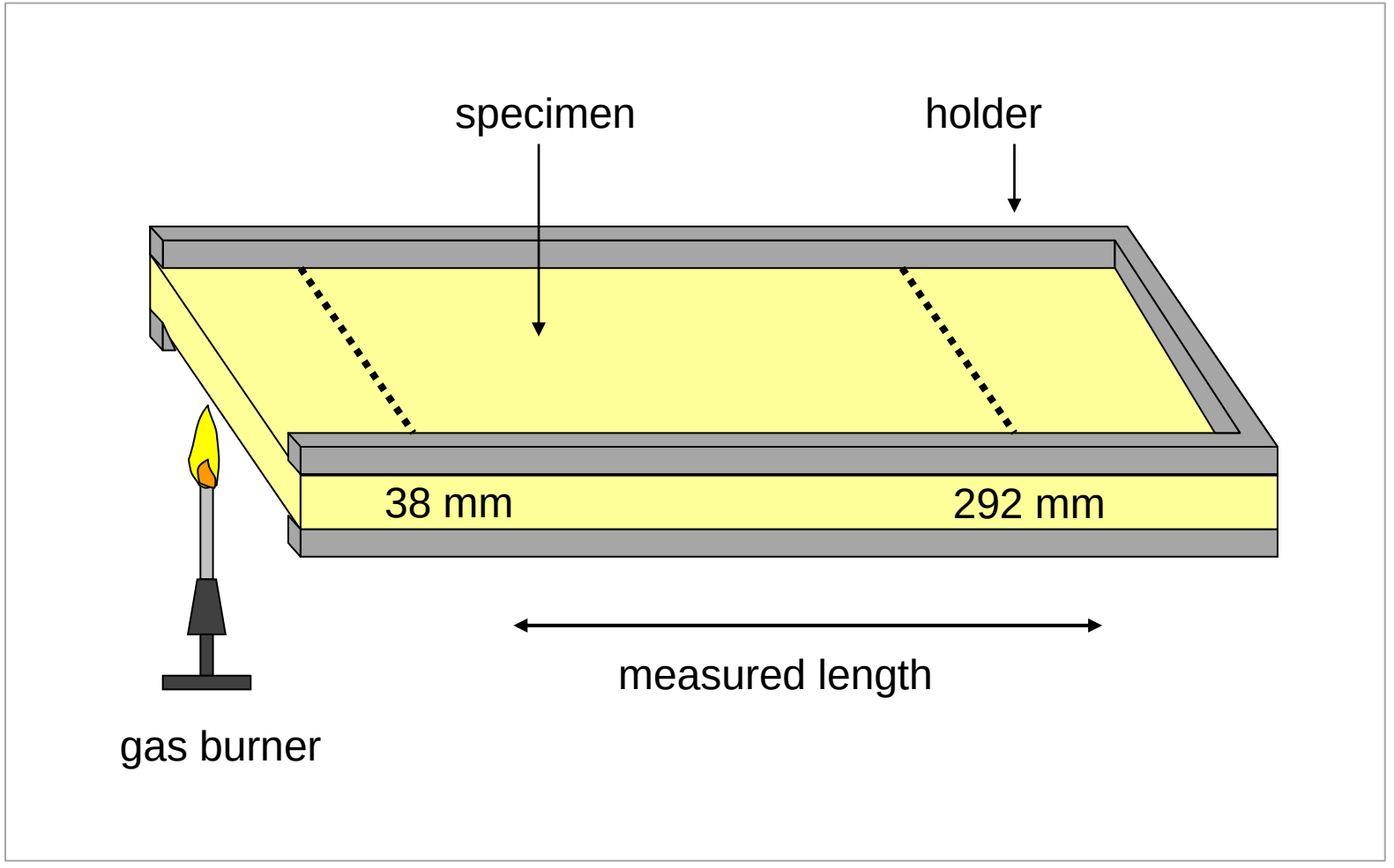
Technical foams

ADD phosphate esters are used as flame retardants in flexible polyurethane (PU) foam

ADD phosphorus based flame retardants offer low volatility / emissions

ADD phosphorus based flame retardants show good aging properties

Fire standard
FMVSS 302 – automotive



FMVSS 302

- Fire standard for vehicles worldwide
- Ignition time: 15 sec
- Flame spread:
  102 mm/min / (4 inch/min)
- Classification:
  - RB (fail)
  - BR (pass)
  - SE/BR (pass)
  - SE/NBR (pass)
  - SE (pass)

Phosphorus based flame retardants increase the flame retardancy of flexible PU foams

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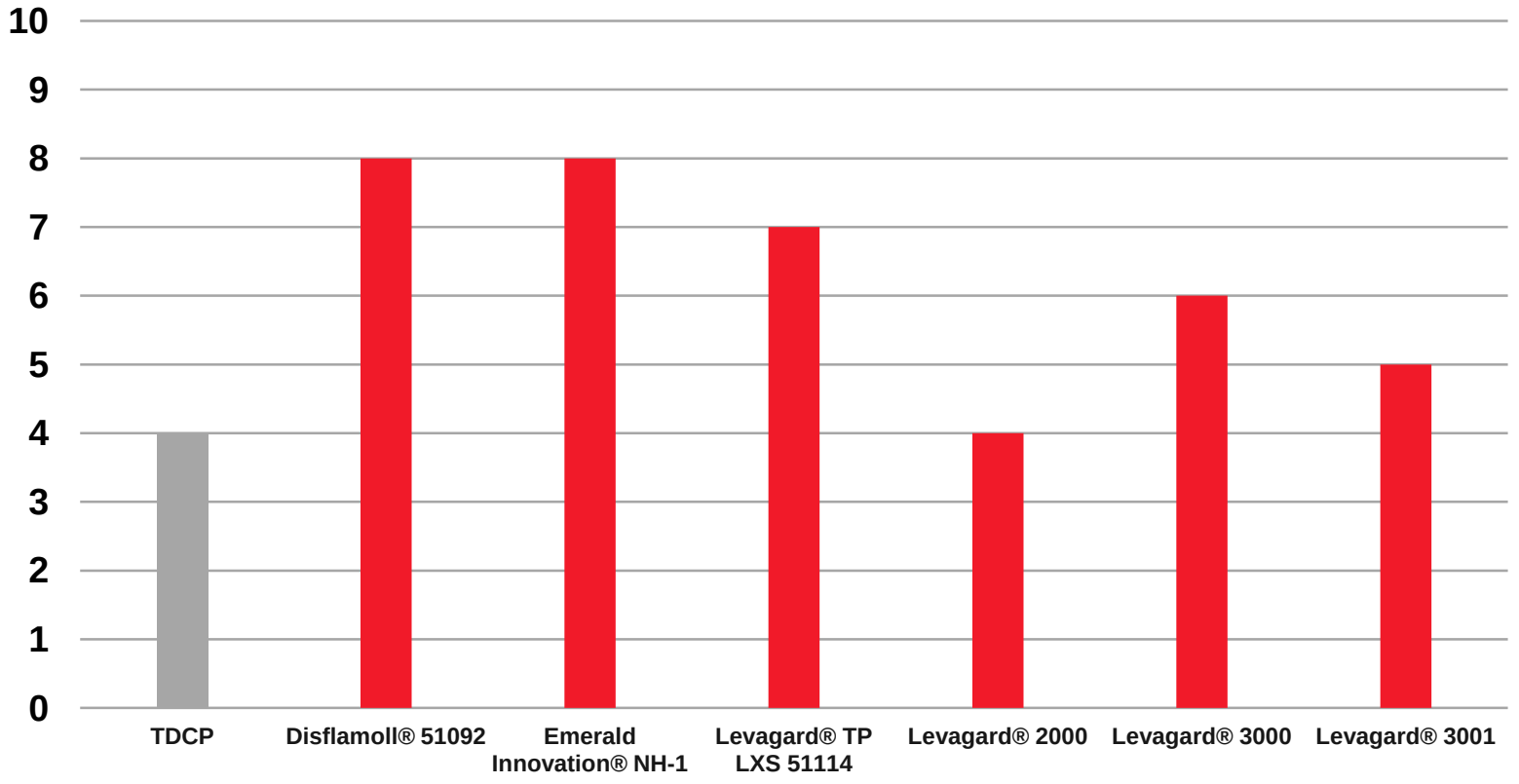
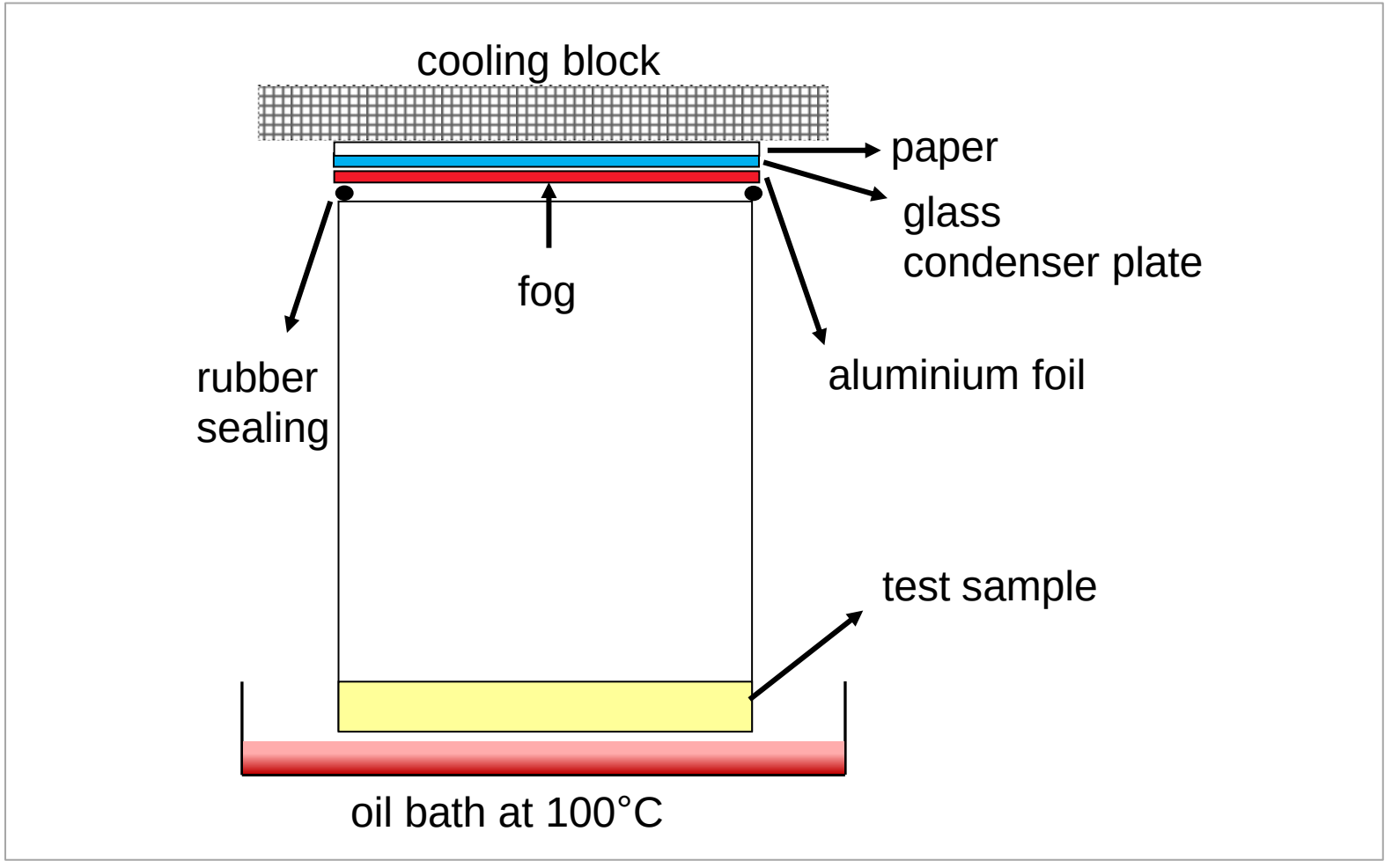
Passing level [php]



FMVSS 302

- Polyether foam with a density of 33 kg/m^3
- Passing level to achieve BR classification was determined

Fogging – DIN 75201
Windscreen fogging test apparatus

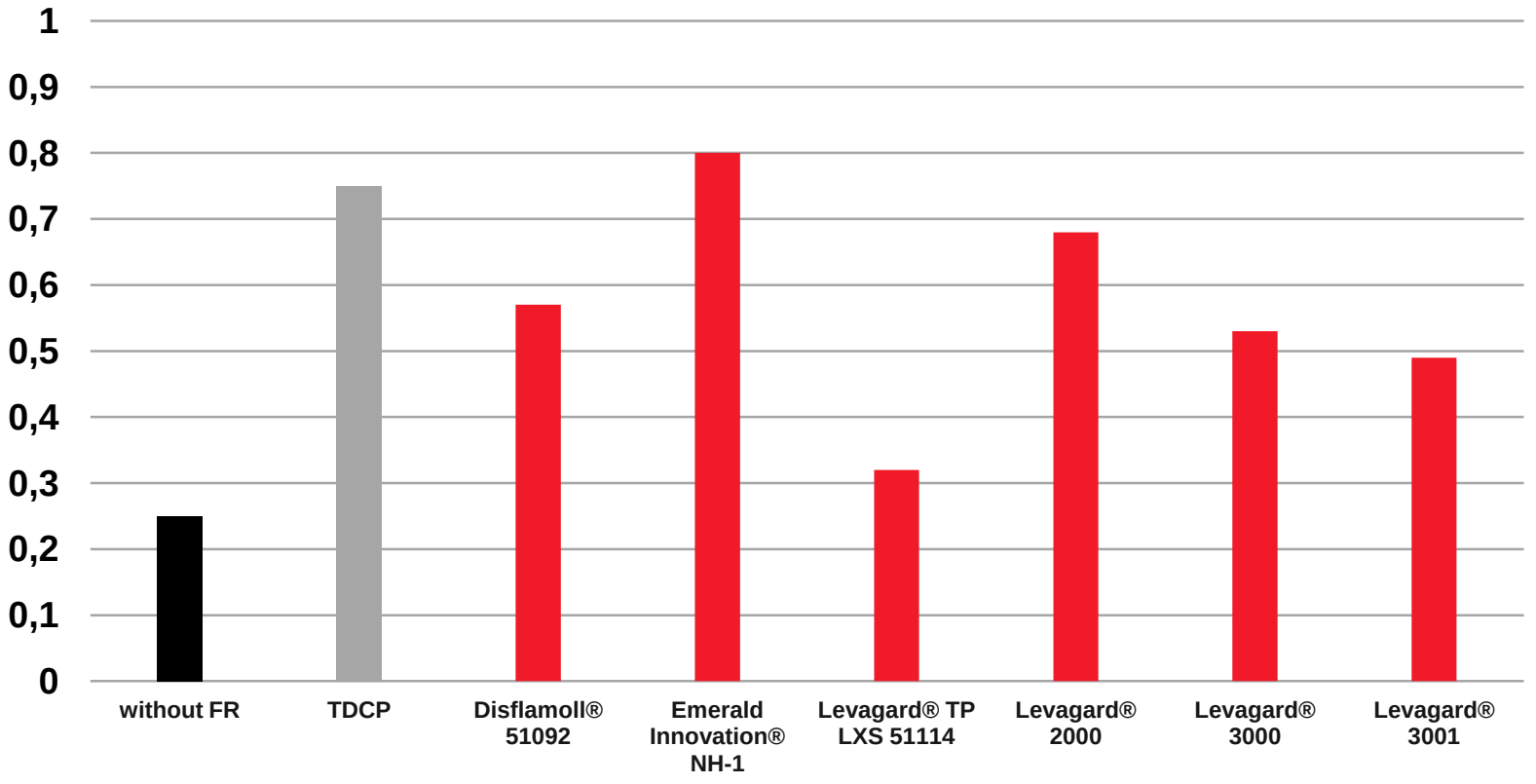


Fogging

- Fogging A
  - 3 h at 100°C
  - Transmission
- Fogging B
  - 16 h at 100°C
  - Gravimetric

Phosphorus based flame retardants show a low contribution to fogging / emission of flexible PU foams

Fogging B [mg]

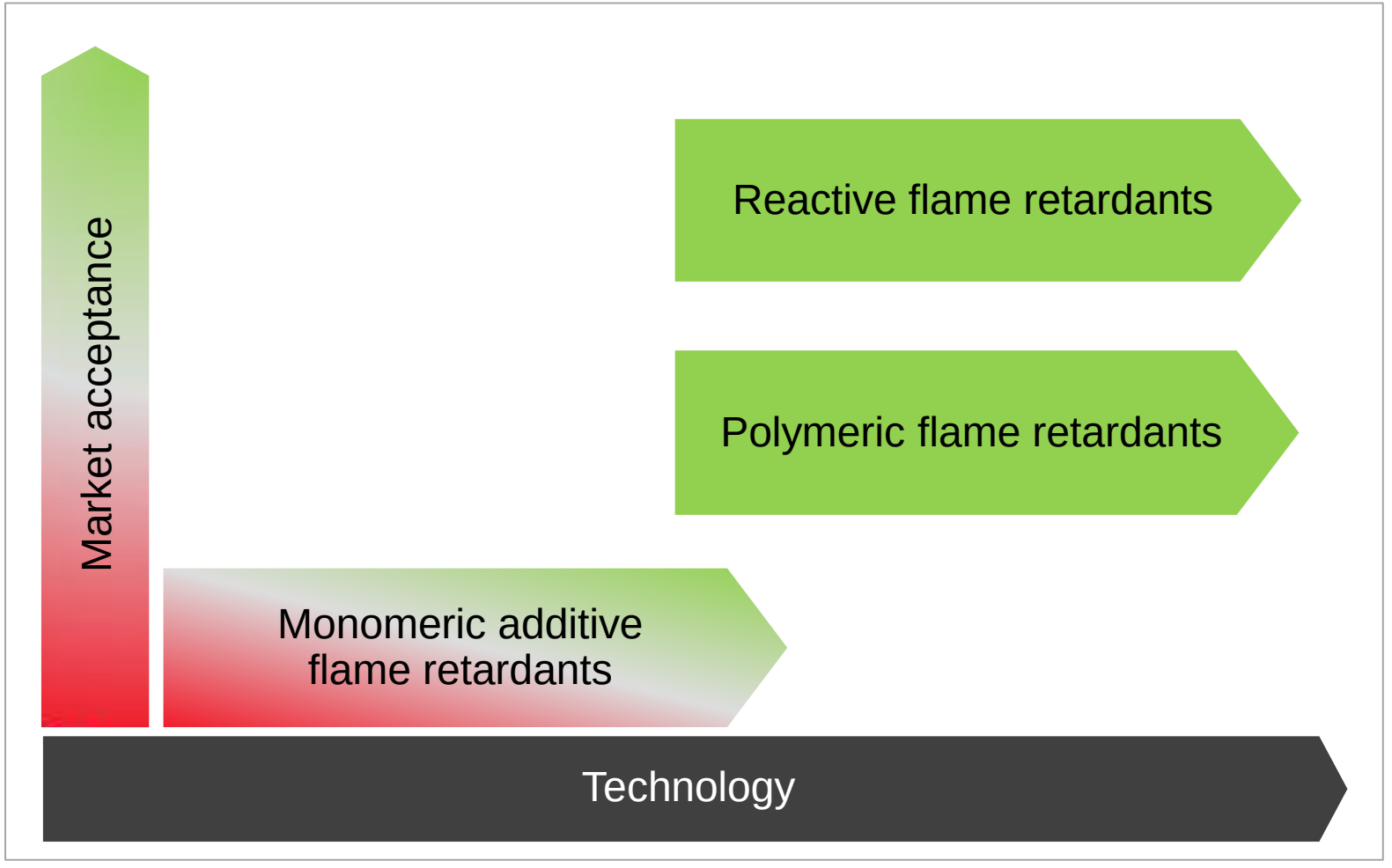


Fogging B

- Polyether foam with a density of 33 kg/m^3
- Fogging of foams containing 6 php flame retardant

New sustainable developments in phosphorus based flame retardants

Concepts for sustainable flame retardants



FR technology trends

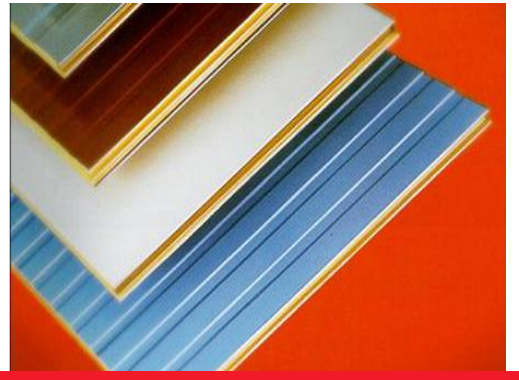
- Increased public sensitivity regarding health effect of chemicals
- Growing awareness of consumer exposure to chemicals
- Additives in polymers may contribute to consumer exposure
- Strategies to reduce emissions:
  - Reactive flame retardants that are chemically bound
  - Polymeric additives, with a high molecular weight, thus a low volatility, a high permanence and no bioaccumulation

Phosphorus based flame retardants in rigid PU foam

Rigid polyurethane foam








Established application for phosphorus based flame retardants

Rigid PU foam

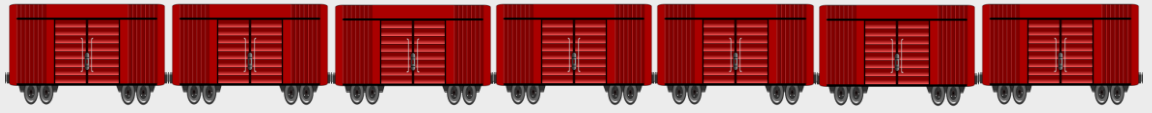
- Phosphorus based additives are most prominent among the flame retardants helping rigid polyurethane foam to comply with various fire standards
- Growing concerns about certain additives used in this application
- Increased market interests in more sustainable flame retardant solutions

Flame retardants for rigid PU foam
New developments

Levagard® 2000

- Phosphorus content: 16,4%
- Viscosity: 100 - 120 mPa·s (23°C)
- Low emission

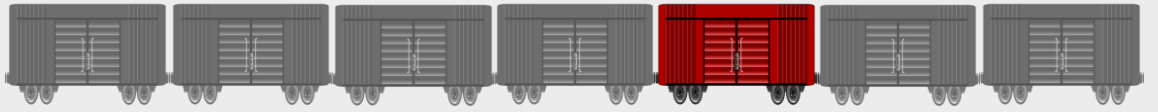
- Oligomeric alkyl phosphate ester



Levagard® 2100

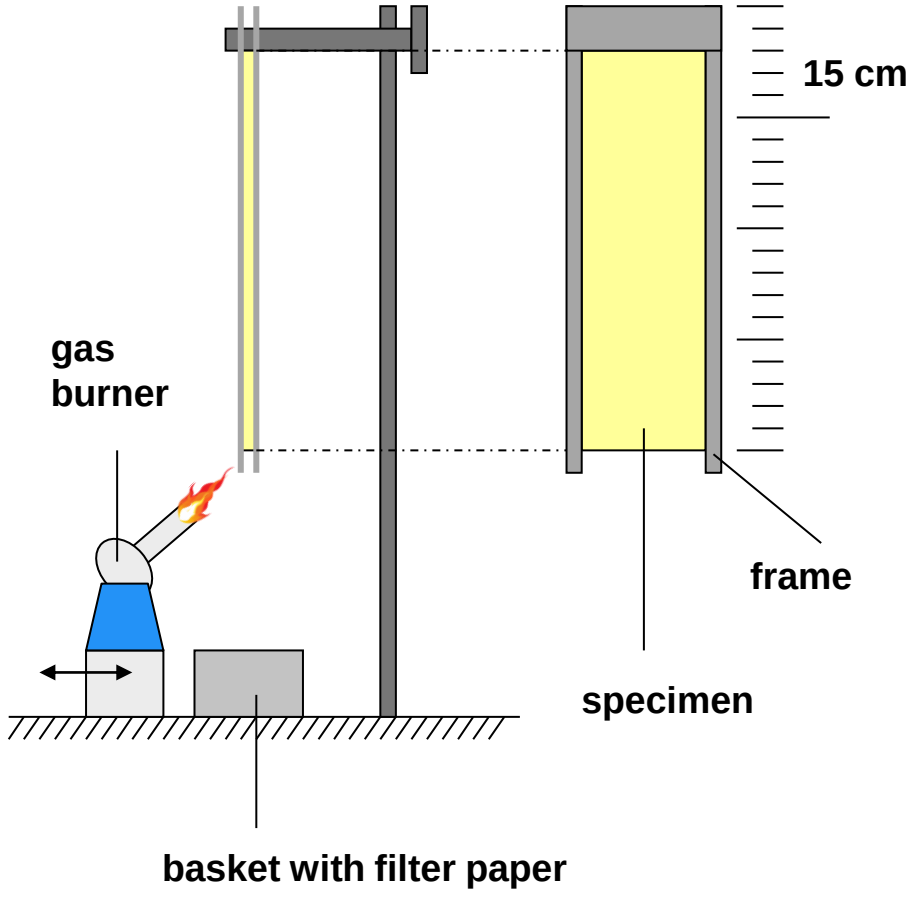
- Phosphorus content: 18,4%
- Viscosity: 25 - 30 mPa·s (23°C)

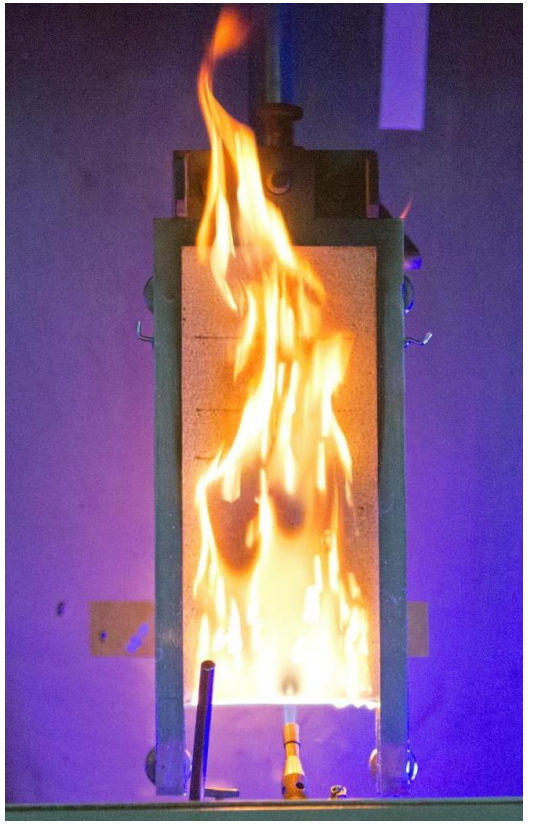
- Reactive organic phosphonate
- Chemically bound into the polymer
- ➢ No emission



ADD has developed new flame retardant solutions for rigid PU foam

Fire standard
EN ISO 11925-2 (DIN 4102 - B2)



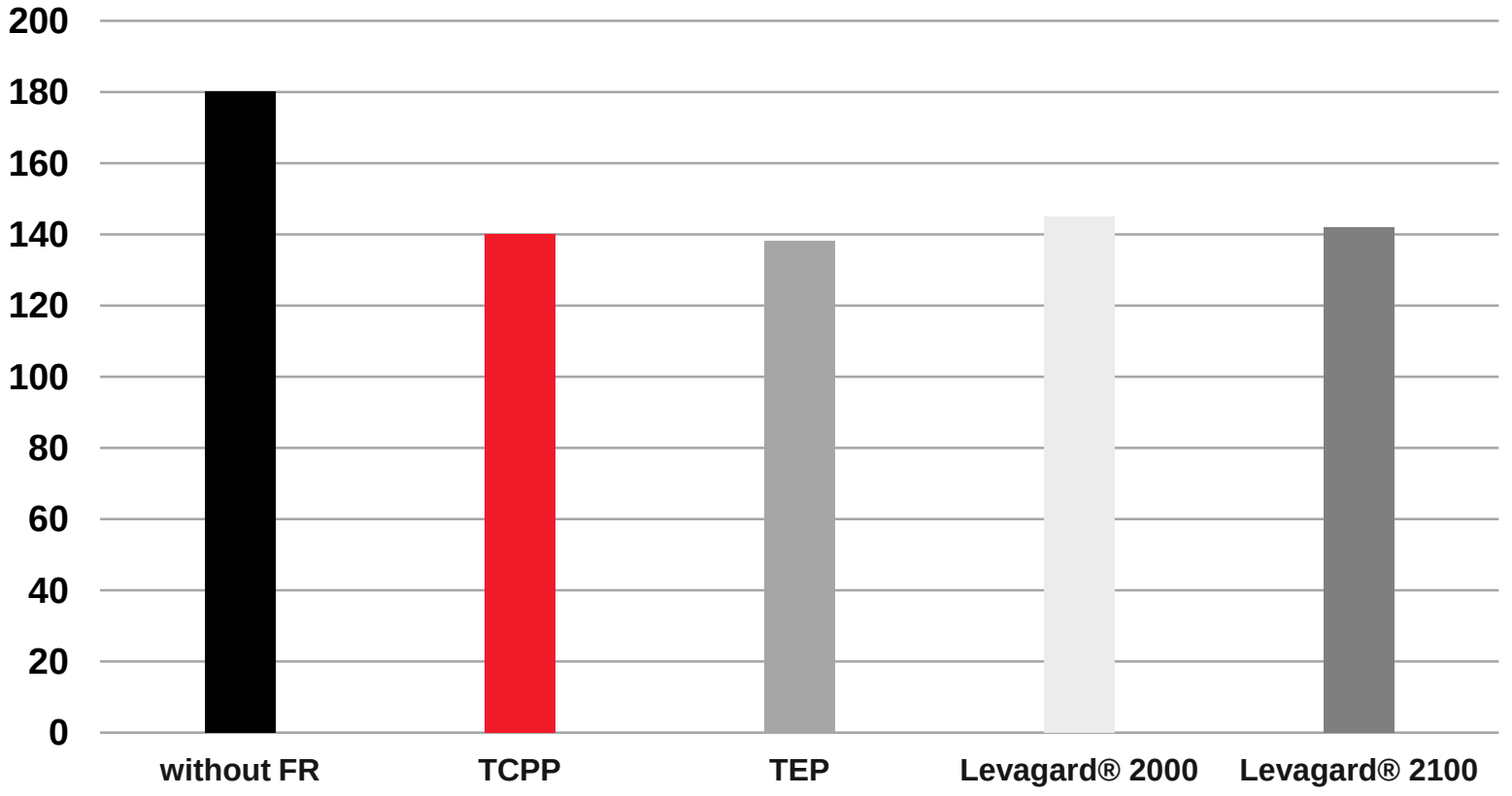


Small burner – EU

- Flame length:
  20 mm / 0.79 inch
- Flame application:
  15 s or 30 s
- Test duration:
  20 s or 60 s
- Requirements:
  - Flame height:
    < 150 mm
    within 20 s or 60 s

PIR foam
EN ISO 11925 – flame height

Flame height [mm]



EN ISO 11925

- PIR foam with a foam density of 28 kg/m^3
- All foams contain 25 php flame retardant

➢ All flame retardants improve the fire performance of the PIR foam

➢ All foams feature a similar fire performance expressed in similar flame heights

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Conclusions

- ADD offers a broad range of phosphorus based flame retardants
- Phosphorus based flame retardants show additional benefits besides flame retardancy
- ADD continues to develop new phosphorus based flame retardants

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Unless specified to the contrary, the values given have been established on standardized test specimens at room temperature. The figures should be regarded as guide values only and not as binding minimum values. Kindly note that the results refer exclusively to the specimens tested. Under certain conditions, the test results established can be affected to a considerable extent by the processing conditions and manufacturing process.

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Business Unit Additives – Polymer Additives


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