PDAE 2009

Polyurea & Fire Safety

Regulations, Fire testing and Flame Retardants

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THOR

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Outline

- Introduction
- Fire Safety notions
- Regulations
- Fire Testing
- Combustion of polymers and FR
  - Chemistries
  - Mechanisms

Why use FR?

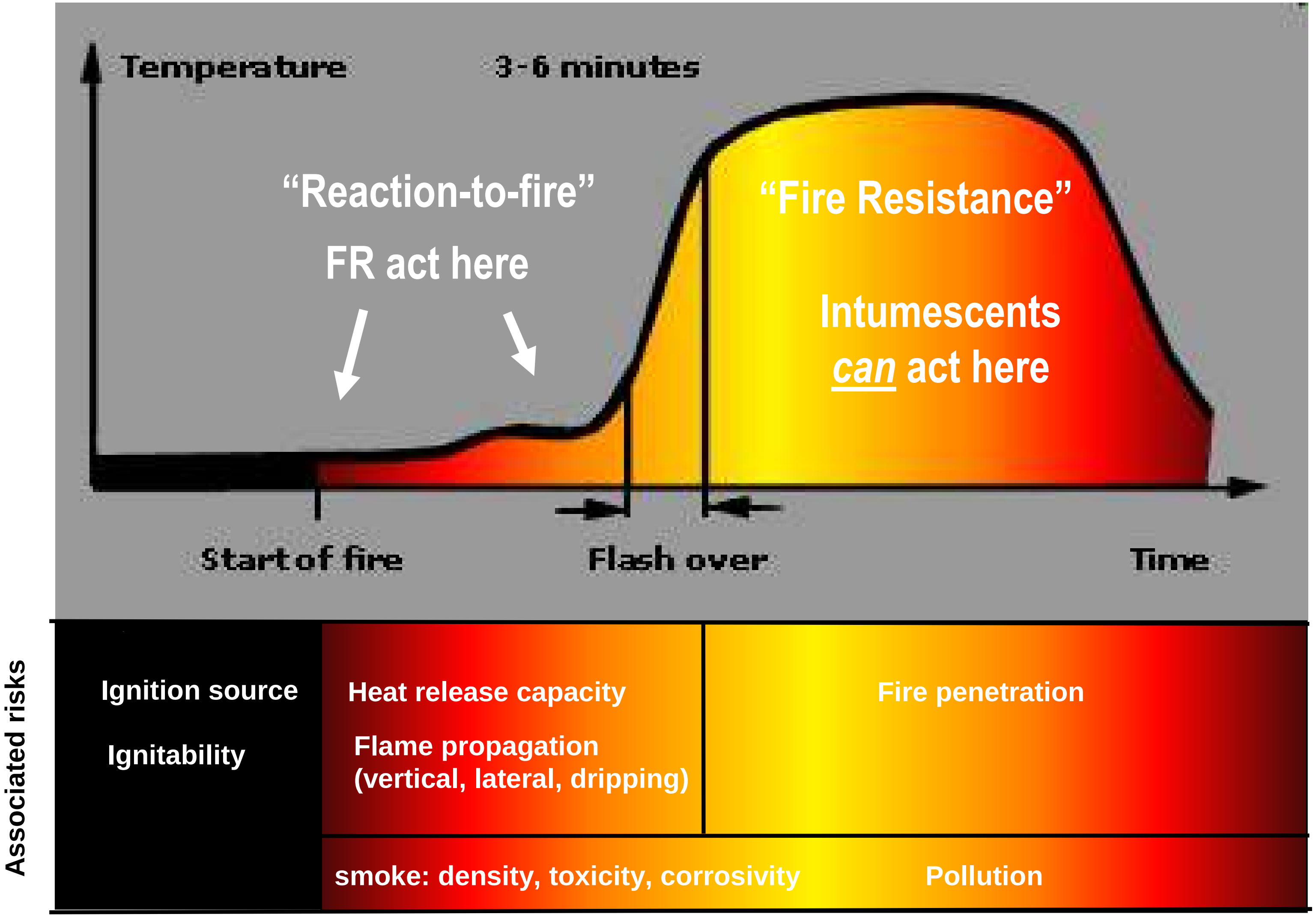
- Polymers are increasingly used in our daily life
  - Consumer electronics
  - Household goods
  - Furniture
  - Decorative materials
  - Floorings
  - Transportation (cars, trains, planes etc)
  - Etc…

- Most polymers are flammable and represent a significant quantity of fuel (fire load)
  - Heat released by a burning TV or sofa is enough to lead to “flash-over” and to set fire to a room or even a whole building

Why use FR?

- Many building materials do not burn, but
  - steel looses its structural strength when temperatures exceed 470-500°C
  - “spalling” of concrete
- In Europe
  - One fire every two minutes
- Fire statistics in Germany
  - Approx. 600 dead victims every year
  - Main cause: poisoning through fire gases (CO…)
  - Approx. 6.000 burnt victims
- Economic costs (2000, Source: GDV):
  - Approx. 6 bn. € incl. 1,9 bn € insurance
  - Approx. 100 000 cases incl. 200+ > 500 000 €

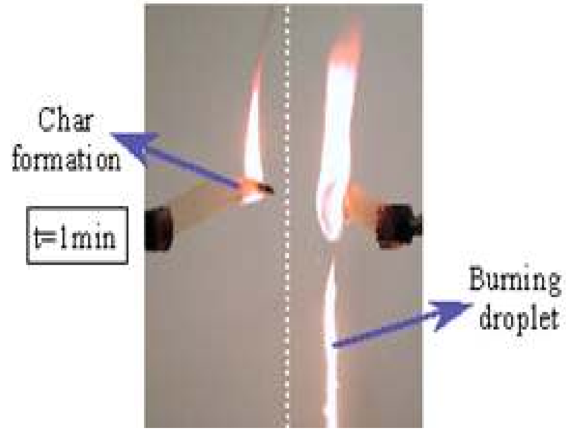
Course of a Fire



Source: EFRA

Fire Safety Notions

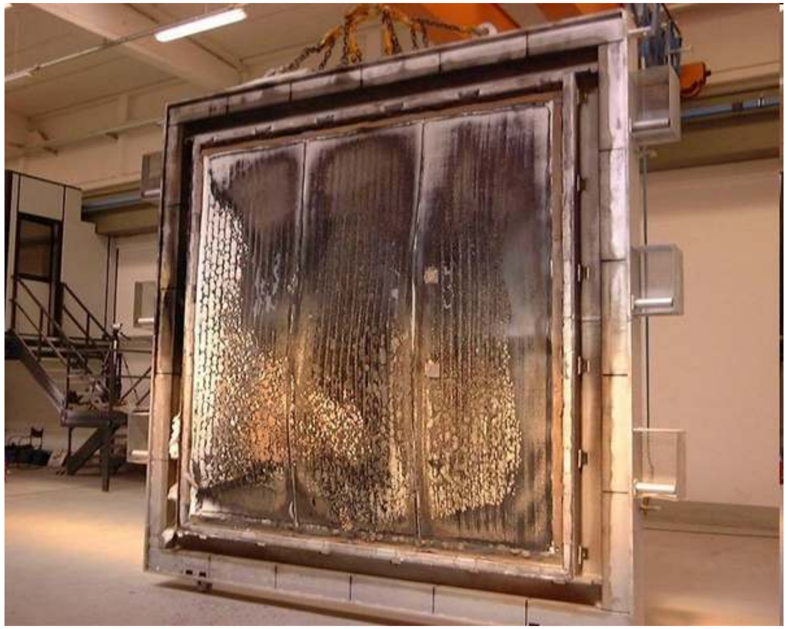
- Reaction-to-Fire: characterizes the burning behaviour of a material under certain defined conditions:
  - Ability to ignite (easy, difficult)
  - Burning rate, spread of flame (slow, quick)
  - Heat release (rate of heat release, peak heat release)
  - Smoke density
  - Smoke toxicity
  - smoke acidity
  - Formation of droplets (burning and/or non-burning)



- May be performed on material or final part
- May be small, large or in a few cases full scale fire tests
- May be binary ("pass / fail") or based on numerical value (e.g. heat release, toxic gases)
- Results are dependant on the testing conditions, thus each fire test has its own "truth"

Fire safety Notions

- Fire Resistance: ability of a part or product, regardless its composition (organic, inorganic) and its reaction-to-fire, to maintain its function for a given time in the event of a fully developed fire.
  - Fire resistant doors
  - Air ducts
  - Load bearing beams or column
  - …
- FRT requirements can range from 15' up to 8 h
- The related fire tests are typically large scale



Source: www.warringtonfire.net

Regulations

1. **Building / Construction**

- The use of fire rated (reaction-to-fire) and fire resistant materials is regulated by:
  - National building codes
  - Some countries, like Germany, have even regional building codes
    (Note: not sure if fire safety requirements are different)

- For Construction Products (CE marking, CPD or ETAG), the test and classification systems are now harmonized, but the requirements may differ from country to country.
  - E.g. for the same application, Euroclass B may be required in Germany and C in Spain

2. **Electrical & Electronic (E&E) applications**
  - Main fire test: UL 94 vertical (5VA, 5VB, V-0, V-1, V-2) and horizontal burning (HB)
  - Sometimes subject to further (different) fire tests, such as glow wire, needle flame test etc.
  - Certain cables have also fire resistance requirements and other specific tests

Regulations

Other applications that typically require flame retarded products

3. **High safety areas** (mostly country specific):
   - Mining and milling sites, chemical sites, offshore platforms
   - Hospitals, retirement homes, jails

4. **Transportation**
   - Cars: FMVSS 302, increasingly completed by OEM specifications
   - Trains: Harmonized TS 45545 (calorimetry + smoke) will replace national standards
   - Planes: FAR 25.853 (Boeing), ABD 031 (Airbus) incl. fire + smoke (density/toxicity)
   - Busses: Directive EC/95/28 will probably be subject to modifications

5. **Furniture**
   - Mainly UK & Ireland (BS 5852:2)
   - Rest of Europe: discussions about upholstered furniture, but no short term changes expected

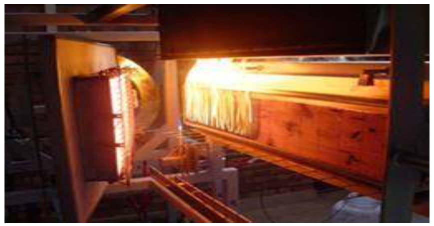
6. **Toys**: EN 71:2 (*Any polyurea used in toys??)*

Common Fire Tests

(focus on Europe and relevant application areas for polyurea)







Source: FTT, WarringtonFire, Currenta

Building/Construction

- Materials regulated by the Construction Products Directive (89/106/EEC) or by European Technical Agreement Guideline (ETAG), and subject to CE marking, are tested according to:
- EN ISO 1182:1999 Non-combustibility test
- EN ISO 1716:1999 Determination of gross calorific value
- EN ISO 11925-2:1999 Ignitibility test
- EN ISO 9239-1 Radiant panel test for floor coverings (only)
- EN 13823:2002 Single Burning Item (not for floor coverings)
- ISO 9705 Full scale room test for surface products (Reference Scenario)

- Results are: Euroclasses (A_1, A_2, B, C, D, E, F)
- respectively B_{fl}, C_{fl} etc. for floorings

- Pending: EU harmonization for roofing applications
  (currently 4 different tests resulting in B_{roof} - E_{roof})
  Expected not before 2013

Building/Construction

- Small flame test (EN ISO 11925-2 – *very similar to DIN 4102 B2*)
- Vertical flame test used prior to SBI and Flooring testing
- Application of flame (edge and surface) for 30 sec (SBI: class B-D) or 15 sec (flooring test + SBI: class E)
- Destroyed area must be <150 mm
- Considers burning droplets (d0, d1)

Building/Construction

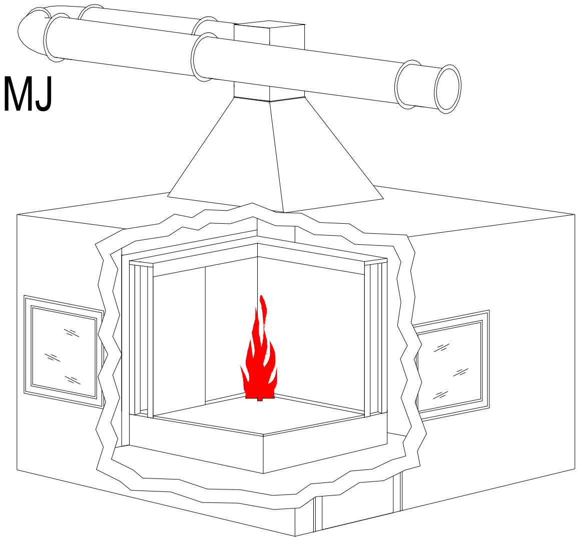
- Floor covering test (EN ISO 9239-1)
- Radiant panel with heat flux 11 to 1 kW/m²
- Horizontal test on specimen 1050 x 230 mm
- Duration: until flames extinguish or max. 30'
- Classification is based on Critical Heat Flux (CHF) below which flame spread is no longer occurring.
- Additional classification based on smoke density (s0, s1, s2)

- B_{fl}: CHF > 8 kW/m² + FS < 150 mm within 20s
- C_{fl}: CHF > 4,5 kW/m² + FS < 150 mm within 20s
- D_{fl}: CHF > 3 kW/m² + FS < 150 mm within 20s
- E_{fl}: FS < 150 mm within 20s

Building/Construction

- SBI: Single Burning Item (EN ISO 13823)
- Two specimen (0,5x1,5m and 1x1,5m) mounted as vertical corner
- Tested three times each
- Exposed to 30 kW gas burner for 20'
- Classification based on Fire Growth Rate (FIGRA), Total Heat Release after 10' (THR_{600}) and maximum Flame Spread
- Additional classification based on Smoke Growth Rate (SMOGRA), Total Smoke Production (TSP_{600}) and droplets/particles

- B: FIGRA < 120 W/s + Lateral FS<edge of specimen + THR_{600} < 7,5 MJ + FS <150 mm within 60s (EN 11925-2)
- C: same except FIGRA < 250 W/s and THR_{600} < 15 MJ
- D: FIGRA < 750 W/s + FS <150 mm within 60s (30s flaming)
- E: FS < 150 mm within 20s (15 sec flaming)



Building/Construction

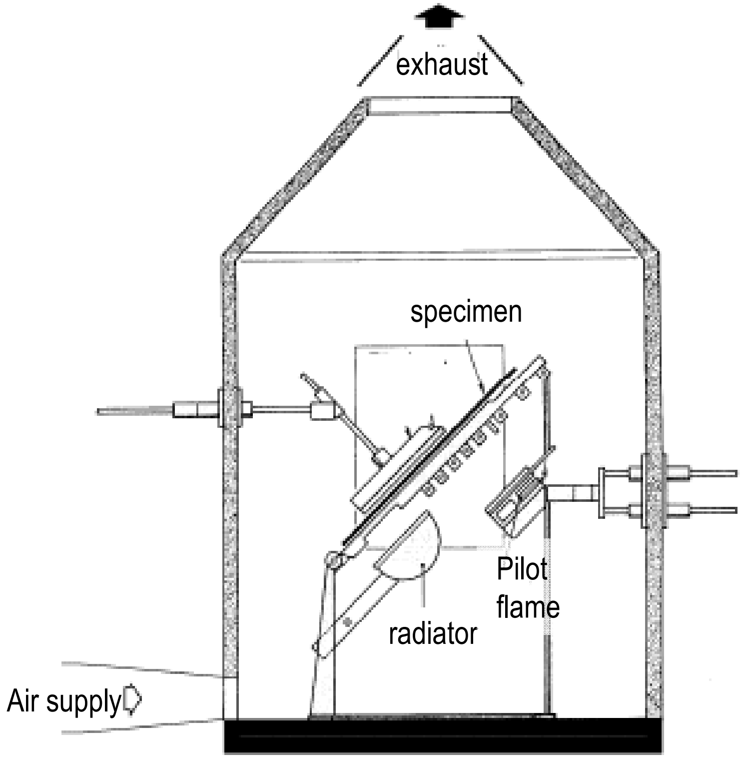
- Materials used in building/construction, but not subject to CPD / CE Marking, are subject to local regulations based on national tests. Main ones are:

- BS 476-7:
  - 6 specimen (885 x 270 mm) tested for 10'
  - Radiant panel (35 kW/m²) + pilot flame (1 cm)
  - Classification (Class 1-3) based on lateral flame spread

- DIN 4102-15 (German “Brandschacht”):
  - 4 specimen (1000x190 mm) vertically oriented (chimney effect)
  - Ring burner for 10'
  - Classified B1 if Tmax of gases < 200°C and rest length > 150 mm and B2-test passed (cf. EN 11925-1)

Building/Construction

- NF P 92501 (French “Epiradiateur”) for rigid materials and flexible materials >5mm:
  - 5 specimen (400 x 300 mm)
  - Radiant panel (30 kW/m²) at 45° with butane pilot flame
  - 20’ testing
  - Classification (M1-M4, n.c.) calculated as an equation between:
    - Time to ignition (1st flame > 5s)
    - Maximum flame height
    - Total burning times



Other tests

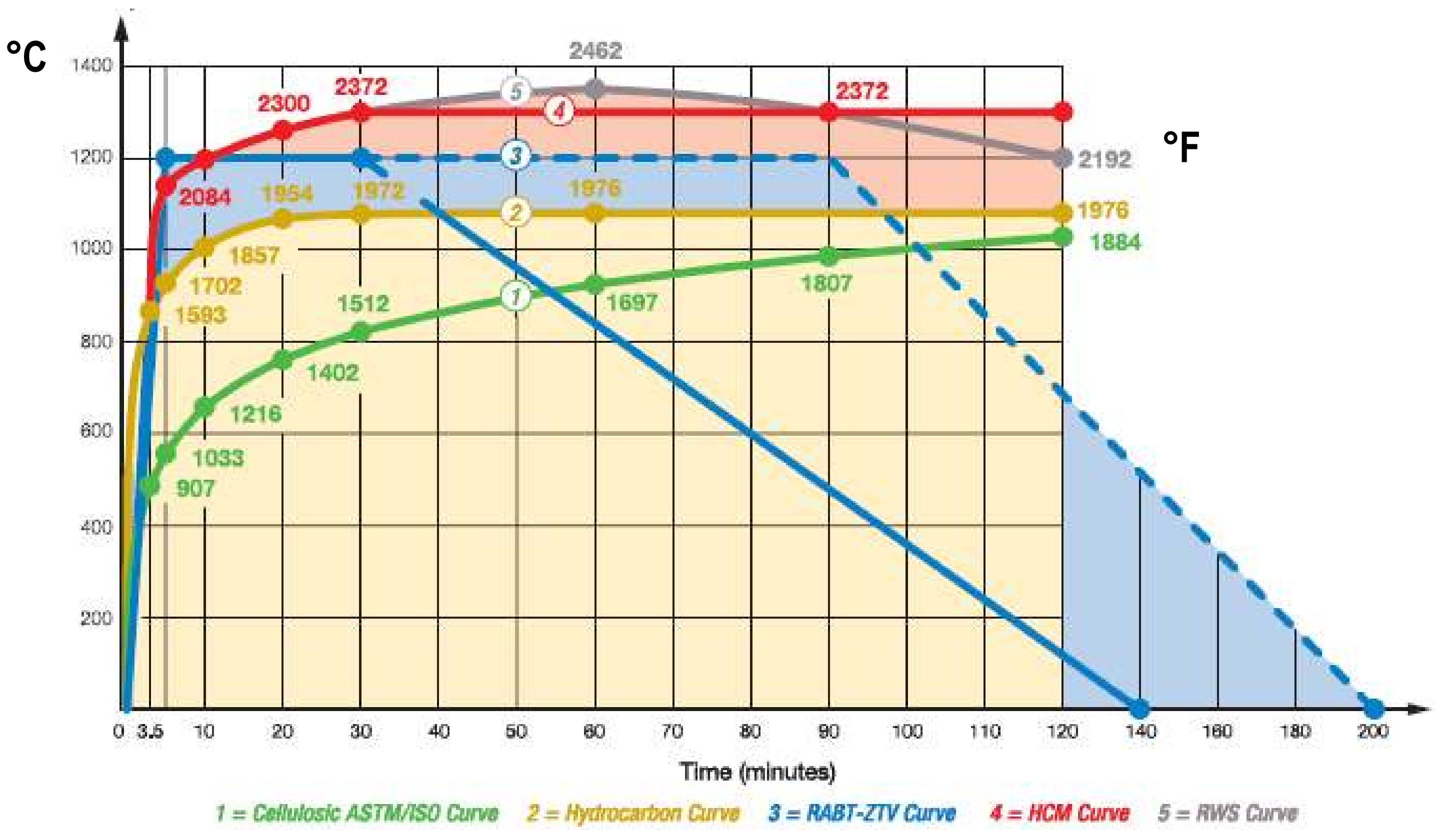
- Furniture
  - UK: BS 5852-2, standardized seat structure tested with different sources, the most frequent one being Crib 5 (5 levels of wood)
  - Rest of EU: no to little requirements, limited to furniture in public places (cinemas, theatres etc)
    - EN 1021-1: cigarette test
    - EN 1021-2: match test

- Marine Applications: IMO Resolution MSC.61(67)

  Fire tests depending on final applications
  - Upholstered furniture: resolution A.652 (16)
  - Bulkhead, ceiling and deck: resolution A.653 (16)
  - Primary deck coverings: resolution A.687 (17)
  - Plastics: ISO 5659-1:1996 (Smoke density)

Fire Resistance Tests

- Determination of the Fire Resistance Time (FRT), as the time needed to reach failure, when exposed to a defined fire scenario.
- Different Time-Temperature curves may apply. The main applied ones are:



Fire Resistance Tests

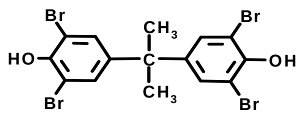
- Important point to consider for Polyurea coatings

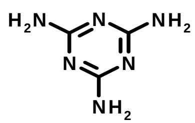
- Polyurea coatings (until now) mostly have requirements in regard to their reaction-to-fire (e.g. Euroclass B, or German B1), but not (yet) in regard to fire resistance.
- BUT
- If coatings are applied on existing load bearing structures (such as concrete or steel), one should carefully check if the coating does not degrade the FRT of the substrate!
- A good reaction-to-fire does not ensure fire resistance properties (this applies to inorganic materials as well).

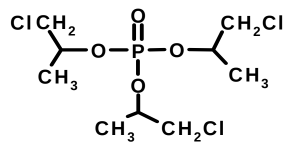
Flame Retardants?

- The term “Flame Retardant” describes the function of these additives, but gives no hint about their chemical or physical nature, or their mode of action.
- There are in fact more than 170 single substances, which can act as FR
- They can be liquid (plasticizing) or solid / organic or inorganic
- They can be additive or reactive (= grafted into the polymer backbone)
- They have different environmental and toxicity profiles (substance specific)
- They have different mode of actions
- They have different price-performance profiles

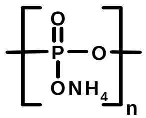
^{35}Cl ^{31}P ^{27}Al



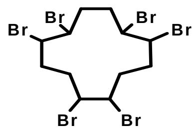




^{80}Br



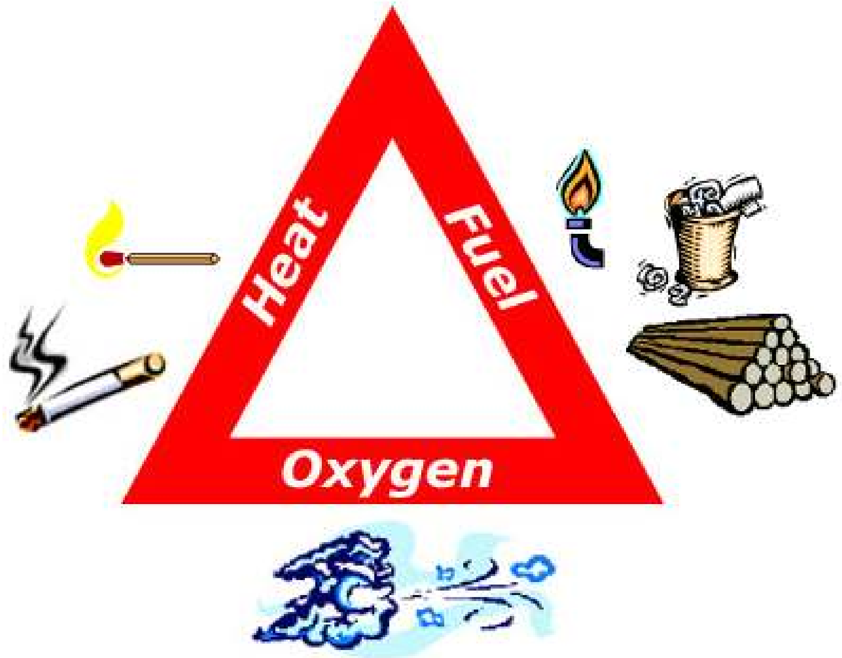
^{14}N



$Al(OH)_3$ ^{11}B ^{24}Mg

Flame Retardants?

- The Fire Triangle (Emmons)

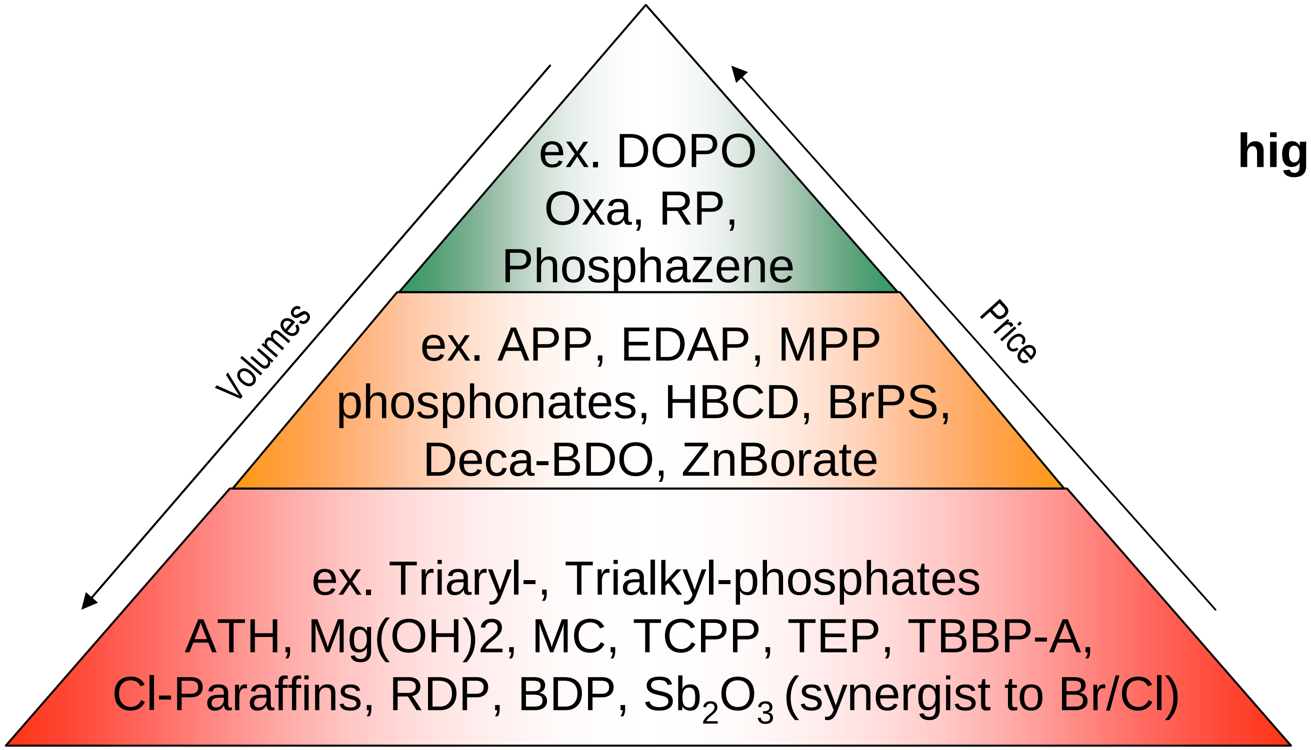


- Fire is sustained only when the three parameters are given at once.
- However, dynamics of combustion depends on exact decomposition path, which is polymer specific
- FR, depending on their nature, act by different means on one or more parameters

Flame Retardants?

	Halogenated FR	Phosphorus FR	Nitrogen FR	Mineral FR	Intumescents
Mode of action	Chemical	Chemical + Physical	Physical	Physical	Chemical + Physical
Place of action	Gas phase (flame)	Mostly solid phase	Gas phase	Gas phase	Solid phase
Mechanism	Release of HBr or HCl traps H-radicals in the flame	Formation of a carbon rich layer which prevents access of oxygen	Release of non-flammable nitrogen, dilute oxygen content	Release of water vapour, cool down and dilute smoke	Formation of an insulative foam at the surface
Compatibility	+	o	o	(o)	o
Effectiveness	+	+	o	-	+
Fire side effects	-	+	(+)	+	+
Cost-performance	+	o	o	++	o

Flame Retardants?



high performance
8 - 40 EUR / kg

performance
3 - 8 EUR / kg

commodities
0,50 - 3 EUR / kg

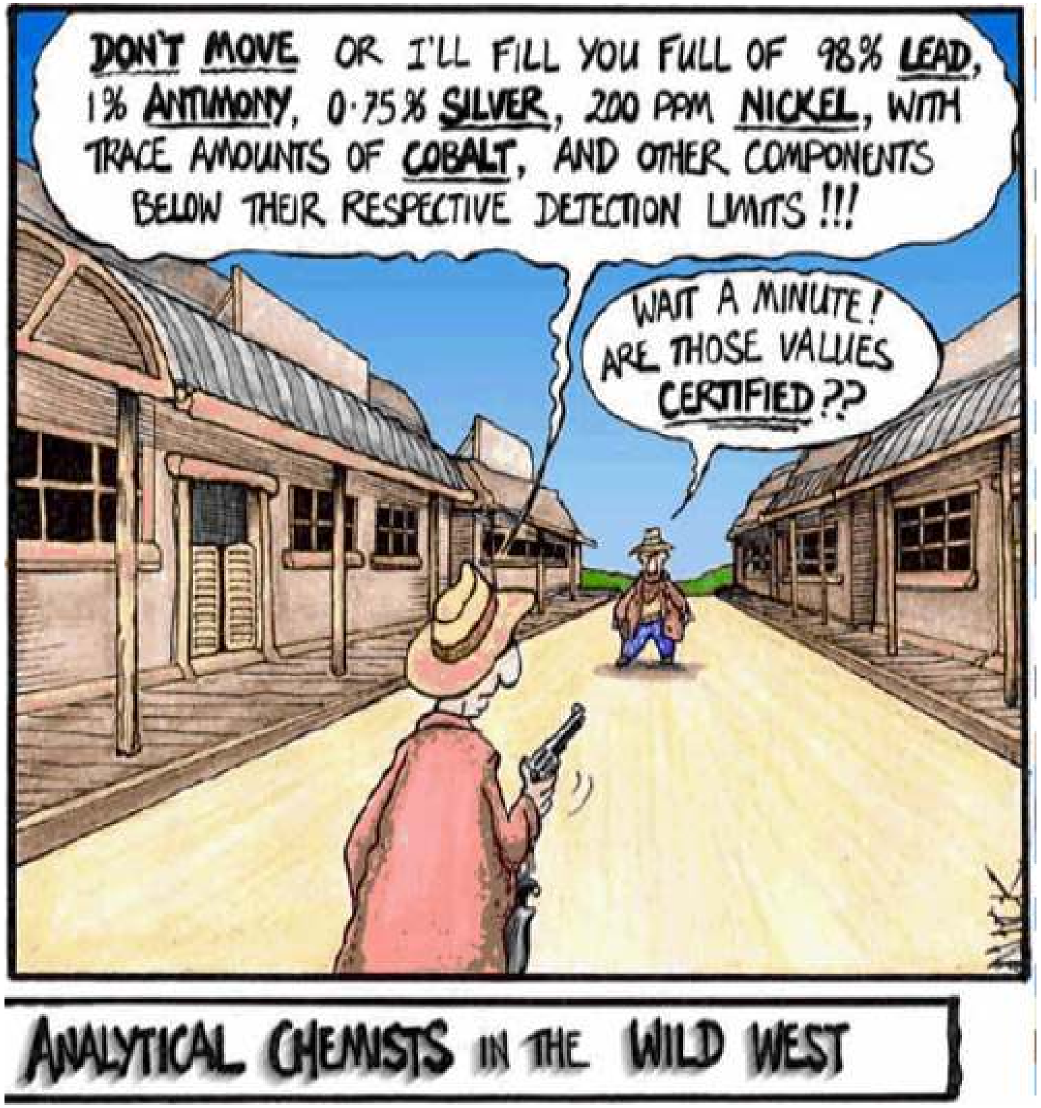
The FR Controversy

- FR save lives and properties, this is undisputed.
- However, concerns are raised about environmental impact and toxicity of certain FRs
  - Scientific studies e.g. in Germany, Nordics, UK and Switzerland
  - Topics: Persistence, Bioaccumulation, Toxicity (PBT)
  - Potential formation of halogenated dioxins & furans
  - FR findings in the Environment, Biota, Indoor Air and dust

- Discussion mainly focuses on halogenated FR, but also a few phosphorus FR
- Highly controversial discussions, e.g. Deca-BDO

- Political agenda: EU risk assessments of 13 high volume FR, REACh implementation
- Increasing role of Ecolabels and Public Green Procurement Policies
- In consumer products, OEM increasingly adopt proactive “halogen-free” stance

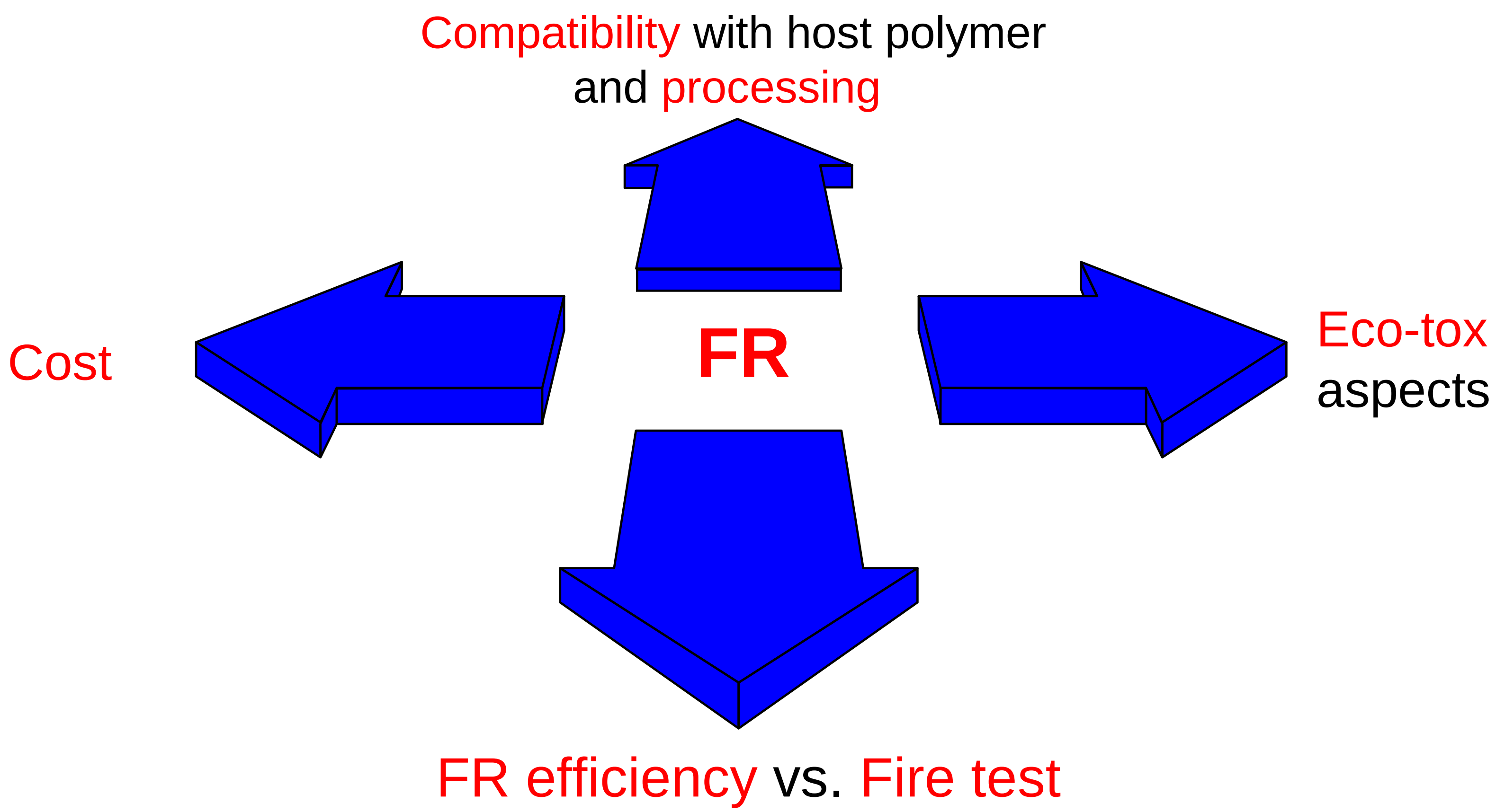
Chemicals & Environment



REACH

The FR challenge

- Selection of FR and formulation work is a complex, empirical process (“trial and error”)
- Often subject to difficult compromises



Summary

- Flame Retardants are an essential part of passive fire safety in a world made of plastics
- Their use is dictated by a complex framework of different regulations (national laws and/or industry standards)
- Material testing is subject to a variety of different fire tests (depending on final use and related fire scenarios) which in turn affect the FR strategy

- The use of FR in polyurea is relatively recent and therefore not extensively explored
- Systems exist but most of them are subject to further improvements
- Many R&D activities ongoing, expected to result in improved formulations (i.e. processing, new fire standards)

- Headaches?

  Seek advice from your raw material producer, formulator or FR supplier

Thanks!

- Thank you for your attention!

- Special thanks to Dr. Volker Butz (Thor GmbH) for his contribution and his promising, ongoing R&D works

- Acknowledgement to Dr. Jürgen Troitzsch and his “Plastics Flammability Handbook”

  3rd Edition (2004), Hanser Publishers

  www.troitzsch.com

- For any question, feel free to contact me:

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