Flame Retardants

pinfa

An introduction to chemistry and technology, applications and environmental aspects

pinfa editorial team
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It is provided by pinfa to the public for any interested party to use, in particular for educational purposes for those interested in the chemistry, testing, applications and environmental aspects of flame retardants.

We focus on non-halogenated (PIN) flame retardant technologies. However, in some cases we reference halogenated flame retardants, because they are still widely used.

Credits & copyright

pinfa

pinfa is the Phosphorus, Inorganic and Nitrogen Flame Retardants Association.

pinfa brings together manufacturers and users of non-halogenated phosphorus, inorganic and nitrogen flame retardants (PIN FRs).

pinfa is a Sector Group within Cefic, the European Chemical Industry Council.

pinfa adheres to Responsible Care® - the global chemistry industry's commitment towards safe chemicals management and performance excellence.

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pinfa China - Jingwen.Chen@clariant.com

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Responsible Care®
OUR COMMITMENT TO SUSTAINABILITY

pinfa's mission

"Members of pinfa share the common vision of continuously improving the environmental and health profile of their flame retardant products.
This vision is coupled with a commitment to maintain high fire safety standards across the world, standards which minimize the risk of fire to the general public."

pinfa's mission targets:
- Fire safety
- Environment and human health impacts of fire and smoke, and of PIN flame retardants
- Commitment to collaboration with stakeholders, regulators, science and industry

pinfa's mission:
https://www.pinfa.eu/about-pinfa/mission

Sources and references

pinfa website
www.pinfa.eu

pinfa Newsletter
Email news on fire safety, regulatory developments, flame retardant industry news and product innovation, environmental and health, etc.

- Past issues online and subscribe (free) here: www.pinfa.eu

Videos
pinfa YouTube channel: https://www.youtube.com/channel/UChb0kX3QSJdcYs1Qjjz0HAw

Some books on fire safety and flame retardants:

- Non-halogenated Flame Retardant Handbook, A. Morgan, C. Wilkie, 2014
- Flame Retardants for Plastics & Textiles, E. Weil, S. Levchik, 2016
- Towards Bio-based Flame Retardant Polymers, R. Sonnier, A. Targuet, L. Ferry, J-M. Lopez-Cuesta, 2018
- Polymer Green Flame Retardants, C. Papaspyrides & P. Kiliaris, 2014
- Fire Retardancy of Polymers: New Strategies and Mechanisms, T. Hull & B. Kandola, 2008
- Plastics Flammability Handbook 3 edition, J. Troitzch, 2004
- An Introduction to Fire Dynamics, 2nd edition, D. Drysdale, 2011

pinfa Members (EU, China & North America)

- A. Schulman
- ADEKA
- AVIENT
- AVAKIAN POLYCHEM
- BASF The Chemical Company
- Budenheim
- CLARIANT
- CTF 2000 Flame Retardant Chemicals & Textile Specialties
- where skin meets fabric dartex
- DSM
- domo The strength of chemicals.
- DUPONT
- FR Adviser LLC From Ideation to Commercialization
- FRX POLYMERS
- Grolman International Distribution
- GREENCHEMICALS
- HUBER
- ICL
- Italmatch Chemicals
- LANXESS Energizing Chemistry
- METADYNEA METAFRAX GROUP
- Nabaltec
- NORDMANN
- OMYA
- Perstorp WINNING FORMULAS
- PolyOne
- RADICI GROUP
- سابك sabic
- Schneider Electric
- SCOTT BADER
- SIBELCO
- tfp
- THOR
- TOLSA
- TOTAL
- williamblythe Excellence in chemistry

1.
Fire safety

Photo © Shutterstock

Fire Safety
Worldwide Fire Statistics

Fire statistics available globally are limited. An overview is provided by CTIF (International Association of Fire and Rescue Services), covering 27-39 countries (depending on the year), representing around one seventh of the world population.

For 2016, all figures are per year and million population:

- World average (for 39 reporting countries)

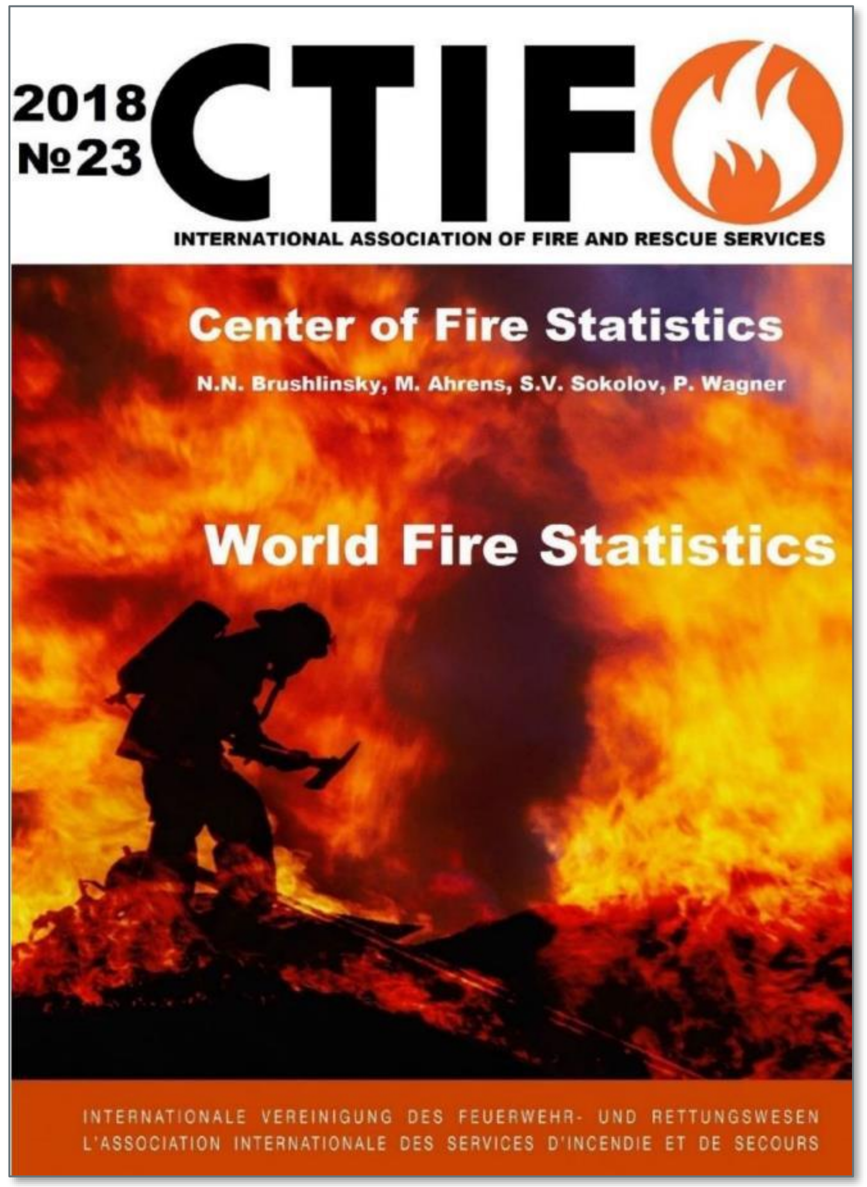
16	**51**	**2,700**
FIRE DEATHS	**FIRE INJURIES**	**FIRES**

- Highest rates of fire deaths (of reporting countries)

60	**57**	**48**
FIRE DEATHS IN RUSSIA	**FIRE DEATHS IN BELRAUS**	**FIRE DEATHS IN LATVIA**

In 2017, the Geneva Association (bringing together nearly 100 insurance companies worldwide) estimated that: **FIRE COST AROUND**

1% OF GDP WORLDWIDE



CTIF report 2018 n° 23 (providing statistics for 2016) – Center of Fire Statistics, World Fire Statistics
https://www.ctif.org/world-fire-statistics
Geneva Association, Bulletin World Fire Statistics n°29, 2014
https://www.genevaassociation.org/sites/default/files/research-topics-document-type/pdf_public//ga2014-wfs29.pdf

Fire Safety
USA Fire Statistics

Fire deaths in the USA have fallen considerably since the 1970's (12,000 fire deaths in 1974) but have been slowly rising since 2012.

For 2017,

1.3 MILLION
FIRE REPORTED
to fire departements

3,400
FIRE DEATHS

14,700
INJURIES

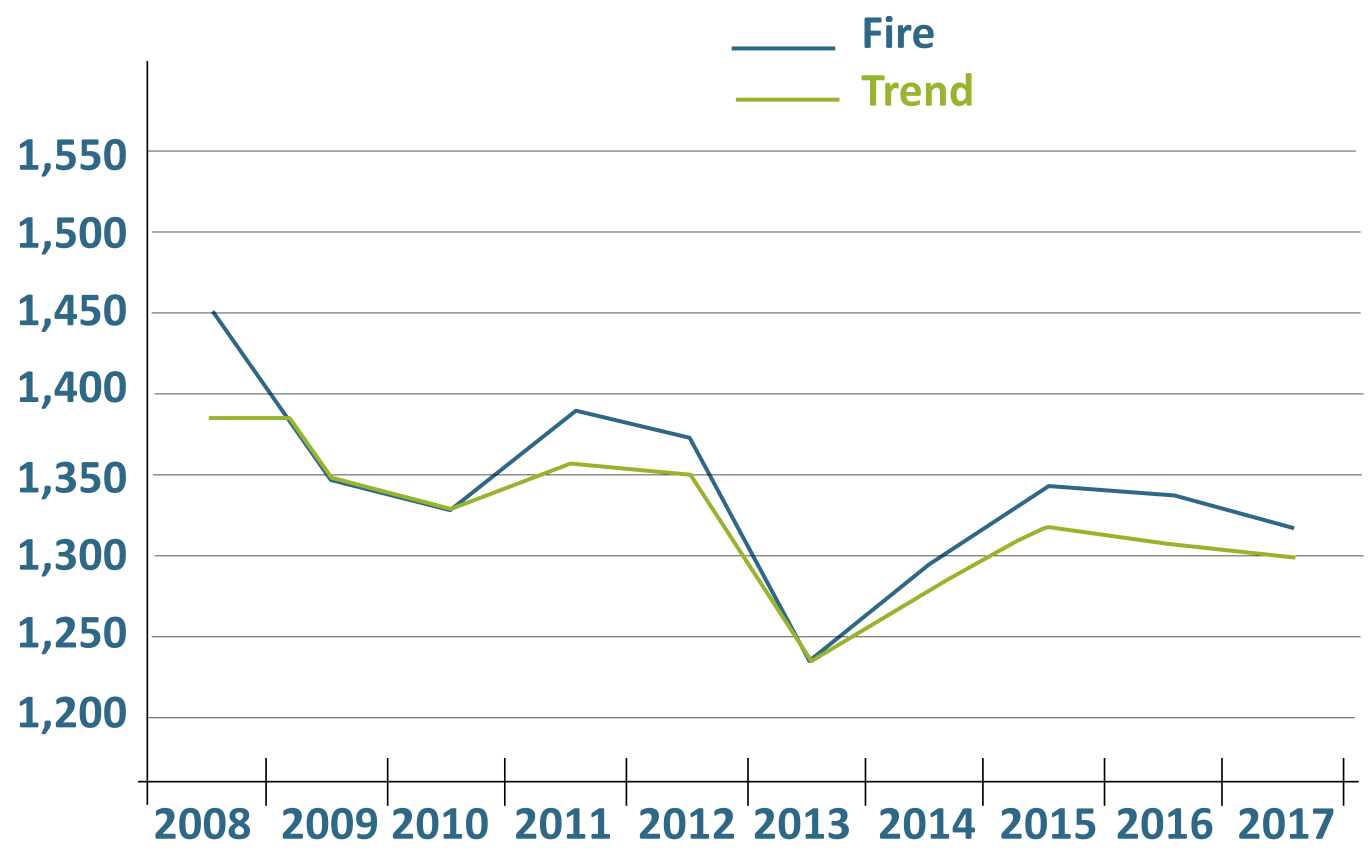
US$ 23 BILLION
LOSSES

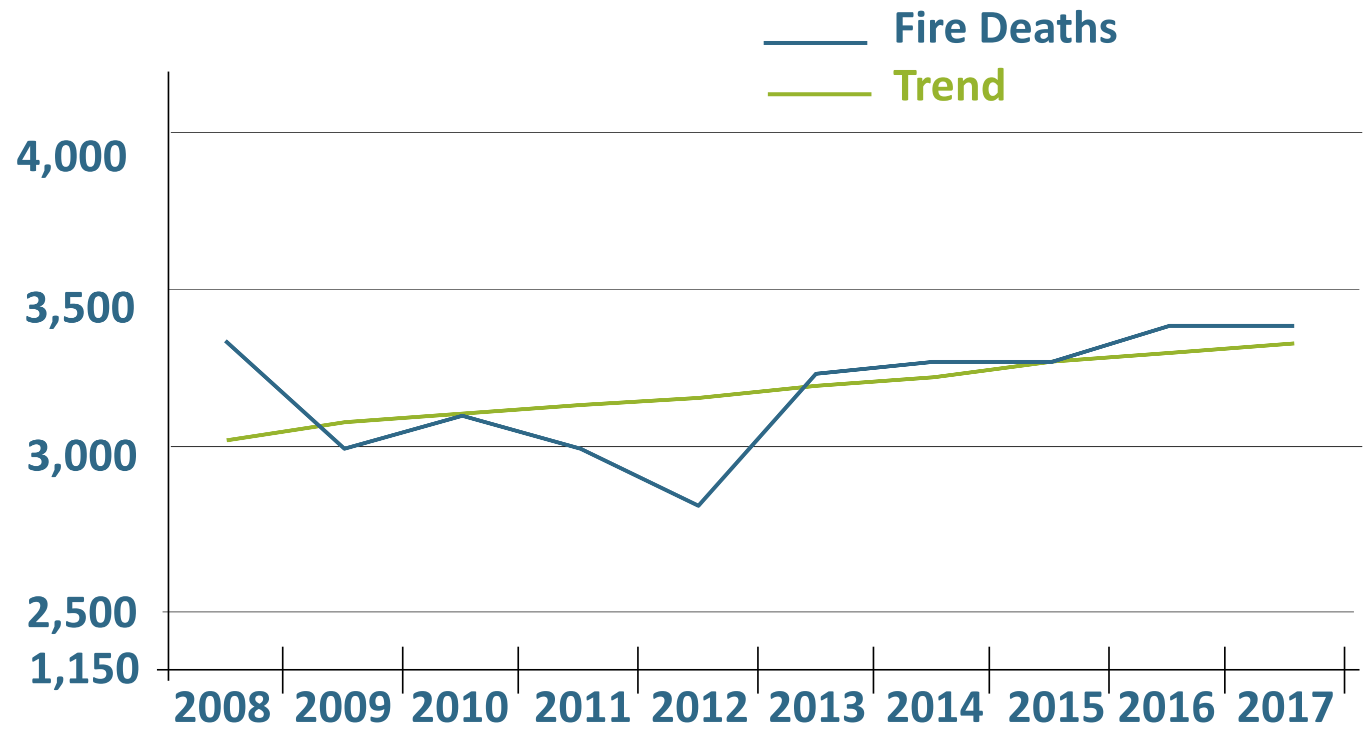
For 2018,
Another source of information is the NFPA (National Fire Protection Association), whose latest report indicate:

3,600
CIVILIAN FIRE DEATHS

15,200
CIVILIAN FIRE INJURIES

US$ 25 BILLION
PROPERTY LOSSES





"Fire in the United States 2008-2017", US Fire Administration – FEMA National Fire Data Center (NFDC); November 2019 https://www.usfa.fema.gov/data/statistics/reports/fius_2008-2017.html
"Fire Loss in the United States During 2018", NFPA, B. Evarts, September 2019 https://www.nfpa.org/News-and-Research/Data-research-and-tools/US-Fire-Problem/Fire-loss-in-the-United-States

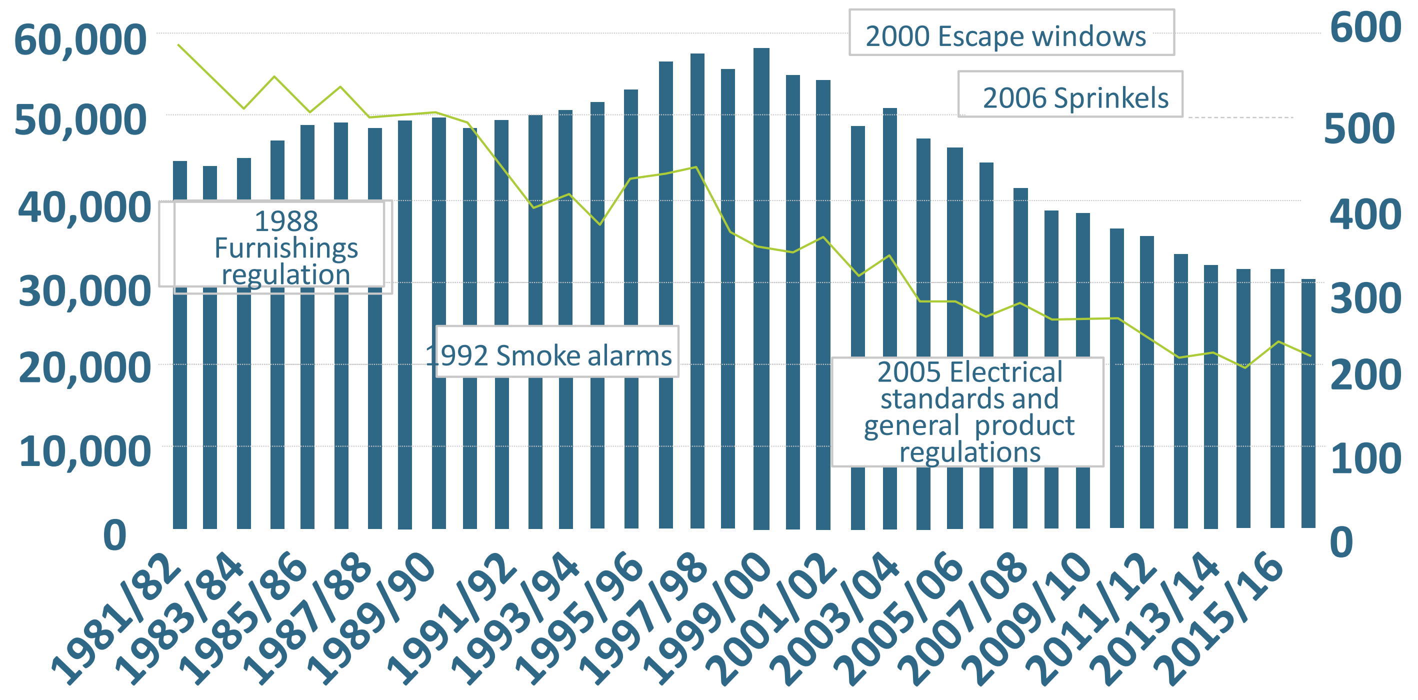
Fire Safety
Europe Fire Statistics

There are no collated fire statistics for Europe. Most countries have fire data, but these are not necessarily comparable.

Estimates suggest that fire kills over 5,000 persons/year in Europe, and injures ten times more.

In many countries in Europe, fire fatalities have fallen significantly over recent decades. This is probably a combined result of:

- Fire safety regulations
- Electrical and other product regulations
- Changes in behaviour, in particular reduced smoking

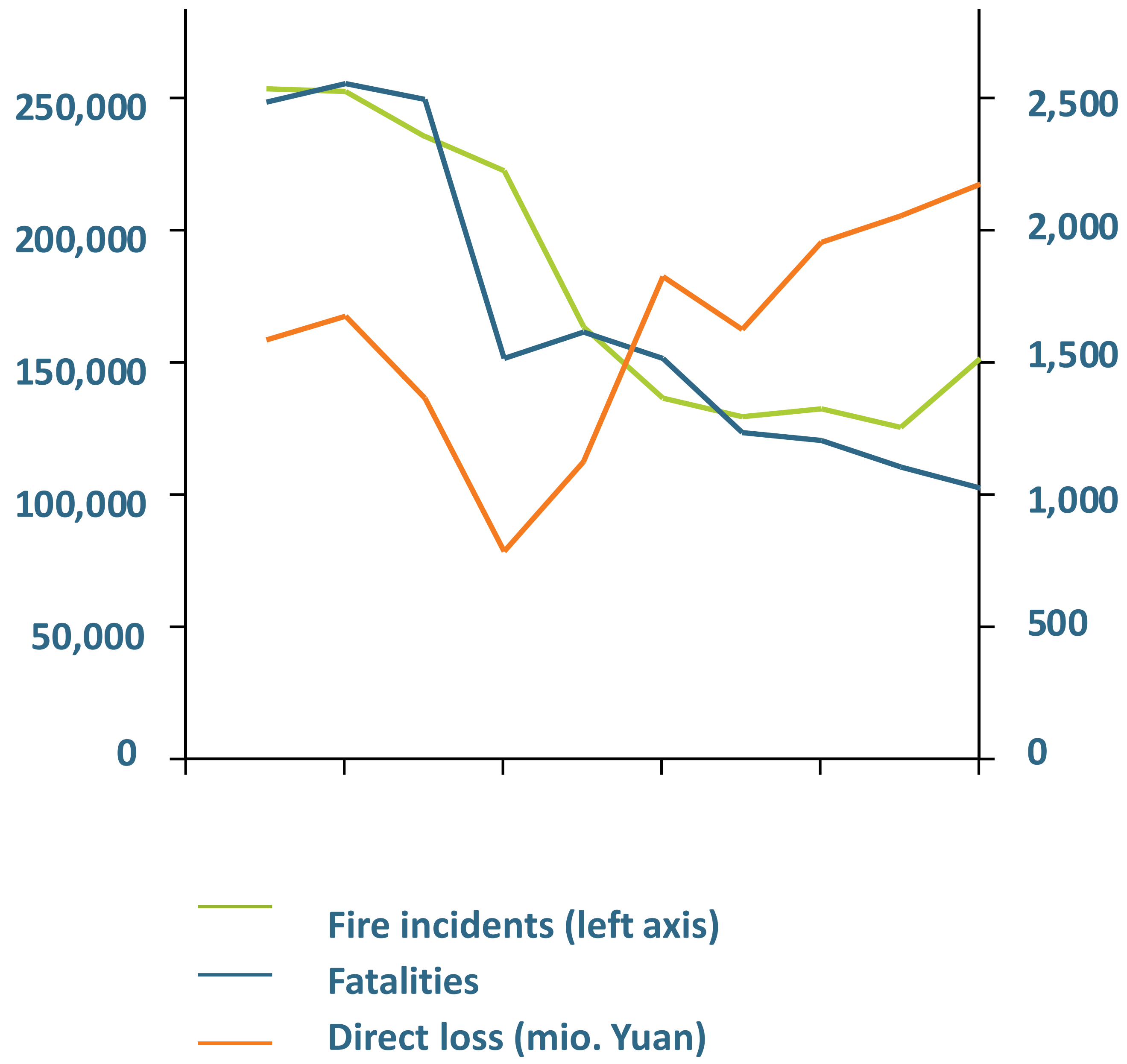


“Focus on trends in fires and fire-related fatalities”, UK Home Office, 12 October 2017 https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/650869/focus-trends-fires-fatalities-oct17.pdf.

Fire Safety
China Fire statistics (2003-2012)

Fire incidents and fatalities have been falling; however, economic damage has increased between 2002 and 2012.

Statistics provided by National Bureau of Statistics of China.



2.

Role of Flame Retardants in Fire safety

Day-to-day Materials and Fire

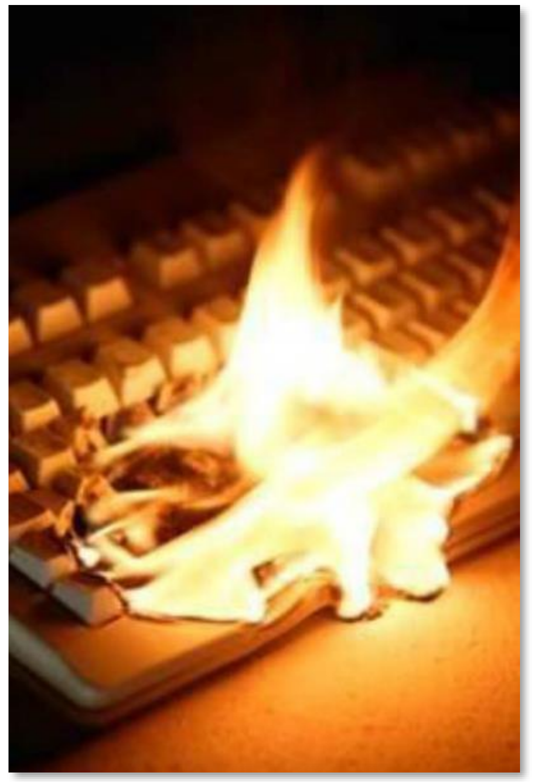
Plastics have a high 'calorific value' (energy comparable to conventional fuels).

Crude oil	43 MJ/kg
Coal	23-26 MJ/kg
Plastics & polymers	19-31 MJ/kg

Natural materials also represent a significant fuel potential in homes and offices.

Wood	14 MJ/kg
Cotton	16 MJ/kg

The heat emitted in a fire depends on oxygen, so foams (which contain air bubbles) or thin plastic components will burn faster and more fiercely.



© Clariant, EFRA

Haight, 2012 "Energy and economic values of non-recycled plastics (NRP) currently landfilled in Canada http://biblioteca.anipac.mx/wp-content/uploads/2017/10/file_Haight_Energy_Value_of_NRP_Study_Final.pdf page 17 and Shen 2008, Life Cycle Assessment of Polysaccharide Materials: A Review, table 5, page 158 https://archive-ouverte.unige.ch/unige:42935/ATTACHMENT01

Escape Time in a Modern Domestic Furnished Room Ranges from 1 ½ to 10 Minutes

FROM 1 ½ TO 10 MINUTES IS THE TIME BEFORE TEMPERATURE REACHES 600–1,000 °C.

These are conclusions of an assessment of > 400 fire tests, including 44 full-scale furnished room tests (2012, 1).

Different non-flame retarded upholstered furniture led to heat release rates of 600–1,000 kW after five minutes (2).

These studies confirm a NIST (USA National Institute of Standards and Technology) study (2007, 3) which showed that escape times have been reduced by around 5x since 1975.

(1) "Der Brand in Räumen Auswertung von Originalbrandversuchen im Vergleich mit analytischen Rechenverfahren- Teil1", in German (Room fires: conclusions from real situation testing compared with analytical modelling), in "vfdb-Zeitschrift für Forschung, Technik und Management im Brandschutz", 6-2, 2012 https://www.baufachinformation.de/Der-Brand-in-R%E4umen-und-seine-Wirkungen/z/2012069003173
(2) "Modelling of heat release rate in upholstered furniture fire", G. W. Zou et al., Fire and Materials. 2018;42:374–385. http://dx.doi.org/10.1002/fam.2502
(3) Access to the revised NIST study, including explanations of modifications, etc. Bukowski, R.W. et al.., 2007, "Performance of Home Smoke Alarms, Analysis of the Response of Several Available Technologies in Residential Fire Settings" NIST Technical Note 1455 (396 pages) https://www.nist.gov/publications/performance-home-smoke-alarms-analysis-response-several-available-technologies

Photo from Blais et al. 2019 https://doi.org/10.1007/s10694-019-00888-8. Room with non flame retarded contents 8 ½ minutes after start of fire test.

The Fire Curve for a Room Fire

The three phases of fire and the protecting features of flame retardants are:

Ignition source

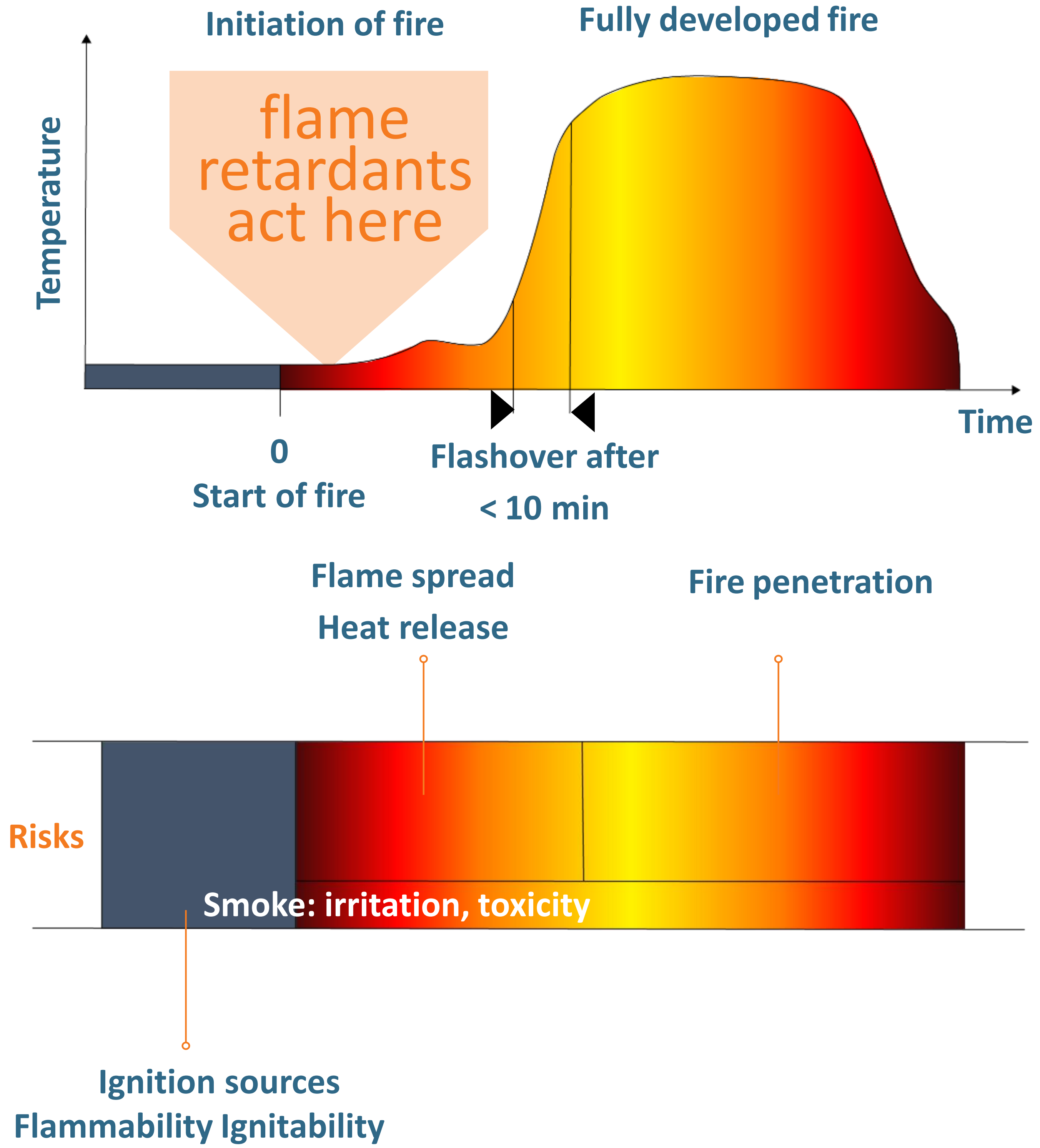
- Prevent ignition
- Possibly self-extinguish

Flame spread

- Slow down flame spread
- Reduce heat release
- Delay flash-over

Fire penetration

- Prevent the collapse of structures, e.g. steel columns protected by intumescent coatings
- Prevent fire moving to adjacent room or building compartment



Flame Retardants Increase the Escape Time by Preventing or Slowing Down Ignition and Fire Growth

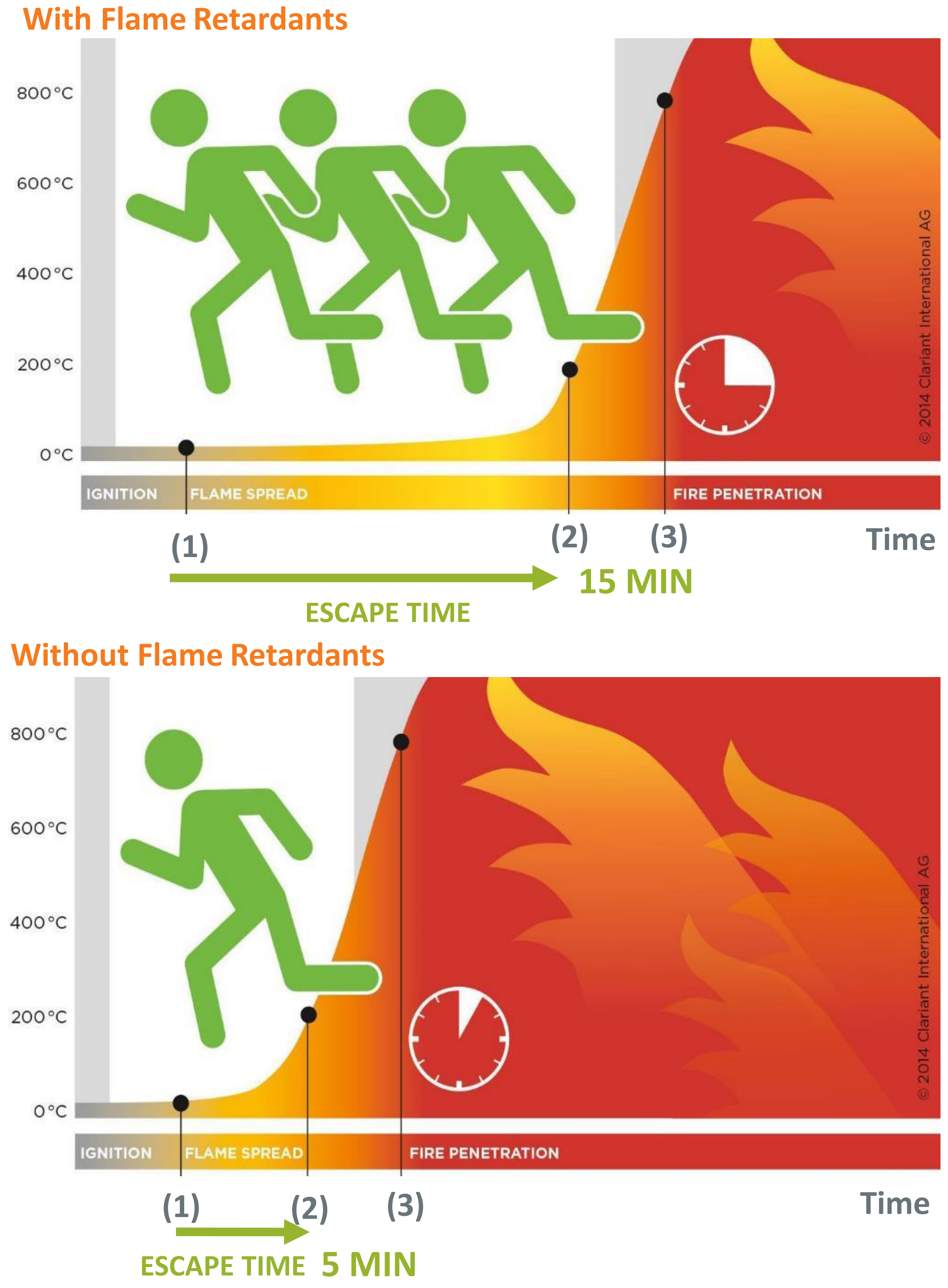
Flame retardants reduce the risk of ignition and fire spread of many plastic and textile materials which results in more available escape time for occupants.

Time to flashover can increase from 5 minutes to 15 minutes which can make the difference between escape and fatalities.

Bear in mind that the escape time includes the time to discover the fire, not alert other people, take the decision to call the fire brigade, take own actions to extinguish or take the decision to evacuate the building.

The times and temperatures in the graphs are typical numbers, but can vary according to the circumstances and materials involved.

How Flame Retardants can increase escape time in fires



(1) Start of fire (2) Flashover (3) Fully developed fire

Case History
Fires Start from Small Ignition Sources (1)

September 2, 1666

The Great Fire of London, started on 2nd of September 1666, in the bakery of Thomas Farriner, in Pudding Lane. Farriner supplied bread to the Royal Navy and later accused a Frenchman of having deliberately lit the fire.

September 6, 1666

Four days later, the fire had destroyed the homes of 70,000 people (85% of the city's population) as well as nearly 90 churches. A melted piece of pottery found by archaeologists shows that the fire reached 1,250 °C in Pudding Lane.

The fire was finally stopped, and prevented from reaching the Royal Court at Whitehall, because the wind dropped, and the Tower of London Garrison used gunpowder to blow up swathes of houses and create effective firebreaks.

85%
HOMES DESTROYED IN THE CITY

90
CHURCHES DESTROYED

THE TEMPAREATURE REACHED
1,250 °C

British Museum collection. Unknown artist.

Case History
Fires Start from Small Ignition Sources (2)

Other historic fires include:

- Helsinki, 1808
- Great fire of Turku, 1827
- Church of the Company, Santiago, Chile, 1863, over 2,000 killed
- Hamburg Great Fire, 1842
- Great fires in Chicago, Michigan and Peshtigo, 1871
- Great Vancouver fire, 1886
- Great Fire of Toronto, 1904

Case History
Grenfell Tower, London, 14-June-2017

On 14th June 2017, just before 1 AM, a fire started in a fridge-freezer on the 4th floor of the 24-storey Grenfell tower housing block, West London. The fire killed 72 people and injured more than 70 others. 127 families lost their homes.

The building had recently been renovated and the fire spread rapidly through external cladding materials and burned for around 60 hours before being completely extinguished.

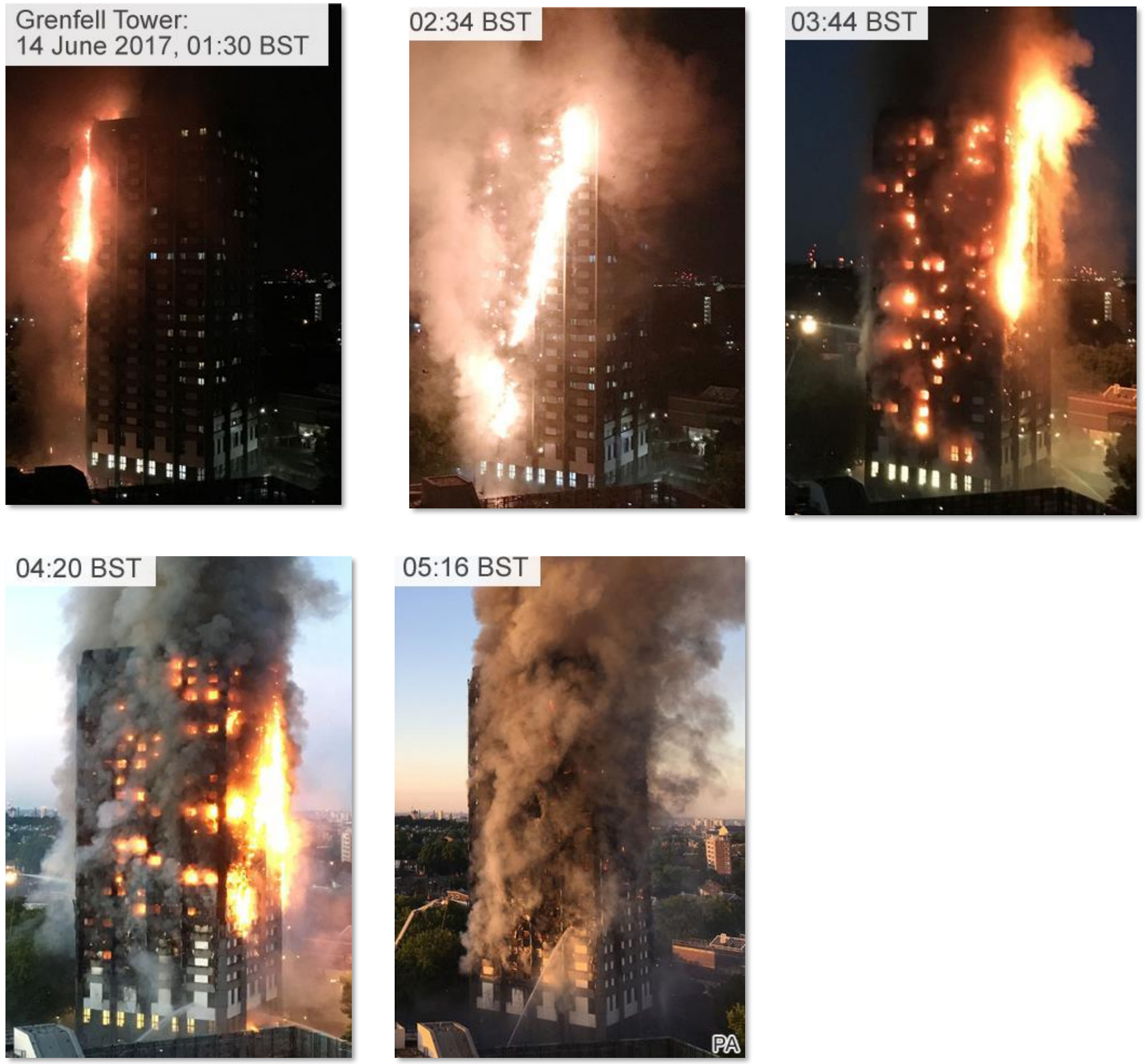
Official statements confirm that the external cladding was not conform to applicable fire safety regulations, and used non flame retardant polyethylene in aluminum sandwich and polyisocyanurate (PIR) boards.

The Times stated that the use of appropriate, fire-safe cladding materials would have added less than 5,000 GBP to the 8.6 million GBP refurbishment cost. Other failures in fire safety contributed to the catastrophic consequences of the fire, including issues with sprinklers, gas supply, fire stops, emergency exits.

Photo: https://prruk.org/no-inquiry-is-needed-the-grenfell-tower-fire-was-a-crime/

The Times https://www.thetimes.co.uk/article/grenfell-tower-fire-resistant-cladding-is-just-5-000-more-expensive-6gjqkg98g

Case History
Grenfell Tower, London, 14-June-2017 Timeline



Photos and timeline: https://www.bbc.com/news/uk-40301289

Case History
Grenfell Tower, London, 14-June-2017

The UK Government identified that the fire started in a Hotpoint (Whirlpool) FF175B fridge-freezer, in which the insulation foam is flammable (but is conform to legal requirements in the UK).

The London Fire Brigade and consumer magazine Which have called for flame retardant backings for fridges and freezers.

The official independent review following the fire concluded "the current system of building regulations and fire safety is not fit for purpose".

Legal action has been engaged in the USA by survivors and victims' families against Whirlpool (Hotpoint), Arconic (cladding) and Celotex – Saint Gobain (insulation).

UK housing fire safety campaign: Grenfell United: https://www.grenfellunited.org.uk/
UK Government report: Hotpoint fridge-freezer investigation https://www.gov.uk/government/publications/hotpoint-fridge-freezer-ff175b-independent-investigation
Official independent report on Grenfell fire (Dame Judith Hackitt):
https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/668747/Independent_Review_of_Building_Regulations_and_Fire_Safety.pdf
London Fire Brigade: https://www.london-fire.gov.uk/news/2015-news/fridge-freezer-delay-putting-lives-at-risk/
WHICH: https://www.which.co.uk/news/2018/02/revealed-the-brands-linked-to-the-most-appliance-fires/

Fire test of a generic fridge freezer.
Photo © EFRA, Ralf Baumgarten

Case History
Dusseldorf Airport, 11-April-1996

c. 13h00

Droplets of solder from welding work on an access road outside Terminal A fall into polystyrene insulation material.

Smouldering fire spreads slowly within a ceiling void.

c. 15h30

Fire is noticed by a taxi-driver in the arrivals area. The airport fire brigade arrives rapidly.

c. 16h00

Flashover occurs, with around 100 m^2 of ceiling material burning, as well as cables. Dense black smoke spreads rapidly through the terminal building.

- 17 people died, all from smoke inhalation, and nearly 90 were injured
- The airport fire services were not trained for this type of fire
- The polystyrene insulation was installed in violation of the building permit ("no combustible insulation")

© A. Beard

See: https://www.grs.de/sites/default/files/pdf/grs-a-3912_0.pdf

Consumer Products
Europe and USA Alert Systems in Place

Europe
RAPEX = Rapid Alert System
for dangerous non-food products

USA
Consumer Product Safety Commission
issues alerts

Coffee machines like this one can burn for more than 30 min. Photo © EFRA, Ralf Baumgarte

Source: https://ec.europa.eu/consumers/consumers_safety/safety_products/rapex/alerts

Consumer products
Flame Retardants versus Smoke Detectors

BAM Germany studies, using room fire tests and modelling of home fires:

Room fire test

Started by a candle flame in a furnished child's bedroom, in contact with non flame retarded mattress for one second:

Smoke alarm in room triggered
2½ MINUTES AFTER IGNITION

Flashover
4 MINUTES AFTER IGNITION

Temperatures reach
400 °C NEAR THE FLOOR, 1, 000 °C NEAR CEILING

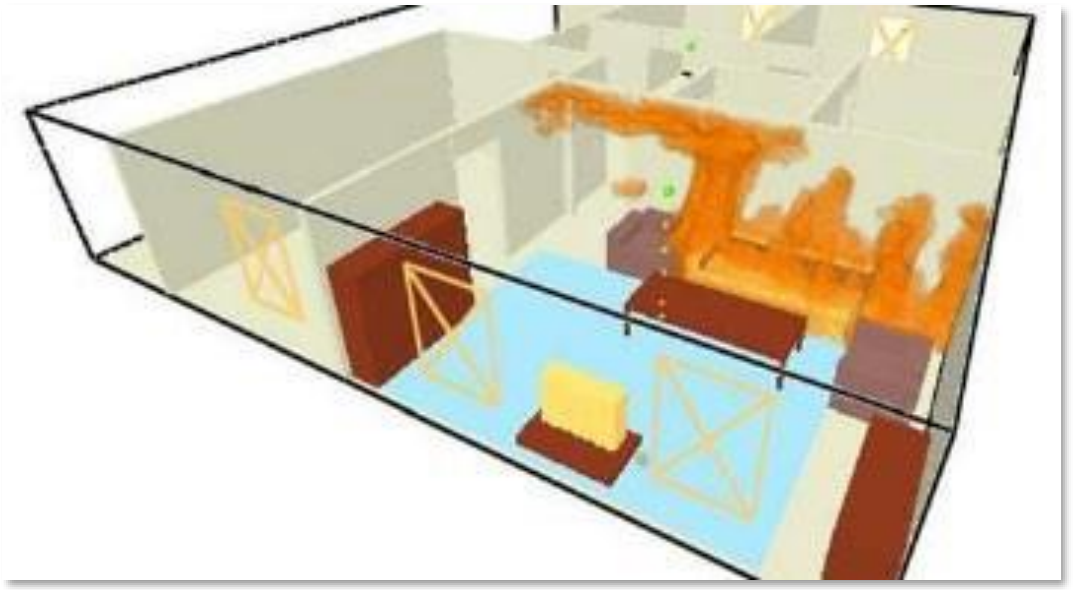
Modelling of fire development

Smoke and fire spread to other rooms and to other flats in the building, considering flame retarded or non flame retarded first item ignited (sofa, TV set)

Flashover
DELAYED FROM 3-4 TO NEARLY 15 MINUTES

Smoke alarms alone
DO NOT GIVE SUFFICIENT TIME FOR ESCAPE, NOR FOR FIRE SERVICE INTERVENTION

FLAME RETARDANTS ARE ALSO ESSENTIAL



A. Hofmann (BAM) et al., Flame Retardants 2006 Conference. Interscience, pp. 195-215 https://www.researchgate.net/publication/290580635_Modelling_fire_scenarios_in_residential_buildings_with_respect_to_the_benefit_of_smoke_detectors_and_flame_retardants_in_high_risk_items and https://slideplayer.com/slide/1688416/

The Plastics Pyramid
Most High-volume Commodity Plastics will burn readily

Thermoplastics:

- High Performance Polymers permitting exceptional end-use-applications, specialized niche products at high costs
- Engineering Plastics with improved performance at higher costs
- Standard Plastics = 65% of EU plastics consumption include Polyolefins, PS, EPS, PVC and PET (Bottle grade)

Thermoset resins:

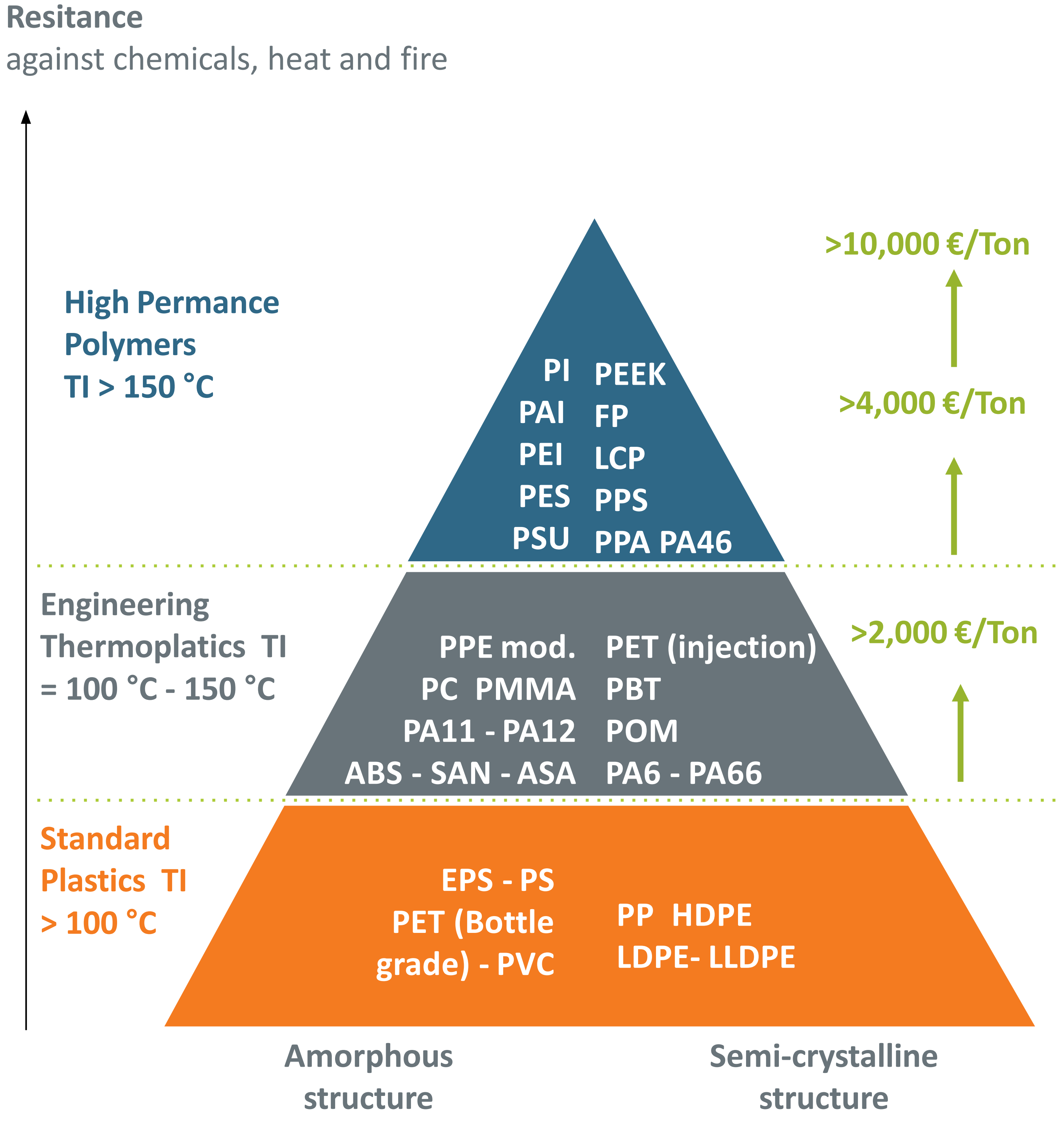
- Acrylic, Epoxy, Polyester, Vinylester, PUR, Phenolic
- Generally stronger than thermoplastics, generally better suited to high temperatures, easy to prototype

360 MIO METRIC TONS

TOTAL GLOBAL CONSUMPTION OF PLASTICS IN 2019

FLAME RETARDANTS CAN BE ADDED TO PLASTICS TO REDUCE EASE OF IGNITION AND SPREAD OF FIRE

Triangle of Thermoplastics
by Structure, Capability and Price



Capability by Temperature Index by Underwriter Laboratories, USA

Source: PlasticsEurope 2016 / Consultic Marketing & Industrieberatung GmbH.
Average 2010 indicative prices. Source: https://slideplayer.com/slide/11216536/
(1) = PlasticsEurope "Plastics – the Facts 2019"
https://www.plasticseurope.org/application/files/9715/7129/9584/FINAL_web_version_Plastics_the_facts2019_14102019.pdf

3.

The Global Flame Retardants Market

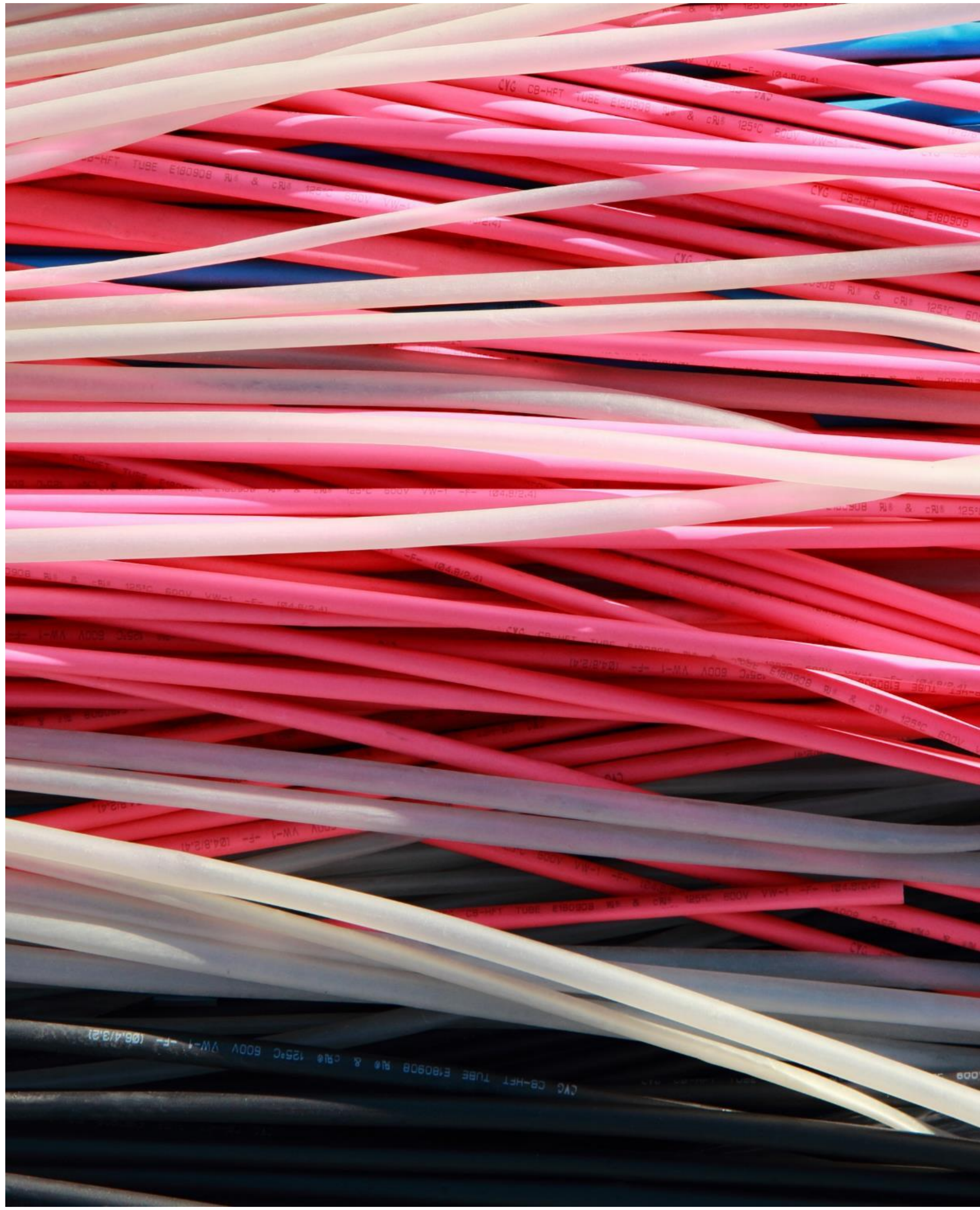


Photo © Shutterstock

The Variety and Classification of Flame Retardants

Phosphorus based

- Inorganic, e.g. red phosphorus, ammonium polyphosphate (APP), aluminum phosphite (AlPi), etc.
- Non-halogenated phosphorus esters, e.g. TCP, TPP, TBEP, etc.
- Organic P compounds, e.g. DOPO, phytate (bio-based), etc.

Inorganic:

- Metal hydroxides, oxides, etc, e.g. MDH (magnesium), ATH aluminium), copper, zinc, boron, molybdenum, iron, etc.
- Expanded graphite
- Natural and synthetic clays and organo-clays

Nitrogen based:

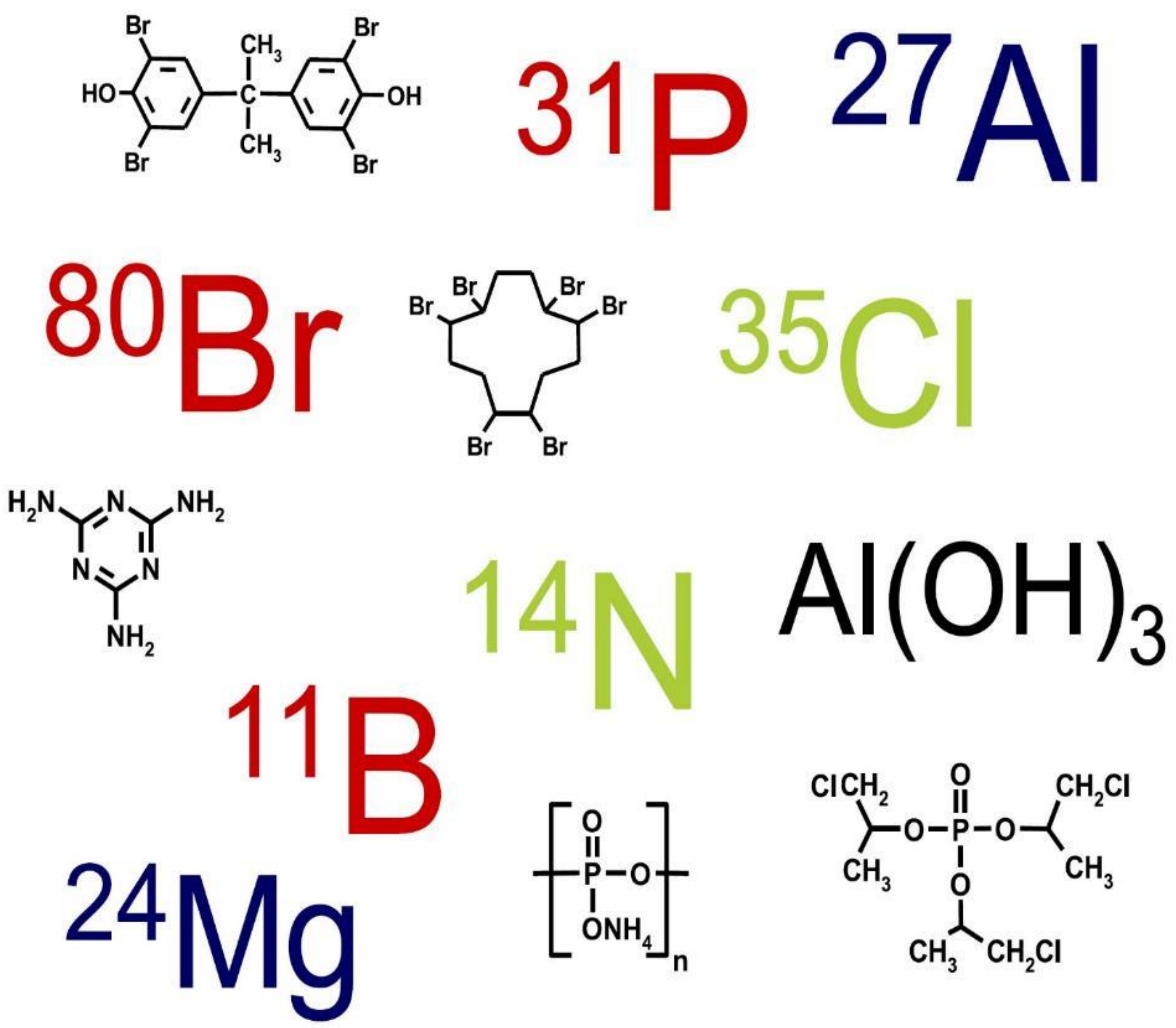
e.g. melamine polyphosphate and other melamine-based compounds, ammonium

Other components: Blowing agents for intumescents (e.g. pentaerythritol), carbon char sources (e.g. lignin, cellulose)

Halogenated flame retardants:

- Brominated or chlorinated, e.g. PBDEs (such as DecaBDE), HBDC, TPPBA, chlorinated paraffins, “tris” (TDCPP), etc.
- These are often used with antimony compounds (ATO)

Many very different chemicals are used as “flame retardants” (FRs) and/or as “smoke suppressants”



Global Consumption of Flame Retardants

~ 10 BILLION USD

WORLDWIDE CONSUMPTION OF FRS CA. 3.5 MILLION TONS A YEAR
(estimate 2020)

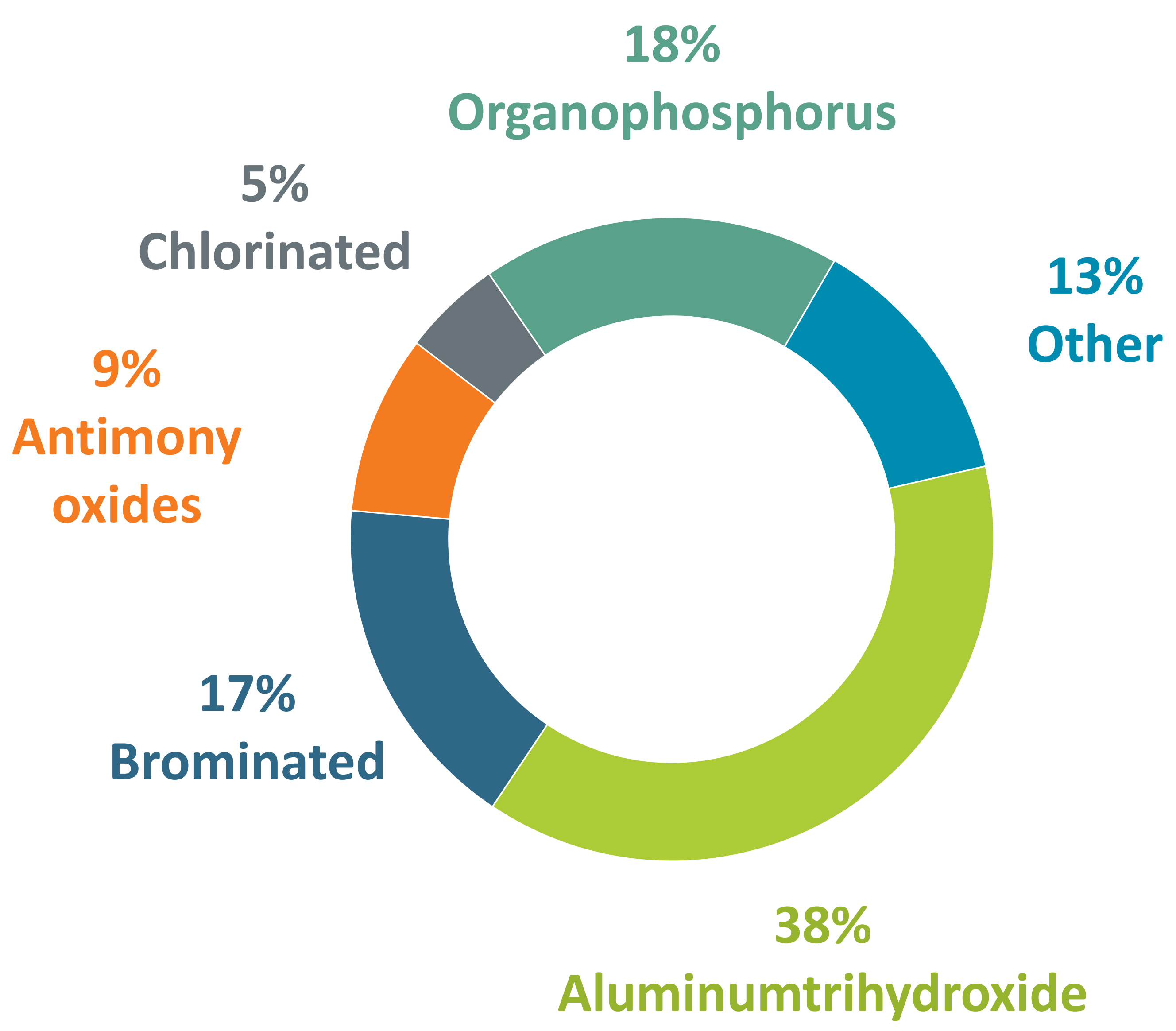
Expected to continue to **GROW AT A GLOBAL ANNUALIZED RATE OF**

~ 6%

PIN FRs (non-halogenated FRs) already have a large share and **ARE GROWING FASTER**

~ 8%

- Use in plastics accounts for approximately 85% of all flame retardants used with textiles, rubber products, wood and timber accounting for most of the rest
- Global FR plastics market estimated at ~ 50 billion USD Ongoing shift to higher consumption in Asia (today > 50% of FR consumption) and a reduction of the share of brominated flame retardants

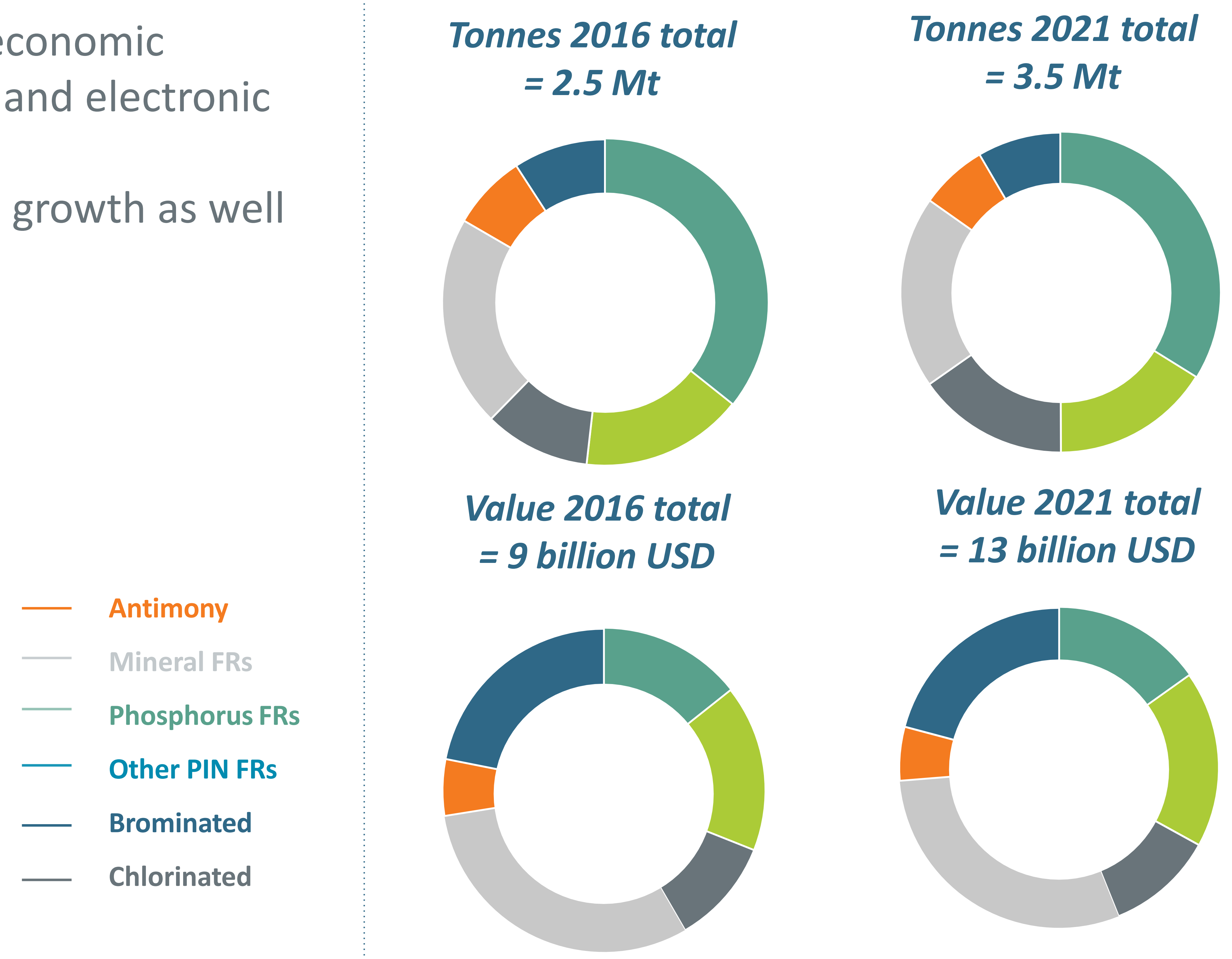


Global Consumption of Flame Retardants by type and by tonnage (2016)

Sources: IHS Flame Retardants Market Report 2017 and J. Crozier, pinfa, at Flame Retardants in Plastics, Cologne, 2018
www.flameretardants-online.com
https://www.lucintel.com/flame-retardant-plastics-market.aspx
https://www.credenceresearch.com/report/flame-retardant-chemicals-market
https://www.marketsandmarkets.com/PressReleases/halogen-free-flame-retardants.asp

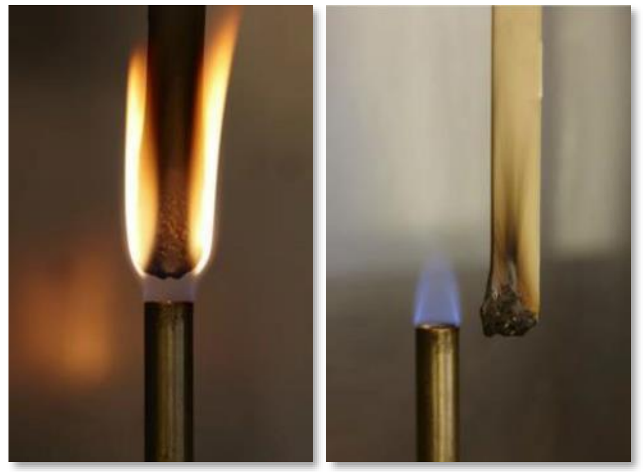
Global Consumption of Flame Retardants will Grow

- Flame retardants consumption growth is driven by general economic development (GDP): more houses, trains, airplanes, electric and electronic equipment means more need for flame retardants
- Increasing safety awareness and requirements contribute to growth as well
- Trend towards more PIN flame retardants



Data from J. Crozier, pinfa, at Flame Retardants in Plastics, Cologne, December 2018, based on secondary data from secondary research, company websites, press releases. magazines, expert interviews, and MarketsandMarkets Analysis

When are Flame Retardants Used?



UL 94 Test

Glow Wire Ignition Test

Smoke density, smoke toxicity

When are Flame Retardants Used?

Flame retardant packages are specific to a given plastic to ensure:

- Material properties: mechanical, electrical, aesthetic, ageing and weathering, resistance to heat or chemicals, etc.
- Compatibility with other additives
- Processability
- Cost

… As well as fire and smoke performance depending on the application.

Photo © Shutterstock

4.

Flame Retardant Mechanisms – How They Work

Photo © Shutterstock

PIN Flame Retardants Inhibit Ignition and Combustion

Flame retardants (FRs) can have one or several modes of action:

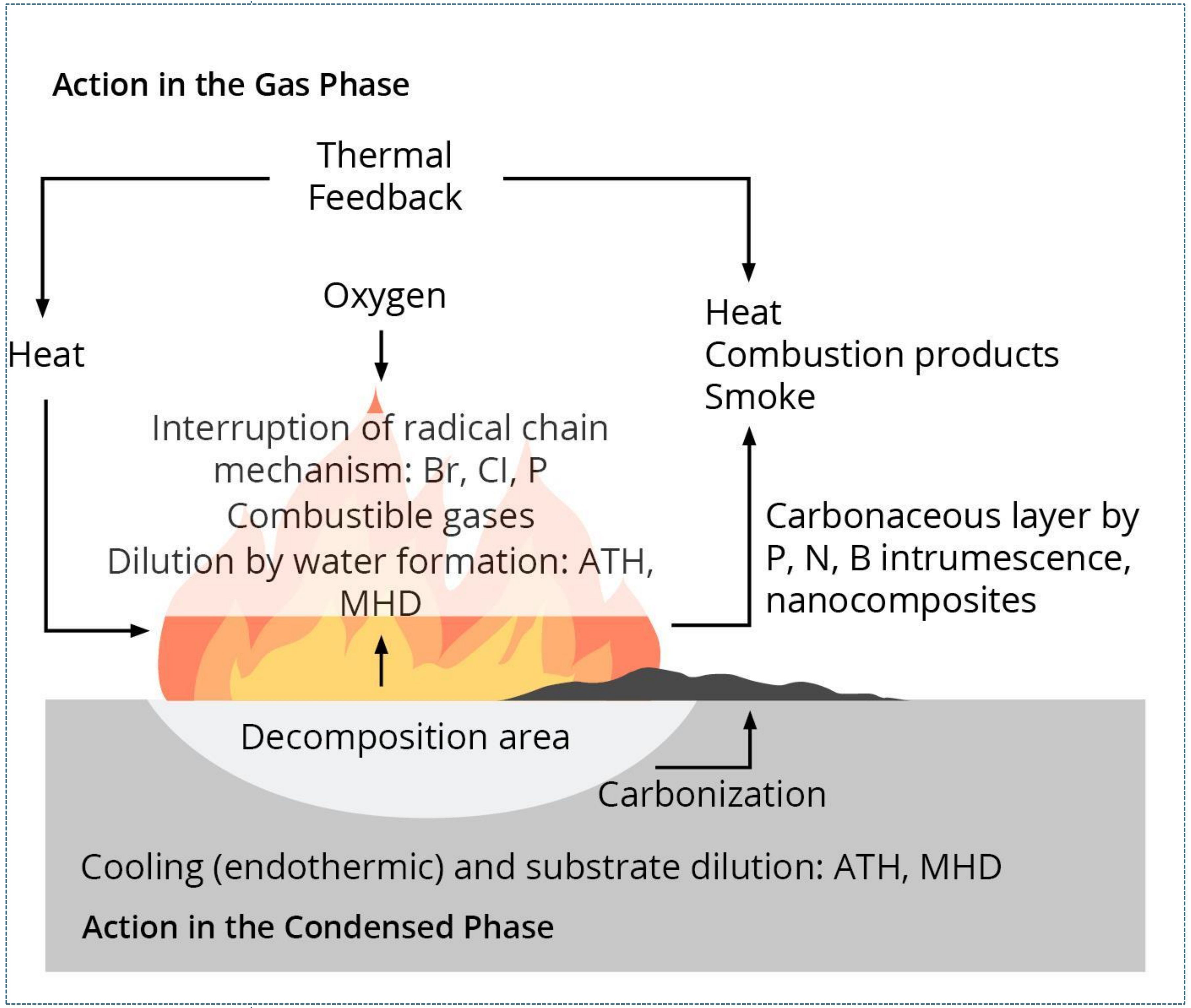
Gas phase:
React with, or remove by catalysis, the reactive OH* and H* radicals which are released by materials under heat and which feed fire.

Solid phase:
Generate a char layer on the material surface, which insulates from heat and prevents contact between oxygen and flammable gases.

Heat buffer:
Endothermic degradation reactions absorb heat energy.

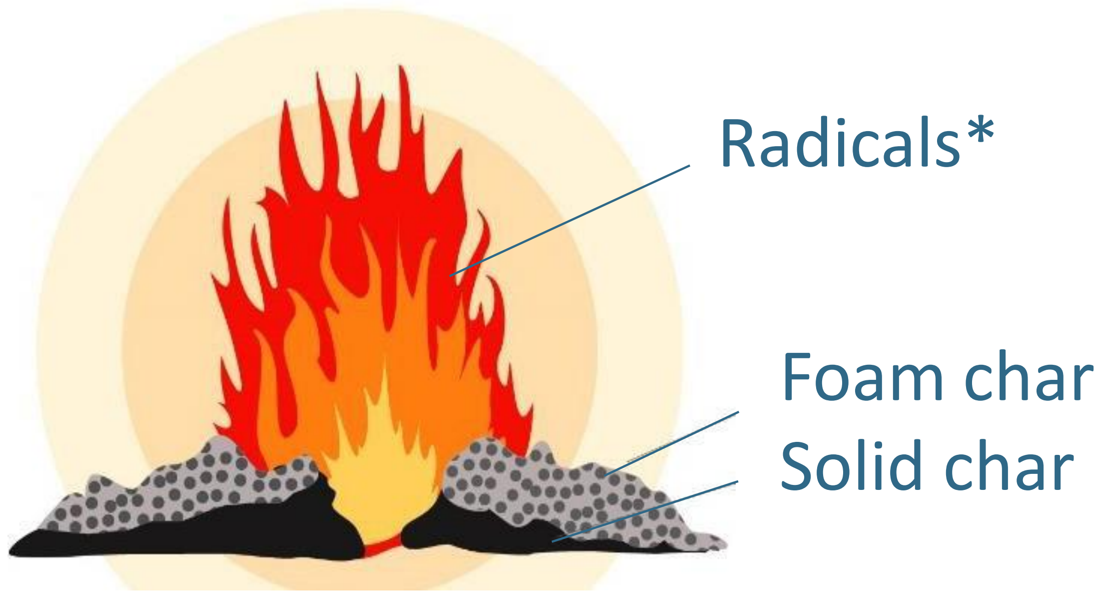
Dispersion:
Release of non-combustible gases (e.g. water, nitrogen), which dilute fire gases and oxygen.

Pyrolysis:
Catalysis releasing poorly flammable molecules.



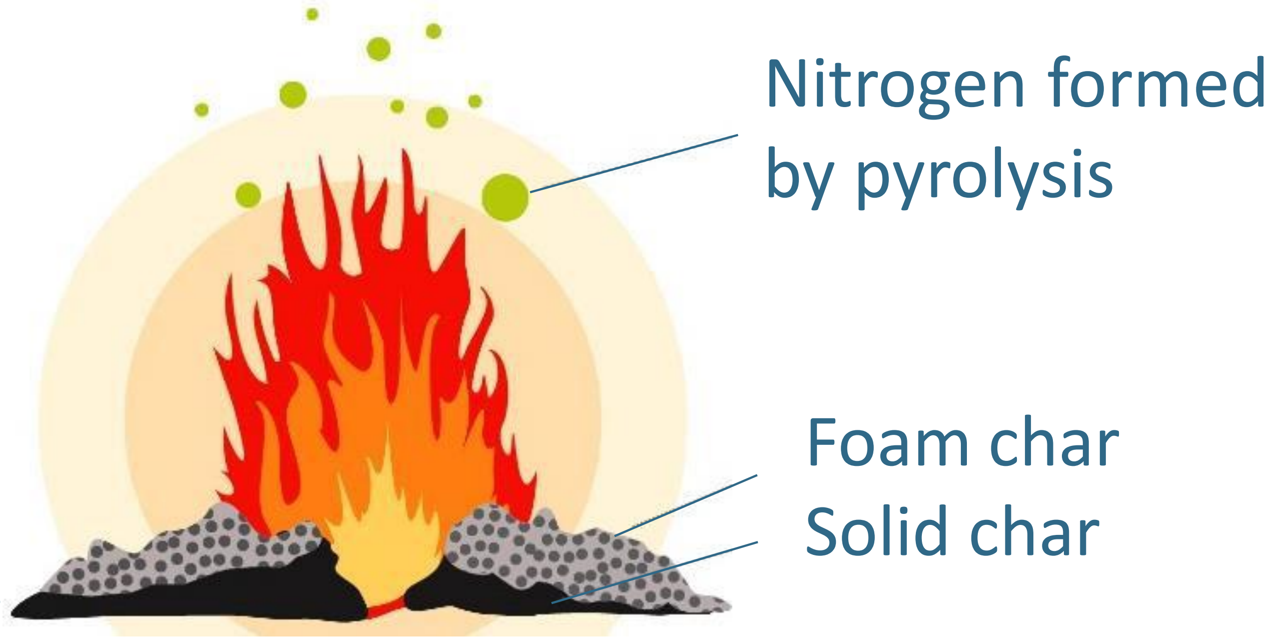
The Different Mechanisms of PIN Flame Retardants

Phosphorus flame retardants

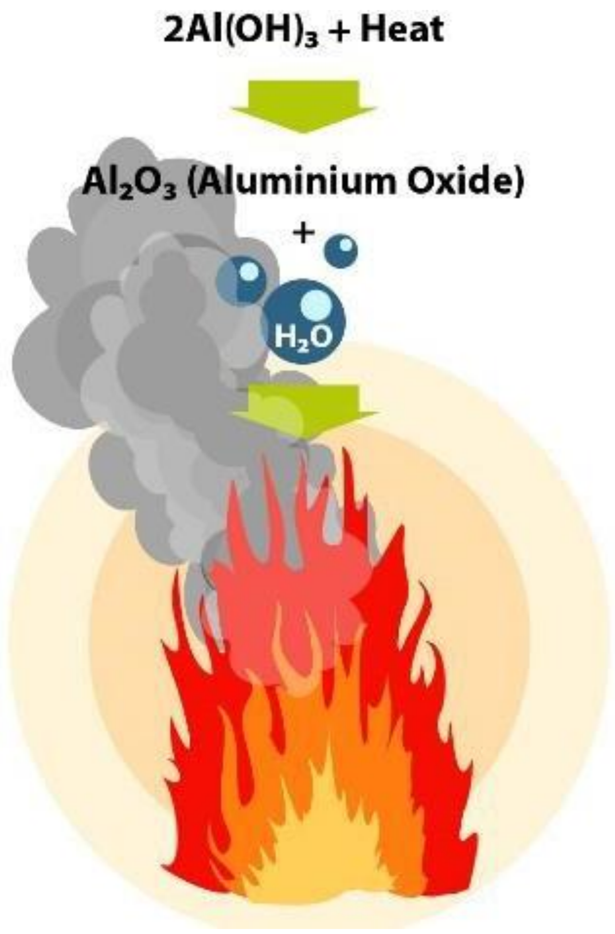


*Some phosphorus FRs release radicals which quench the combustion reactions

Nitrogen flame retardants

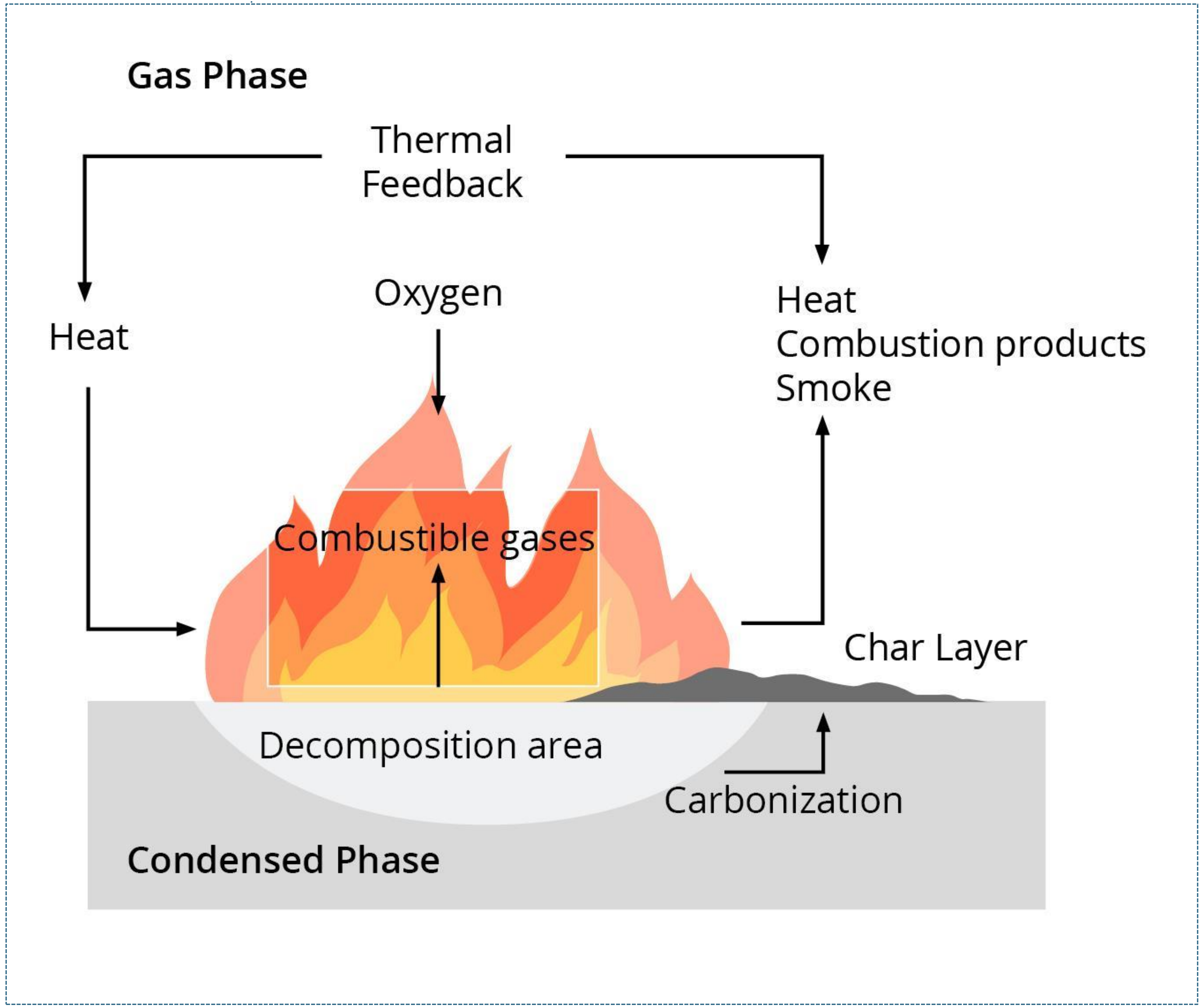


Inorganic flame retardants
- quench and cool -



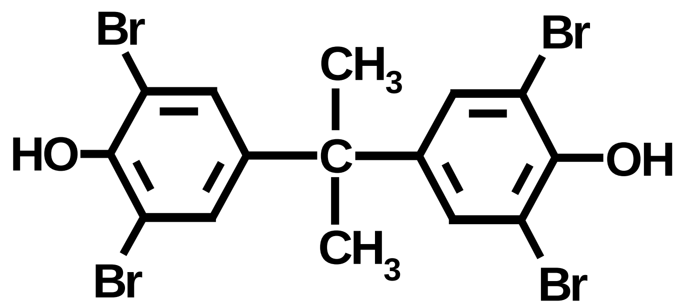
Halogenated Flame Retardants Interrupt the Chemical Reactions in the Gas Phase

- Halogenated flame retardants are organochlorine or organobromine chemicals
- In fire, halogen radicals are released (Br* or Cl*)
- In the flame zone (gas phase) these neutralise the energy rich radicals (H* and OH*), interrupting the chain reaction of combustion
- This results in incomplete combustion, leading to significant smoke production
- Halogen acids are formed (HBr, HCl)
- Halogenated flame retardants are often used in combination with antimony trioxide

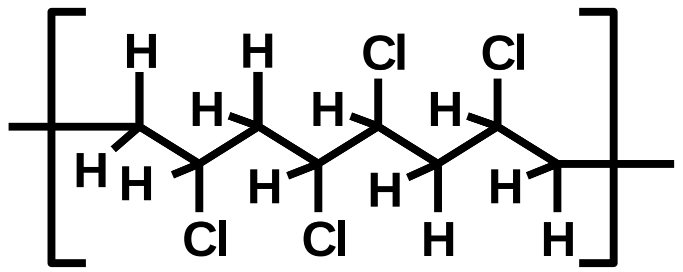


See: https://www.flameretardants-online.com/flame-retardants/bromine-chlorine

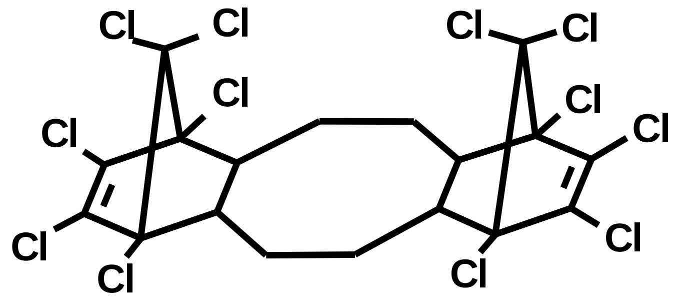
Halogenated Flame Retardants Examples



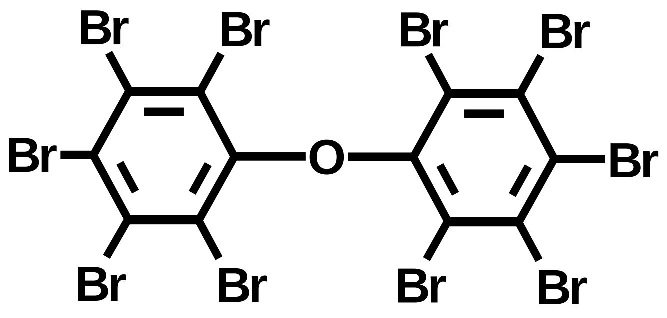
Tetrabromobisphenol A (TBBA)



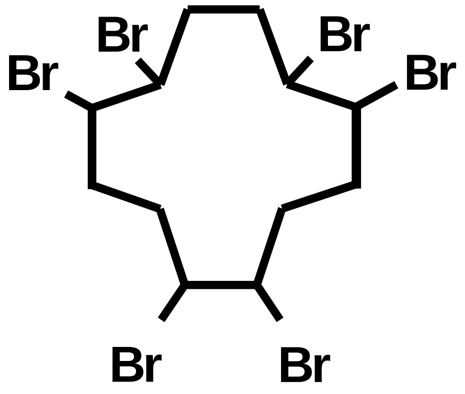
Chlorinated Paraffins



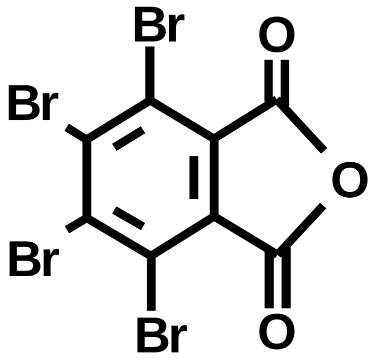
Dodecachloropentacyclooctadecadiene (Dechlorane)



Decabromodiphenylether (Deca)



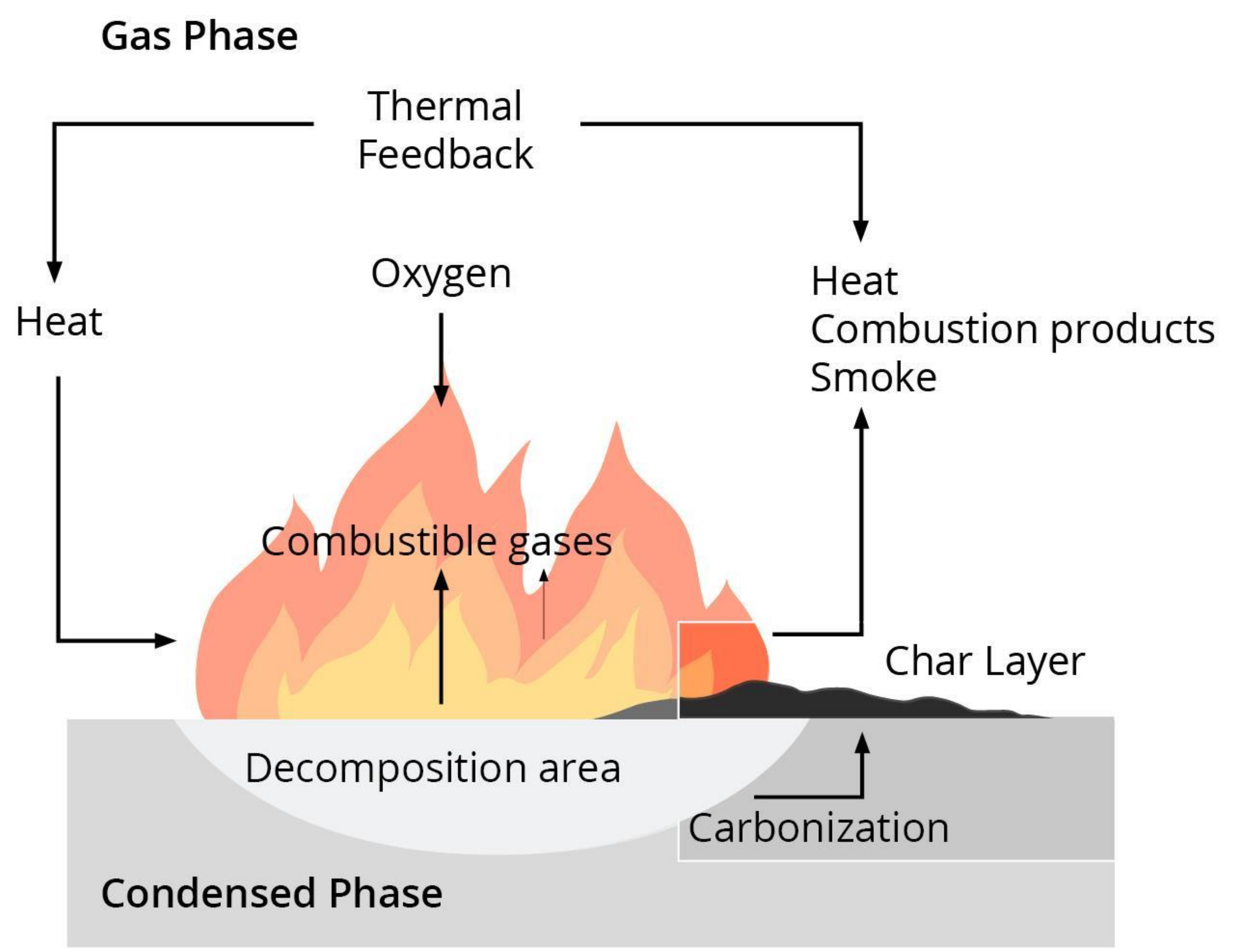
Hexabromocyclododecane (HBCD)



Tetrabromophthalic Acid Anhydride

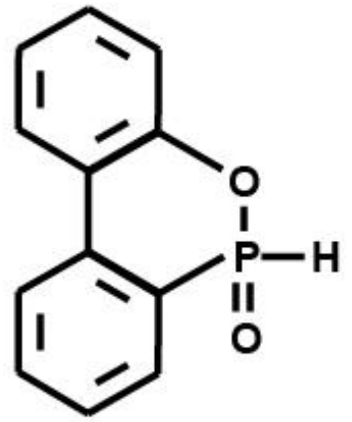
Phosphorus-based Flame Retardants can Form a Protective Char Layer or Work in the Gas Phase

- Elemental (red) phosphorus, inorganic and organic phosphorus compounds are used.
- Main mechanism is by formation of a char layer at the material surface (solid phase), stopping the contact between fuel and air. Combined with intumescence, foam-like char also provides a thermal protection effect.
- Phosphorus flame retardants can also have some gas phase effect (phosphorus radicals) which leads to incomplete combustion.
- Char formation results in generally less smoke, because there is no forced incomplete combustion and because release of volatile compounds is limited by the barrier effect.
- Phosphorus flame retardants generate considerably less acidic gases than halogenated flame retardants.

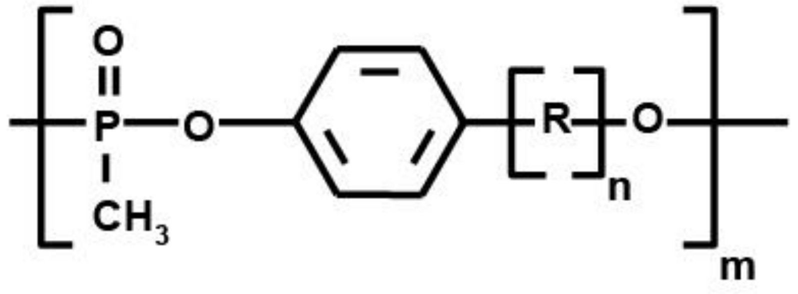


Phosphorus-based Flame Retardants Examples

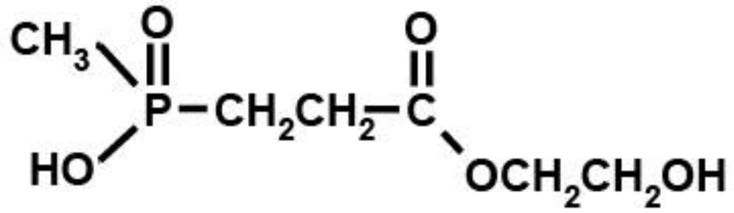
- Specific interactions with different polymers – no one size fits all
- No simple correlation of activity vs. P-content
- Different mechanisms, solid phase (surface charring + intumescence) and/or gas phase
- Low fire emissions, soot; no corrosive gases
- No negative impact on UV stabilizers
- Many have excellent environmental and health profile

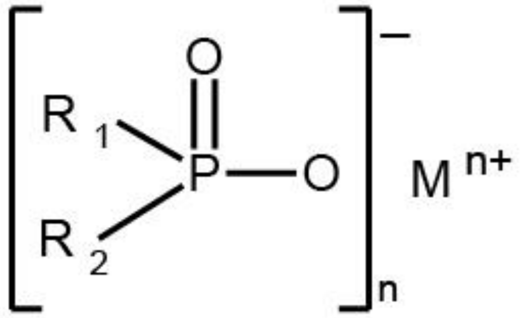


DOPO



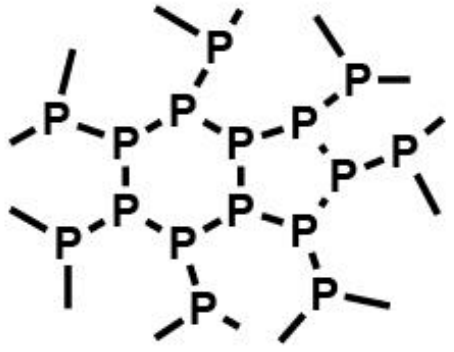
Polyphosphonate



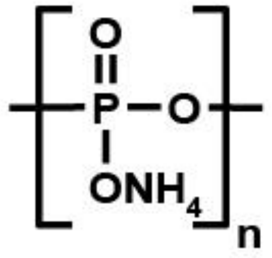


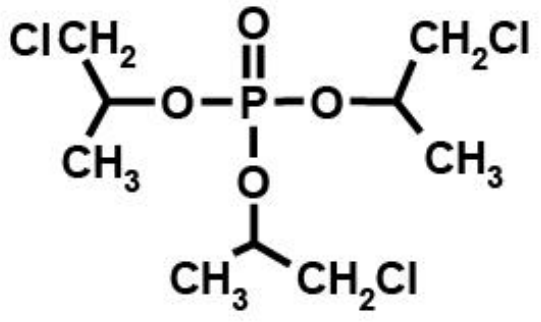
Phosphinic acid derivatives

Newer developments

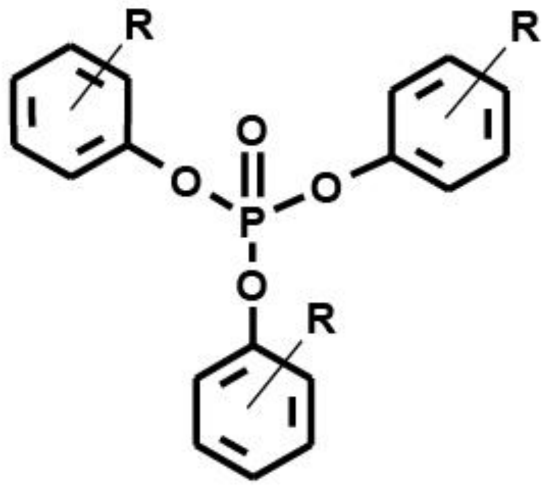


Red Phosphorus





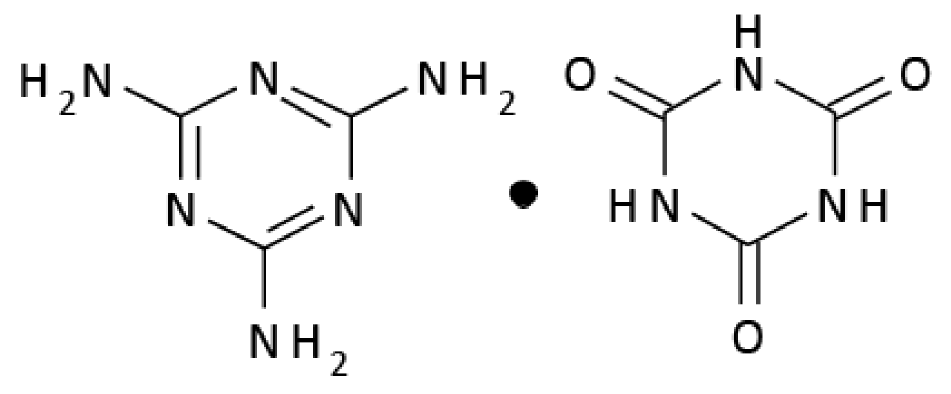
Ammonium polyphosphate (APP)



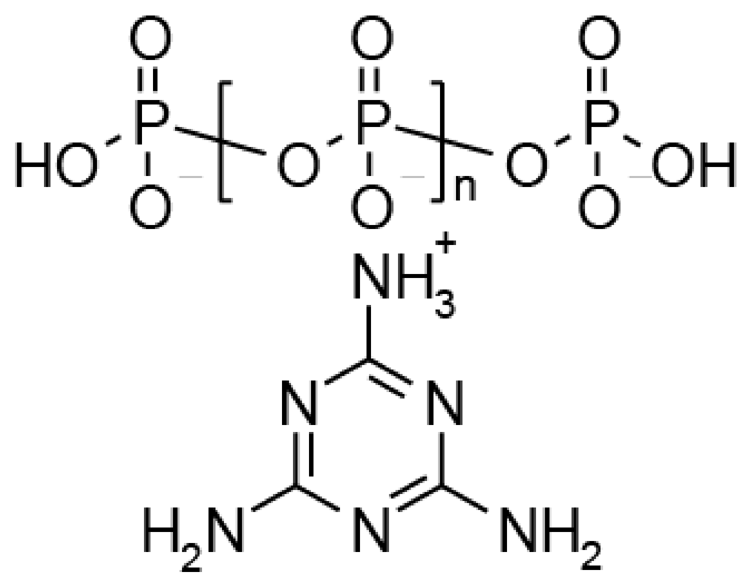
Triarylphosphates

Nitrogen-based Flame Retardants Act by Endothermic Decomposition, Releasing Inert N_2

- Melamine on its own or in derivatives like melamine cyanurate (MC) and melamine polyphosphate (MPP) are the most common N-based FRs
- Releasing inert nitrogen (N_2 so diluting fire gases), acting as cooling agents by endothermic decomposition, also as blowing agents in intumescent systems
- They can promote polymer degradation ➔ polymer melts away from flame front, e.g. MC in polyamide
- N-based FRs are often combined with phosphorus based FRs



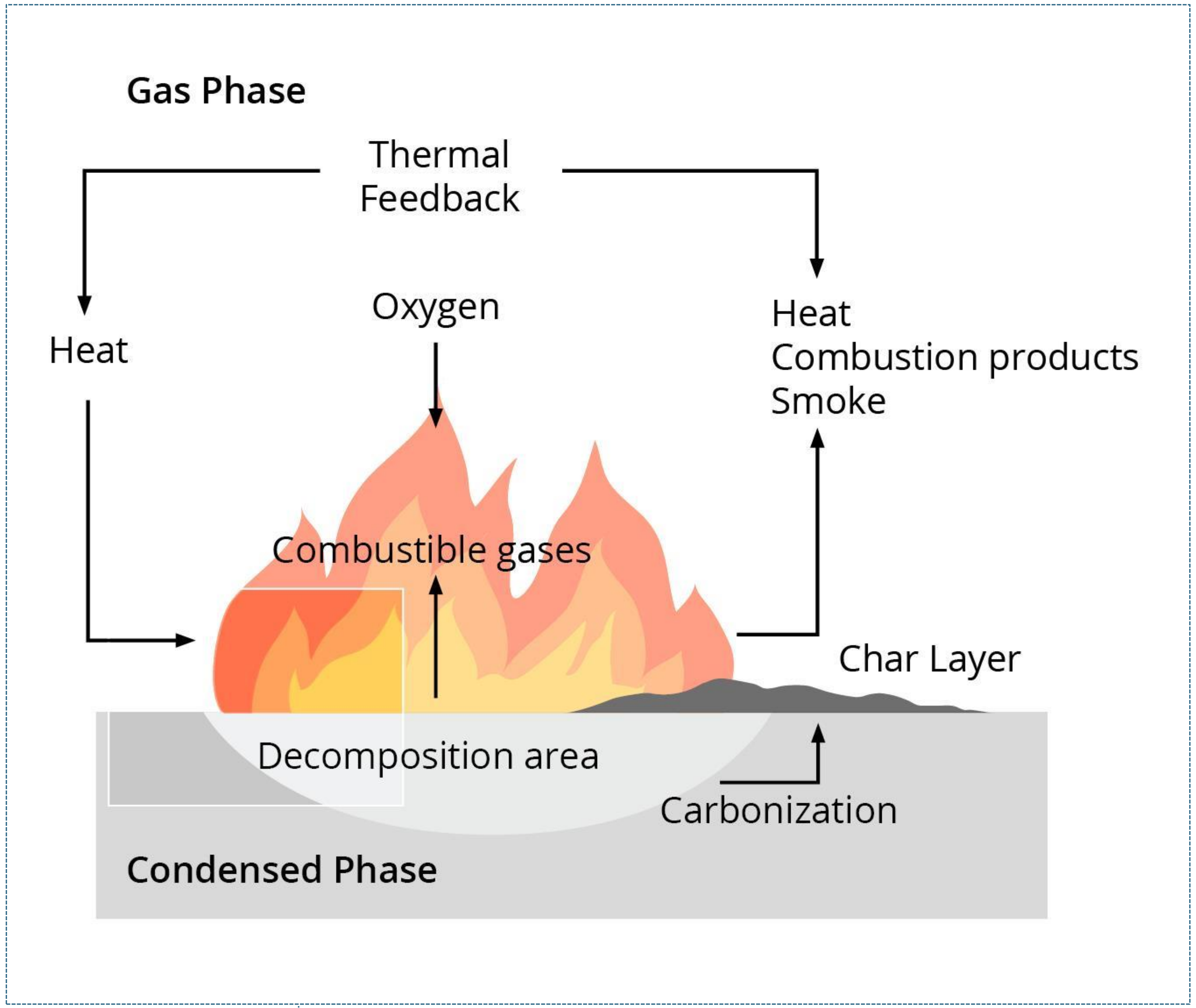
Melamine cyanurate



Melamine polyphosphate

Inorganic Flame Retardants Release Water

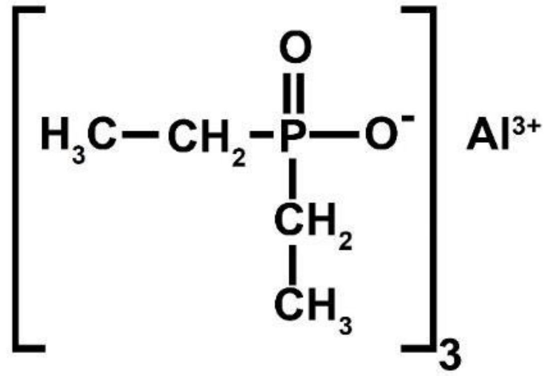
- Aluminum and magnesium hydroxides are the most common
- Quench: water is released upon heating, leading to a cooling of the combustion zone and dilution of fire gases
- Cool: release of water is an endothermic reaction
- Solid phase action: minerals, such as aluminum, can also contribute to glassy char formation
- Physical effect is less efficient: high loadings are necessary
- Less smoke, because no forced incomplete combustion, no acidic gases



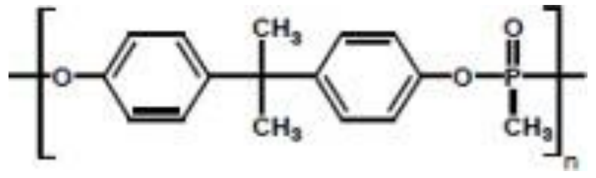
$Al(OH)_3$ + energy ➔ $Al_2O_3 + H_2O$

$Mg(OH)_2$ + energy ➔ $MgO + H_2O$

Notable PIN Flame Retardants Innovation: Commercial Products 2000-2020



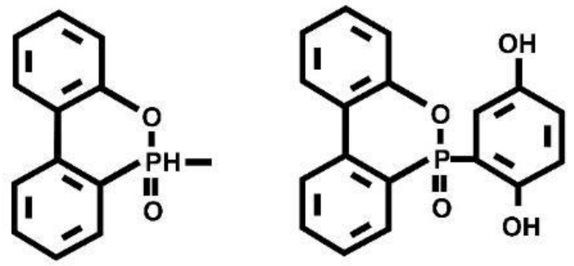
***DEPAL (Clariant)



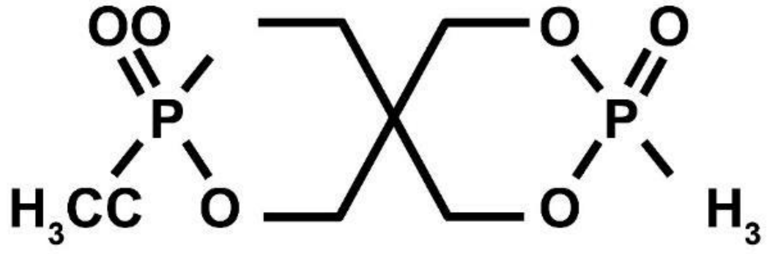
*Polyphosphonate (FRX Polymers)

$[H_2PO\text{-}O]_n\ M^{n+}$

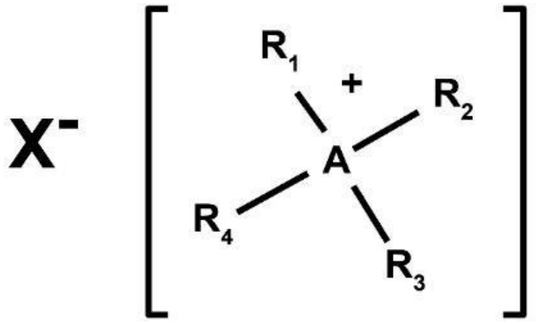
***Metal hypophosphites (Italmatch)



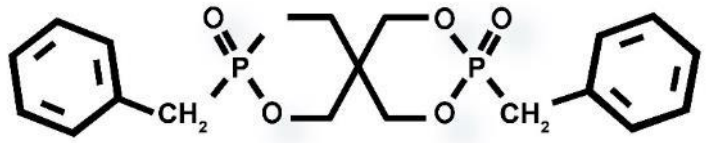
**DOPO & DOP-HQ (Schill & Seilacher)



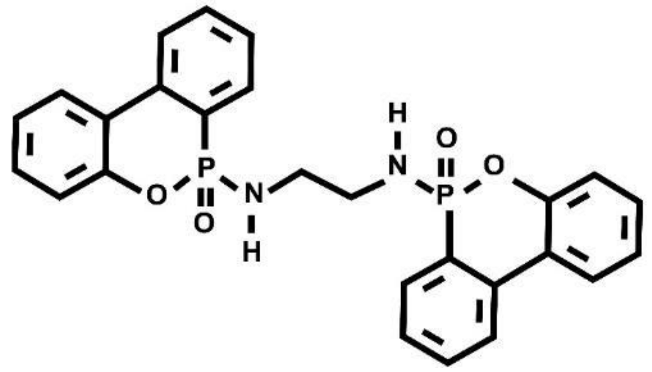
***NH P-FR (Thor)



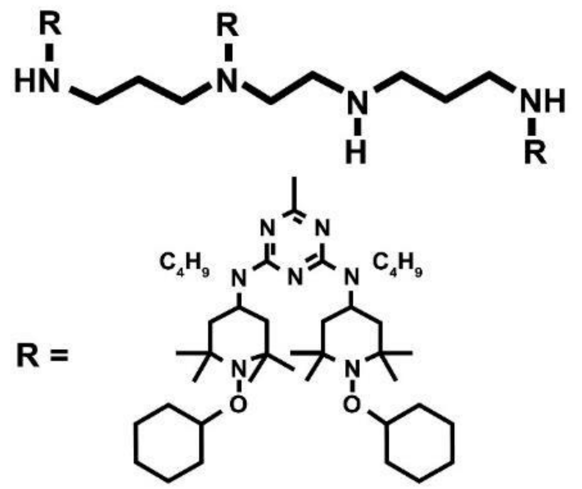
***Ionic Liquids (Inovia)



***Arylphosphonate (Teijin)



***EDA DOPO (Metadynea)



Flamestab NOR 116 (BASF)

*Polymeric FR - **Reactive FR - ***Additive FR

Smoke and Toxicity

- All fires generate toxic smoke, the inhalation of smoke is the main cause of death for fire fatalities (> 70%)
- The total toxicity of gases emitted in fires is principally related to the quantities of materials burned
- Dense smoke can make orientation impossible, and so prevent escape
- Acutely toxic components prevent escape, can cause injury and death
  - narcotic: CO, HCN - deadly within minutes; but also CO_2, O_2-deficiency
  - irritants for eyes and breathing: HCl, SO_2, NO_x, aldehydes
- Compounds with long term effects pose significant concerns for firefighters and other professionals repeatedly exposed to smoke or soot:
  - polycyclic aromatic hydrocarbons (PAHs)
  - halogenated dioxins + furans (PCDD/F)
  - mostly adsorbed to soot, so inhaled in smoke particles

Fire and smoke demonstration at firefighter training centre PIVO, Brussels, pinfa Advisory Board meeting 2019. Screenshot from video "Flame retardants & fire safety Television sets with (Philips) and without (Thomson) flame retardants – burn test by Berlin fire service" https://www.pinfa.eu/media-events/photo-video/

Do PIN Flame Retardants Make Smoke More Toxic?

In 2019, the French institute CREPIM completed a study testing 94 polymer samples from 12 companies, with and without FRs.

Results highlight that phosphorus, inorganic or nitrogen-based flame retardants have no significant negative impact on the evaluated smoke parameters of the study (CIT_{NLP}, $CIT_{4\ min}$, $CIT_{8\ min}$ and Ds values) under the testing conditions.

Effect compared to neat polymer

- Much worse
- Slightly worse
- Neutral
- Neutral to Better
- Better

In fact, several flame retardants can have a positive impact on the evaluated parameters when used judiciously.

CREPIM evaluated the smoke toxicity and the smoke density according to two well-recognized protocols: the norm NF X 70-100 at 600°C (tubular furnace) and the ISO 5659-2 with Annexe C of EN 45545-2 method (smoke chamber) at 50 kW/m2. Evaluated parameters were the Conventional Index of Toxicity for non-listed products and toxicity index at 4 or 8 minutes (CITNLP, CIT4 min, CIT8 min as per EN 45545-2) as well as smoke density values at various time intervals (DsMAX, Ds10, Ds4, Ds1.5 and calculated VOF4 values). Study funded by pinfa. Summary of results in pinfa Newsletter n° 109 at www.pinfa.eu

Polymer	Toxicity Concern	PIN FR Effect Toxicity	Smoke Density	Halogen / Br-FR Effect Toxicity	Smoke density
Polyolefins (PE, PP)	CO, CO_2				
Polystyrene (PS)	CO				
Polycarbonates (PC)	CO, CO_2				
Polyesters (PBT)	CO, HCN, NO_X			Not evaluated	Not evaluated
Epoxy resins	CO, HCN				
Polyamides (PA6, PA66)	CO, HCN, NO_X				
Polyurethanes (PUR, PIR)	CO, HCN, NO_X				
Polyvinylchloride (u-/p-PVC)	HCl	(1)	(1)	(1)	(1)

(1) **Minor impact of flame retardants on toxicity and smoke, however, in all cases huge contribution from HCl exceeding threshold values by far**

Smoke Suppressants Can Significantly Reduce Emitted Smoke And Also Act As Flame Retardant Synergists

Mode of action:

- Catalysis of cross-linking of carbon compounds in fire, so stabilising char and preventing the release of smoke and of soot particles
- In gas phase, vaporised metal compounds react with hydrogen radicals
- Release of water from hydroxides at high temperatures or release of ammonia which acts in the gas phase
- In halogenated polymers (e.g. PVC), volatilisation of metal halides, which act as flame retardant catalysts in the gas phase

Examples:

- Molybdenum minerals, e.g. ammonium octamolybdate
- Zinc minerals, e.g. zinc oxide, zinc phosphate, zinc stannates, zinc borate
- Calcium, copper, iron, nickel, silicon, tin minerals

Ignition of a sofa by a cigarette.
Photo EFRA © R. Baumgarten

5.

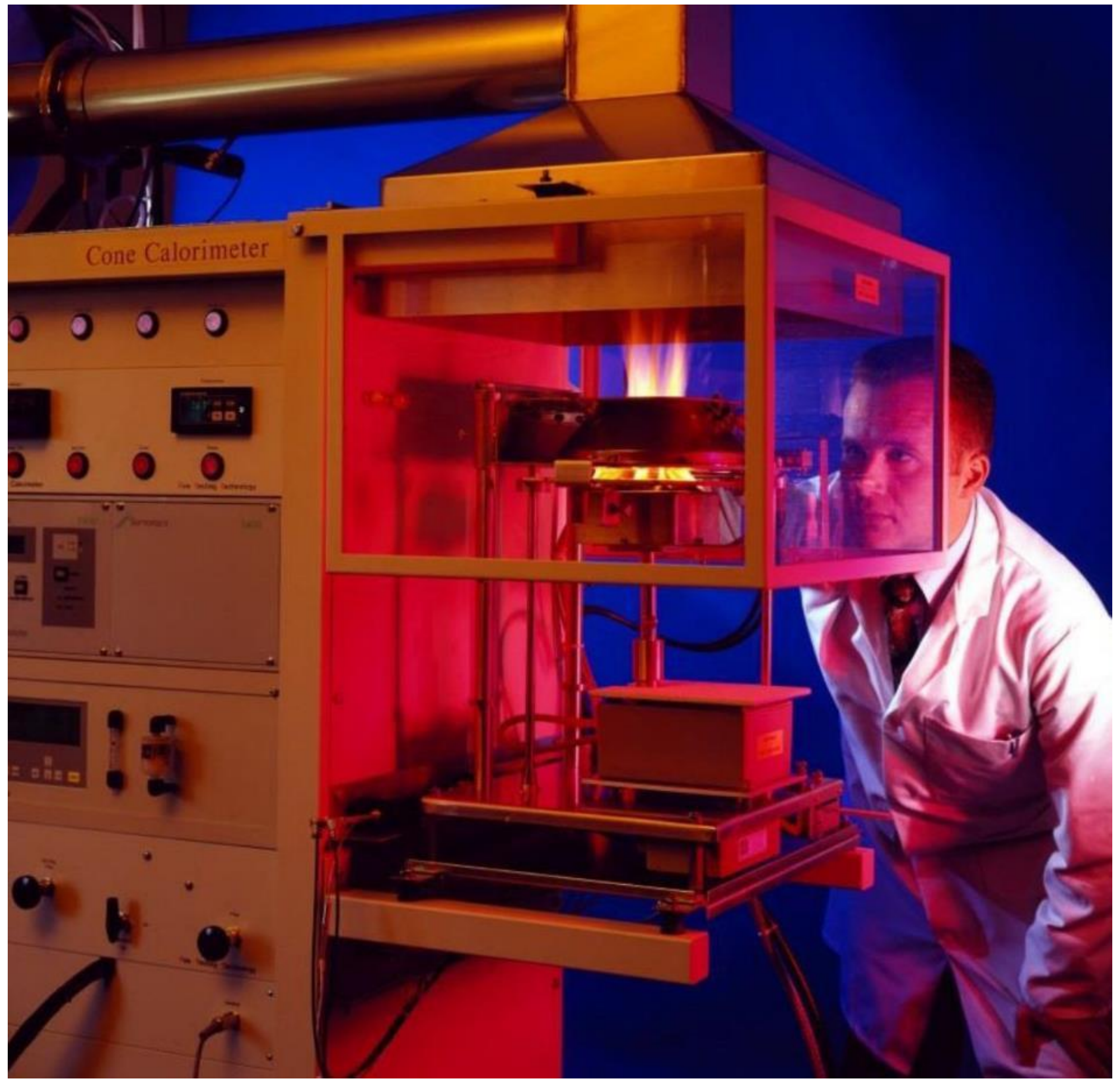
Fire Tests and Standards

Photo © Clariant, R. Baumgarten

Fire Standards and Fire Tests

- Standards are defined by regulation or by industry voluntary agreement
- Standards specify that in certain applications, materials must respect certain requirements, which can include fire performance
- Standards will usually specify which fire test must be used, and under what conditions, to verify conformity to the required fire performance. In some cases; standards may authorise use of other tests to show equivalent performance

The objective is to ensure protection of people and property against risks of fire and smoke.

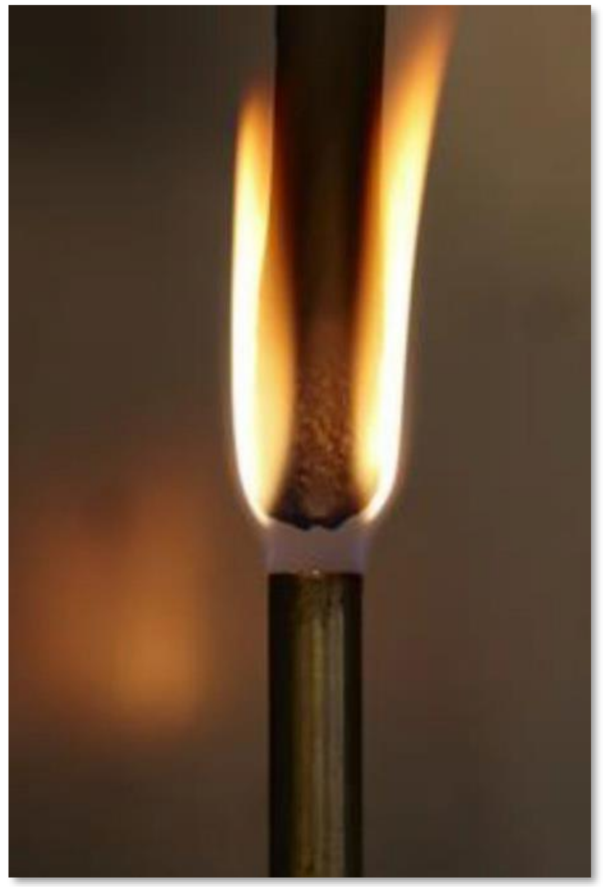


Cone calorimeter fire test. Photo: courtesy of Fire Testing Technology, UK

Fire Tests and Flame Retardants

Flame retardants are generally used as required to ensure that a material passes Fire Test(s) specified in a Standard or by a customer.
Thus, the loading of flame retardant used is defined to ensure to reliably pass the fire test(s). Although this may seem like "box ticking", the aim is to ensure fire safety:

- **Standards define what fire and smoke performances are required for materials**
- **Fire tests are designed to test these performances**
- **Flame retardants are used to ensure that performance is achieved**



UL 94 vertical fire test. Simulates resistance against ignition by a small flame.
Photos © Clariant R. Baumgarten

Fire Tests Evaluate the Behaviour of Specimens Under Defined Conditions (1)

Testing material properties:

The heat of combustion (as measured by oxygen bomb calorimetry) is a fire parameter which is a real material property. Generally, fire tests involve specific scenarios.

Testing a scenario:

most fire tests assess material fire behaviour under specific conditions, designed to simulate aspects which are significant for fire risk and fire impacts: e.g. thickness and horizontal or vertical orientation of specimen, size and kind of ignition/energy source.

Different scales:

Small scale fire tests cannot directly be extrapolated to predict behaviour in full scale fires. Fire and smoke tests are designed to compare materials, not to estimate impacts of full-scale fires.

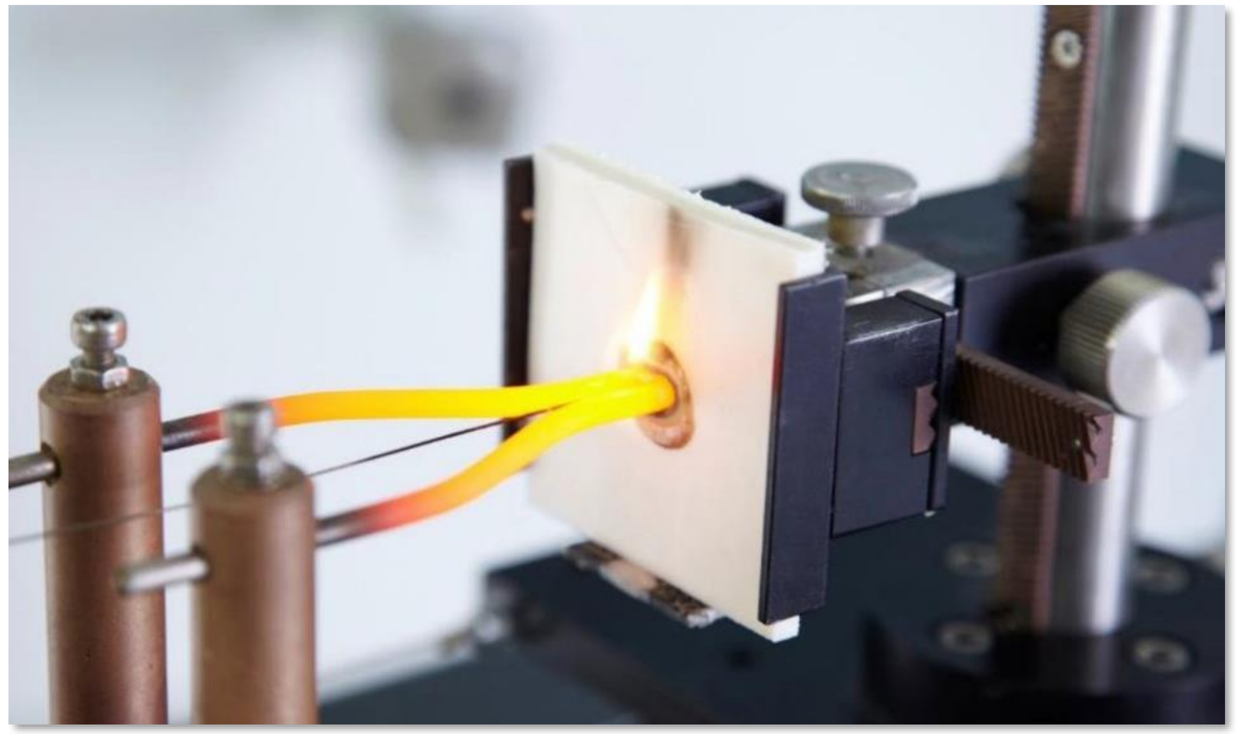


Photo © Budenheim. Glow wire fire test. Used widely for electrical and electronic equipment. Simulates resistance to ignition or fire spread from a localised, high temperature heat source, comparable to electrical faults.

Further explanations here: https://www.ifsecglobal.com/uncategorized/fire-resistance-and-reaction-to-fire/

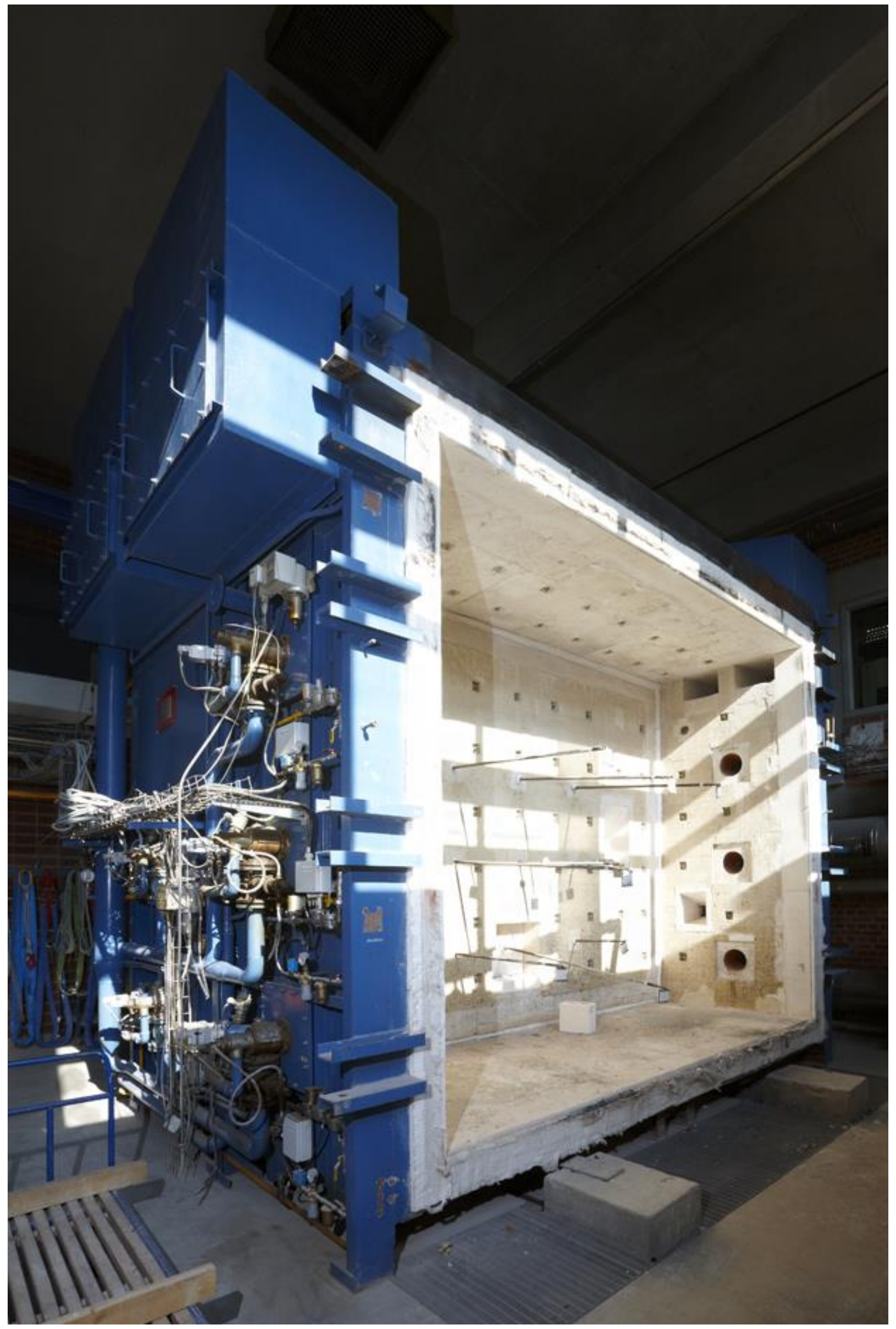
Fire Tests Evaluate the Behaviour of Specimens Under Defined Conditions (2)

Reaction to Fire:

Reaction to Fire means resistance to ignition (prevent fires starting) or prevention of fire spread, including contribution to the development and impacts of a fire (e.g. heat release, melting dripping, smoke release), especially during the early phases of a fire (relevant for escape and extinguishing).

Fire Resistance:

The term designates the ability of products and construction elements to prevent the spread of fire (e.g. fire wall) or withstand the impact of fire (e.g. steel beam) for a specified time under defined fire conditions (e.g. temperature development curves defined in standards).



Large scale test oven for Fire Resistance of walls.
Photo © Clariant, R. Baumgarten

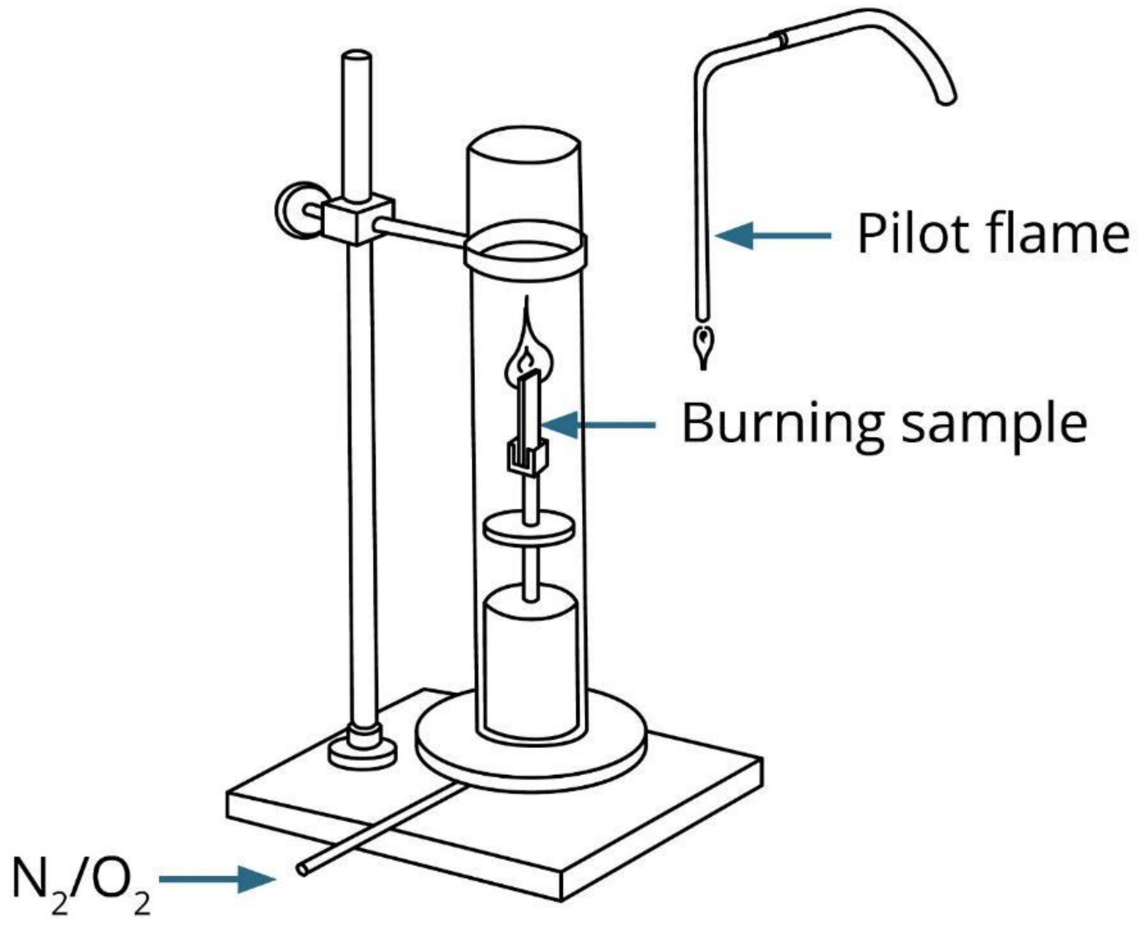
Further explanations here: *https://www.ifsecglobal.com/uncategorized/fire-resistance-and-reaction-to-fire/*

The Limiting Oxygen Index (LOI) is Widely-used to Indicate Relative Flammability

HIGH LOI
= LOW FLAMMABILITY

The test measures the minimum level of oxygen (mixed with inert nitrogen) which can sustain a flame in the material.

This is not directly comparable to real fire conditions, but provides an indication of relative flammability, useful for material development, quality control, etc.



https://www.fire-testing.com/oxygen-index/

Further explanations: LOI values for different neat polymers: https://omnexus.specialchem.com/polymer-properties/properties/fire-resistance-loi

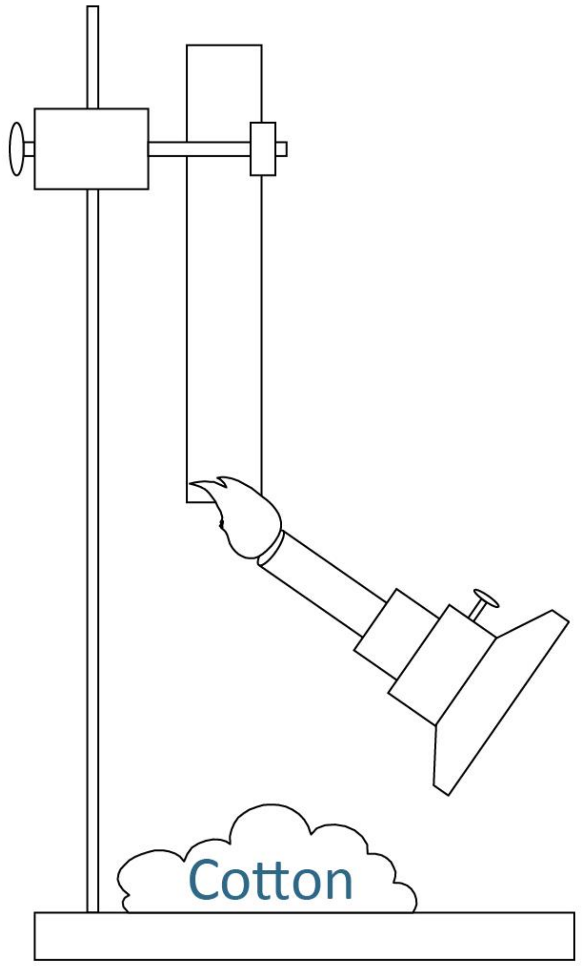
Underwriters Laboratories UL 94 Vertical Test

Usually conducted on a ca. 13 x 1,5 cm specimen, with defined thickness, typically from 0,4 to 3,2 mm. 5 specimens per test.

Results depend on specimen thickness:

- The same UL-V rating for a thinner specimen indicates higher fire performance
- Indicating “UL94-V0” without specifying the thickness is not meaningful

Other classifications apply to low density foams (HF-1, HF-2, HBF) or thin films (VTM-0, VTM-1, VTM-2).



Class	V-5A	V-5B	V0	V1	V2	HB	Not Rated
Low inflamability – High Fire Performance						High inflamability – Poor Fire Performance	
Individual afterflame time			≤ 10 s	≤ 30 s	≤ 30 s	> 30 s	
Total afterflame time: sum of t_1 and t_2 for the 5 specimens			≤ 50 s	≤ 250 s	≤ 250 s	> 250 s	
Ignition of cotton			No	No	Yes	Yes	
Examples of applications	Automotive Circuit boards		Electrical (E&E)		Office automation		

More information: “UL 94 Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliance” https://standardscatalog.ul.com/standards/en/standard_94

Harmonised with IEC 60707 / 60695-11-10 / 60695-11-20 / ISO 9772

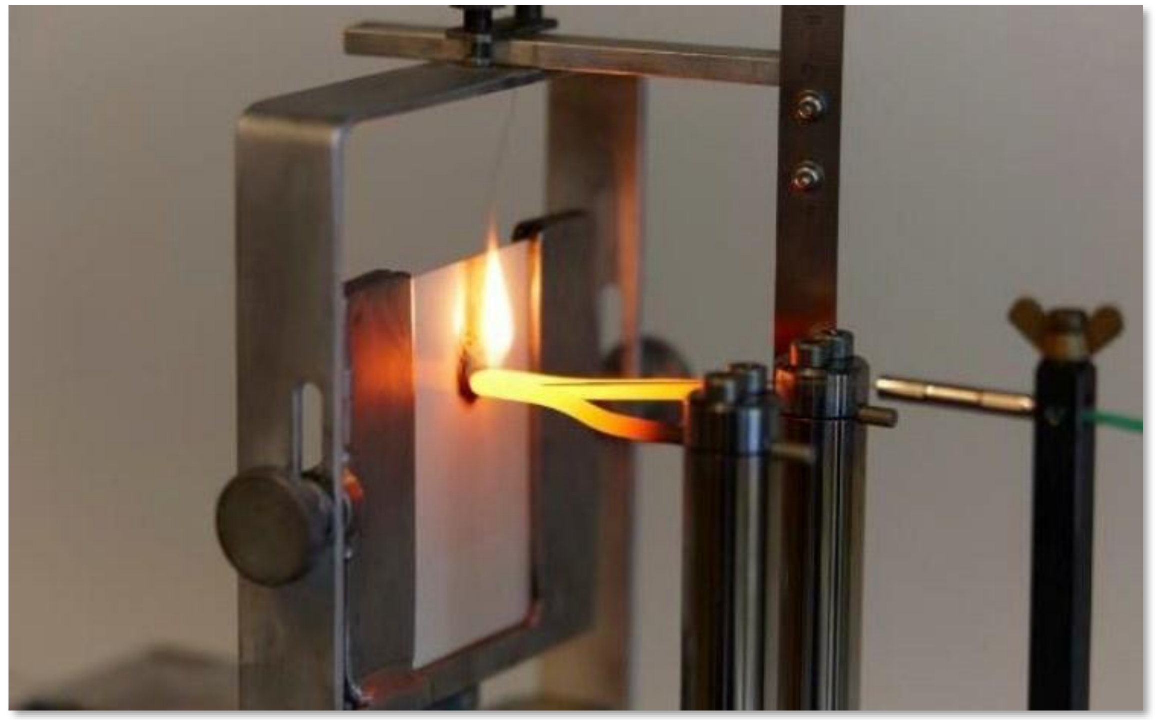
Glow Wire Ignition
Test is Common for Household Appliances

DIN EN 60695-2-11 and -12

Temperature of wire will be heated to a pre-determined temperature, wire will be pressed against a sample (set force of 1N) for 30 seconds.

TEST CRITERIA:

Is sample ignited (duration, flame height, drips, tissue paper below ignited)?



Glow wire test. Photos © Clariant, R. Baumgarten

The Cone Calorimeter

The Cone Calorimeter is widely used to assess fire behaviour of small samples of materials (approx. 100 x 100 mm).

A conical heater enables controlled heat levels to be delivered to the sample, and when using an additional enclosure of the sample space, ventilation conditions can be controlled.

The apparatus provides comparable data on ignition time, mass loss, heat release rate and combustion emissions, including smoke density and soot production.

Cone calorimeter fire test. Photos courtesy of Fire Testing Technology, UK

ISO 5658-2 Evaluates Flame Spread Laterally

ISO 5658-2 evaluates flame spread laterally along a vertically mounted material sample, next to a gas burner of 50-1,200 kW/m^2.

It is used to classify materials under the European railway fire safety standard EN 45545-2.

The aim is to ensure that the material, when used in vertical interior panels, does not spread fire along a rail carriage or similar.

ISO 5658-2 lateral flame spread fire test. Photo © RiSe.

Single Burning Item Test, EN 13823

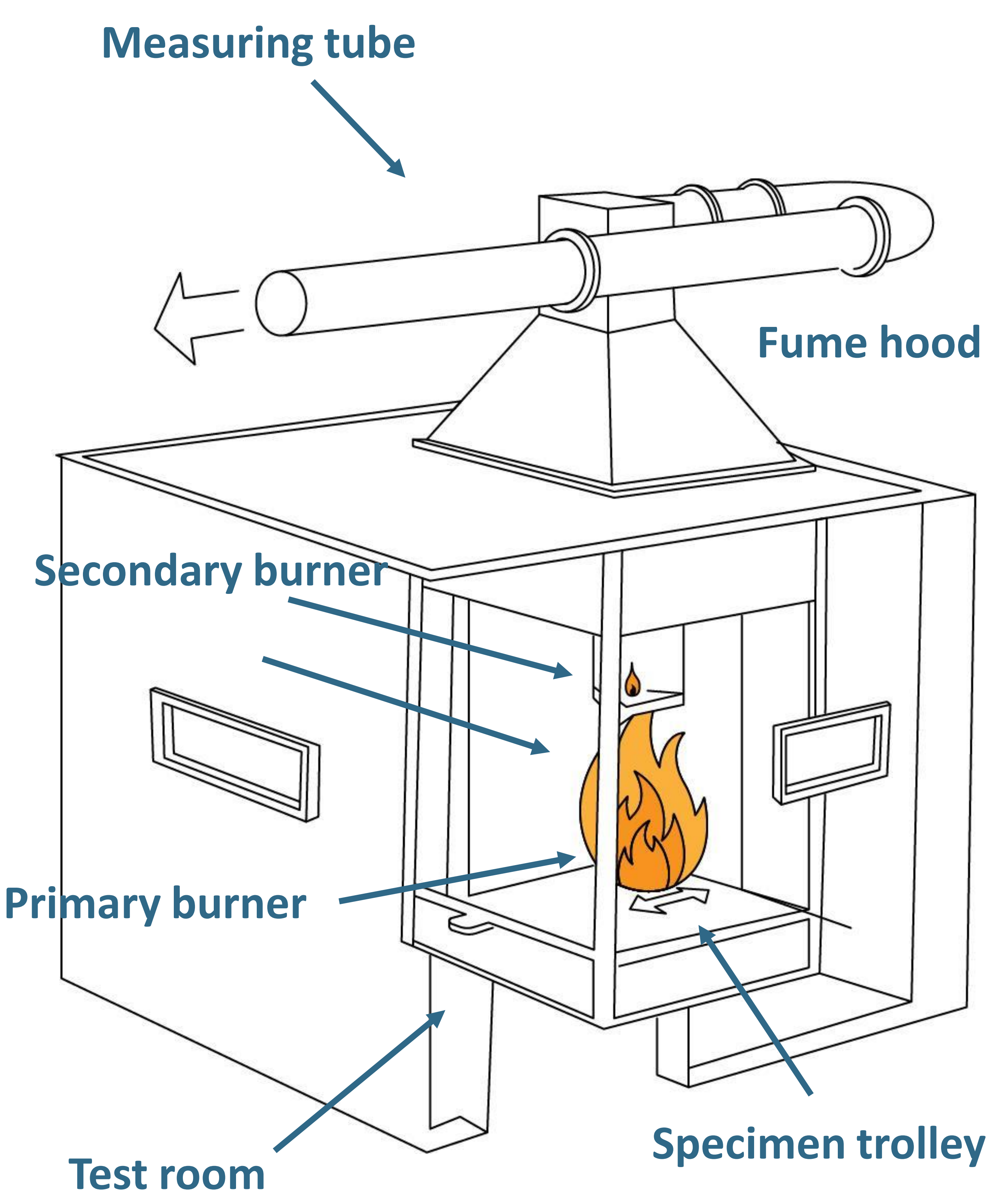
Applications:
- Construction/building

Specimen:
- 2 specimens: 1,500 x 1,000 mm
- 1,500 x 500 mm

Test:
- Gas burner 30 KW, mimicking a burning waste paper basket
- 20 min flaming

Classification criteria:
- Rate of heat release
- Smoke density
- Dripping

Performance classes:
- Euroclasses B, C, D



Re-drawn according to EN 13823

ASTM E84 - Steiner Tunnel

ASTM E84 is the most used fire test standard in the USA to characterize flammability of plastics.

A specimen (7.3 m x 0.56 m), either in one unbroken length or in separate sections joined end to end, is mounted face downwards so as to form the roof of a horizontal tunnel.

The fire source, two gas burners, ignites the sample from below with a 89 kW intensity and the combustion products are carried away by a controlled linear air velocity of 73 m/min. Flame spread index (FSI) and a smoke-developed index (SDI) are measured.

FIRE SOURCE

2 GAS BURNERS

89 KW

INTENSITY SAMPLE

73 M/MIN

LINEAR AIR VELOCITY CARRIES AWAY COMBUSTION PRODUCTS

FSI & SDI

ARE MEASURED

Building – ASTM E84
(" Steiner Tunnel Test " mainly used in USA)

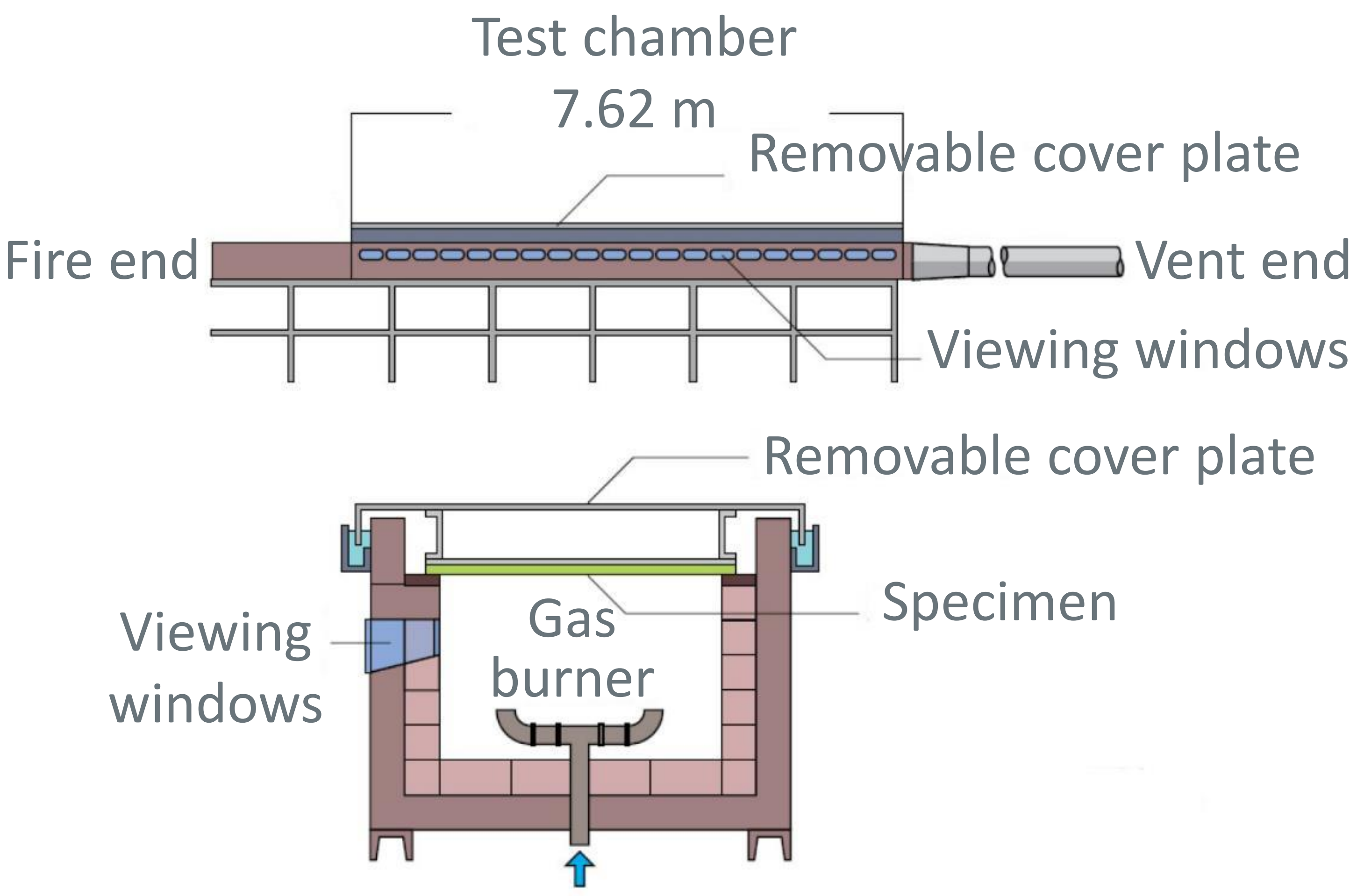


Table 8: ASTM E84 Classification of the interior finishes

Class	Flame Spread	Smoke Index
A	0-25	0-450
B	26-75	0-450
C	76-200	0-450

Fire Standards and Fire Tests

The CE-mark attests that a Construction product is certified (by a "notified body") to have achieved the stated CPR classification according to the specified testing standard. It means that the product can be placed on the EU market.

Example: EU Construction Products Regulation (CPR) 203/2011

EN 13501: "Fire classification of construction products and building elements" is a harmonized standard under the CPR and defines classes of reaction to fire.

A1 → **F**

A_{CA} → **F_{CA}** (cables)

Non combustible — **Fire characteristics cannot be determined**

This reflects heat release and flame spread/flame propagation.

s1a-s3	low to high smoke emission
d0-d2	burning droplets
a1-a3	smoke acidity

A cable may thus have a CPR classification looking like this: $B2_{ca}$- s1a, d1, a1

For example, in the UK (since 2019), cladding materials on most buildings > 18 m tall, must be classified (under CPR) at least A2 s1, d0 or A1.

A1	Will not contribute in any stage of fire, including fully developed fire
A2	Will not significantly contribute to fire load & fire growth in fully developed fire
s1	Weak or no smoke
d0	No flaming droplets

Smoke Density ISO 5659-2

- Optical density of smoke produced from a horizontally positioned test specimen subjected to 50 kW/m^2 in a sealed chamber
- Continuous real-time smoke analysis
- In combination with annex C of EN 45545-2 (FTIR*): Instantaneous analysis of: CO_2, CO, HCl, HBr, HF, HCN, NO/NO_2 and SO_2 for toxicity calculation, where each gas is weighted by its inherent toxicity

Observed values:

$CIT_{8\ MIN}$

Conventional Index of Toxicity at 8 min, sum of weighted toxic gas concentrations, normalized to a reference scenario (room size and smoke releasing surface)

DS_{MAX}

Maximum smoke density optical density, obscurance

VOF_4

Characterizes the total obscuration during the 4 minutes of the test

Smoke chamber ISO 5659.
Photo © courtesy of Crepim

*FTIR = Fourier Transform Infrared Spectroscopy
VOF4 = Ds1 min + Ds2 min + Ds3 min + (Ds4 min/2)

Smoke Toxicity
Example NF X 70-100 (France)

NF X 70-100-2:
Fire tests, Analysis of gaseous effluents - Part 2: Tubular furnace thermal degradation method

Test duration:
20 min at defined temperature

Steady and well-ventilated burning

Analysis of

- 3 Asphyxiating gases: CO, CO_2 , HCN
- 5 Respiratory irritant gases: HCl , HBr , HF, SO_2 , NO_x

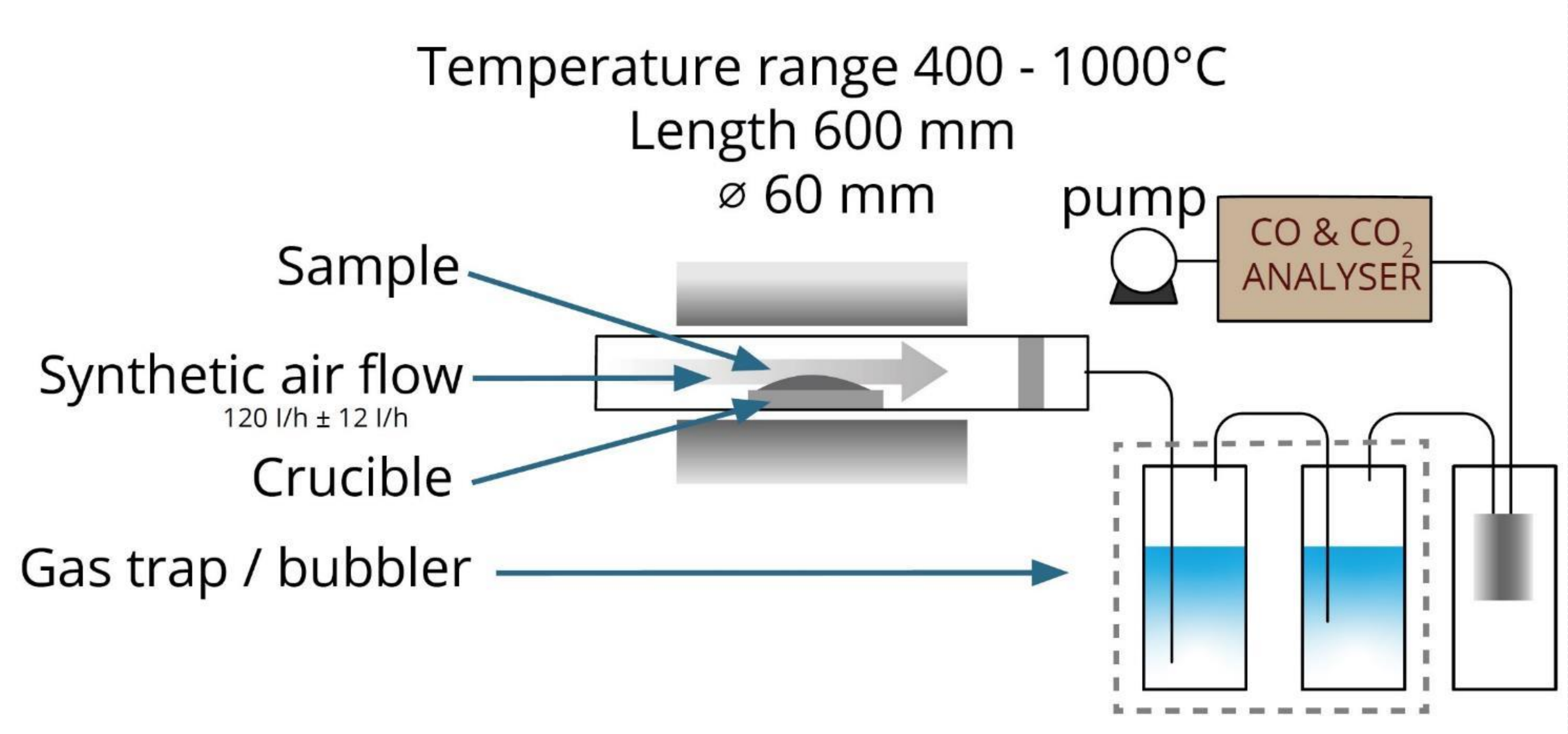


Chart courtesy of Crepim

6.

Applications for Flame Retardants

Photo © Shutterstock

Flame Retardants in Building and Construction

Many modern construction materials are flammable: e.g. insulation, decoration, flooring and ceiling materials, external claddings, windows and doors, wiring and cables, coatings and coverings, piping and ducting.

Sustainability objectives accentuate:

- External and internal insulation, both polymer foams and natural materials such as recycled textiles or cellulose
- Use of timber and wood, both structural and for decoration
- Air tightness of buildings and urban densification increase fire risk

Non-flammable structural elements also require fire protection, in particular steel beams which can fail in the heat of a fire if not protected.

Specific fire performance is required of elements intended to prevent fire spread: fire doors, fire stops on void penetrations etc.

Fore more detailed information see the pinfa brochure on Building & Construction applications of PIN flame retardants.

PIN intumescent coatings protect flammable materials, timber, steel or concrete from fire, Photos: © Clariant

Flame Retardants in Electric and Electronic Equipment

FRs are commonly used in E&E, because electricity is a fire risk: e.g. malfunctions and short circuits can lead to the release of enough energy to ignite the plastics used as insulating or enclosure materials.

Cables also have to comply with safety standards in most applications, be it within an E&E product or installed in a building.

Product safety standards e.g. for computers or displays define which flammability performance certain parts must meet.

Typical flammability standards are the UL 94 vertical standard or those using the glow wire apparatus (see test section above). These tests typically check the resistance against a small flame or low energy ignition source.

For more detailed information see the pinfa brochure on FRs in E&E

Photo © Shutterstock

Flame Retardants in Wires and Cables

Around 1/5th of flame retardant use in Europe is for wires and cables: electrical, telephone, data, both copper-core and fiber-optic.

Fire safety treatment of the insulation and sheathing materials of cables is important:

- Wires and cables can transmit fire from one room to another, because they cross through walls and between floors. Also, they are present in ceiling voids, attics, technical spaces where a developing fire will not be detected.
- Cables can start fires in cases of overheating or electrical faults
- Cables must continue to function in case of fire to enable operation of alarms, communications, fire equipment

A typical large building contains several km of cables.

Photos © pinfa brochure B&C

https://ifpmag.mdmpublishing.com/for-arts-sake-its-got-to-be-prysmian/

https://ifpmag.mdmpublishing.com/for-arts-sake-its-got-to-be-prysmian/

Flame Retardants in Transportation

Cars, trains, buses, ships and aircraft are built increasingly with flammable materials (polymers, carbon fiber, composites) for design, performance and energy savings (weight).

OVER 50%
OF THE AIRBUS
380 IS COMPOSITES

Fire safety and smoke emissions are critical in transport, because escape can be impossible, fire risks are increased by fuel and engines, and many passengers are in a small space.

Fire safety standards are increasingly demanding, for example:

- Aircraft: FAR 1964, significantly updated in 1984 and currently (2019 ongoing) under review
- Shipping: IMO mandatory code adopted 2010
- Railways: Europe EN 45545 (2013)
- Buses and coaches: UNECE 118 (2014)

Fore more detailed information see the pinfa brochure on transportation

Photos © pinfa Transportation Brochure

Electro-mobility Poses New Challenges for Fire Safe Polymers

Long-term reliability:
Component and orange colour stability at elevated temperatures

Increased safety:
Stable dielectric strength over temperature and UL94-V0 flame-retardance standard

Miniaturization:
Enabled by maximum tracking index (CTI 600 V)

Complex shapes:
High-flow capability allowing thinner walls, design flexibility and size reduction (miniaturization)

Design flexibility:
High elongation at break and good balance of mechanical properties

Increased productivity:
Robust processing with minimum outgassing and corrosion through wider processing window

Easy part traceability:
UV laser marking

Halogen-free:
Avoids electrical contact (galvanic) corrosion

Photo © Sutterstock

7.

Environmental and Health Aspects

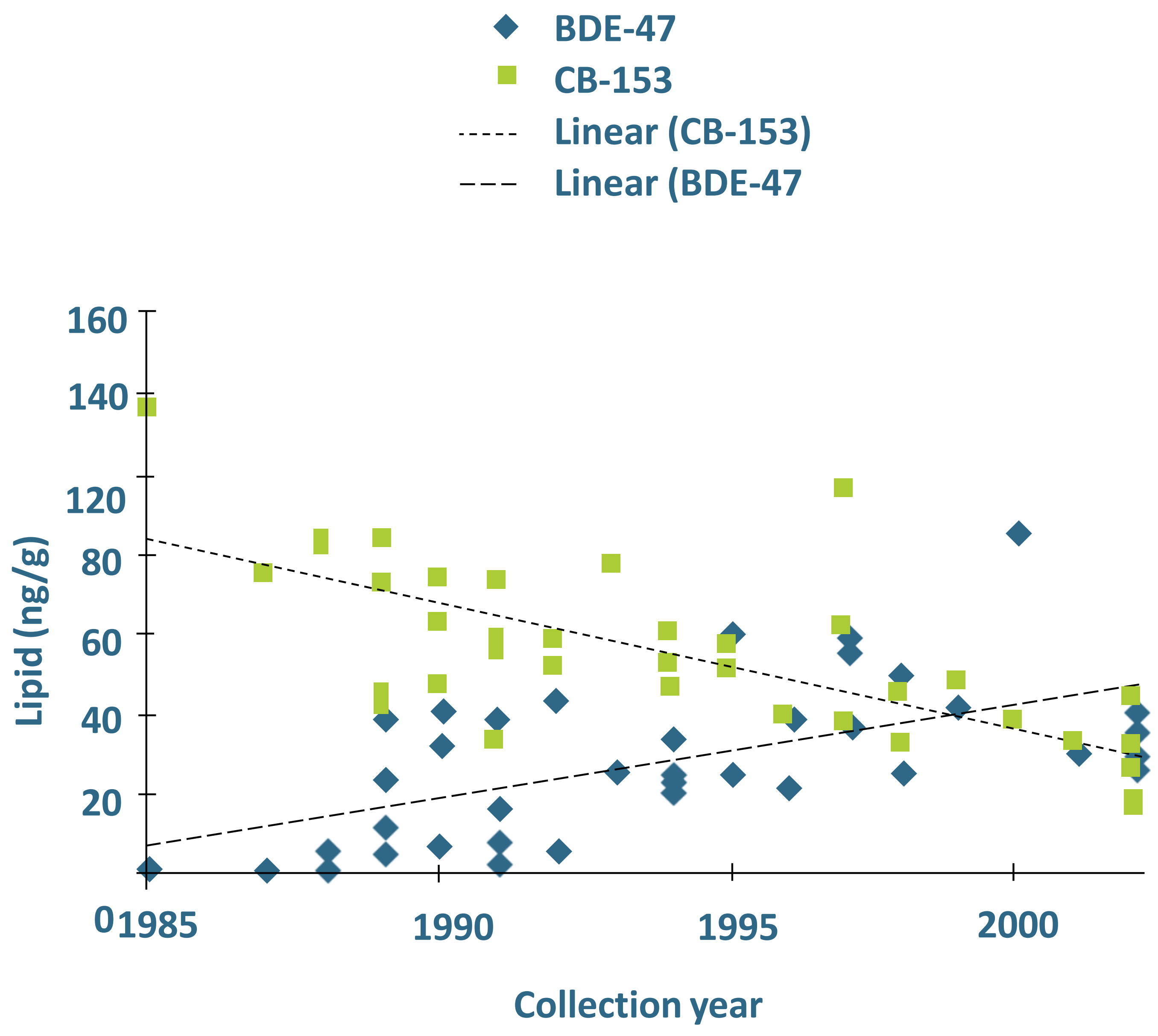
Special disclaimer for the following slides on regulations: The slides reflect the status as of March 2021, to the best of our knowledge. For legal certainty, please check and confirm with the original sources, also for potential changes or updates, as regulations and restrictions of substances change over time.

Photo © Shutterstock

Concerns on Environmental and Health Impacts Have Lead to Flame Retardant Restrictions

Several halogenated flame retardants, such as Decabromodiphenylether (DecaBDE), Hexabromocyclododecane (HBCD) and Short Chain Chlorinated Paraffins (SCCPs), all widely used until recently, have been found in many environmental compartments and biota. In addition, they were found to have persistent, bioaccumulative, toxic (PBT) properties. Consequently, they were designated Persistent Organic Pollutants (POP).

There are no PIN FRs on the UN Stockholm Convention 'POP' list.



Human blood levels of polychlorinated biphenyls (green) have been decreasing from 1985-2003, whereas polybrominated diphenylethers (blue) showed an increasing trend (both groups represented by a commonly found congener). This and other findings lead to the restriction of polybrominated diphenyl ethers.

Graphic source: Created for ES&T by Andreas Sjödin of the U.S. Centers for Disease Control, shows the levels of the most bioaccumulative PBDE congener, BDE-47, and the most bioaccumulative PCB congener, CB-153, in U.S. human blood samples. ES&T, 37, p. 384, 2003

Environment and Health Challenges for Flame Retardants

pinfa works in partnership with stakeholders, regulators, scientists and industry to:

- ✓ **Develop safer PIN flame retardants, based on phosphorus, nitrogen and inorganic minerals**
- ✓ **Accept that FRs may have acute hazard phrases, so work to minimize exposure and release risk**
- ✓ **Develop information and address data gaps**
- ✓ **Improve compatibility of PIN FRs with product end of life and recycling**

There are specific challenges for flame retardants, e.g.

- Flame retardants have to be 'durable', in order to remain effective in materials or equipment over time. Yet it is desirable to avoid 'persistence' in the environment.
- Compatibility with plastics can mean a risk of bioaccumulation for organic flame retardants, if they are lipophilic.

Photo © Shutterstock

SEE THE PINFA **MISSION**

Flame Retardant Restrictions in Europe

Banned or restricted FRs	Halogenated FRs	PIN FRs	Reference
United Nations **Stockholm Convention** (**POPs** Persistent Organic Pollutants list)	HBCD, PBDEs inc. DecaBDE , SCCP (chlorinated alkanes)	None	http://chm.pops.int/TheConvention/ThePOPs/ListingofPOPs/tabid/2509/Default.aspx
EU **RoHS Directive** 2011/65 Restriction of Hazardous Substances in Electrical and Electronic Equipment	HBCD, PBBs, PBDEs inc. DecaBDE . Additionally: TBBPA, antimony (ATO) and MCCPs (chlorinated alkanes) currently under consultation (2020)	None	https://ec.europa.eu/environment/waste/rohs_eee/index_en.htm
EU **WEEE Regulation** 2012/19 Waste of electrical and electronic equipment	Requires separation and specific treatment of E&E waste containing brominated FRs	None	https://ec.europa.eu/environment/waste/weee/index_en.htm
EU **Ecodesign Regulation**: electronic display parts	All halogenated FRs banned in stands and enclosures of electronic screens	None	https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32019R2021
EU REACH – already restricted	Penta and octa BDEs	None	https://echa.europa.eu/substances-restricted-under-reach
EU REACH “candidate list” (possible SVHC Substances of Very High Concern)	Dechlorane Plus, DecaBDE, HBCD, SCCPs , Tris (2-chloroethyl) phosphate	Boric acid, disodium borate, trixylyl phosphate	https://echa.europa.eu/fr/candidate-list-table
Furthermore, brominated flame retardants are limited in usage by standards requiring low smoke low toxicity (e.g. railways, aircraft, shipping) and by voluntary industry Substance Declaration Lists or similar			

REACH and Flame Retardants (1)
Principles

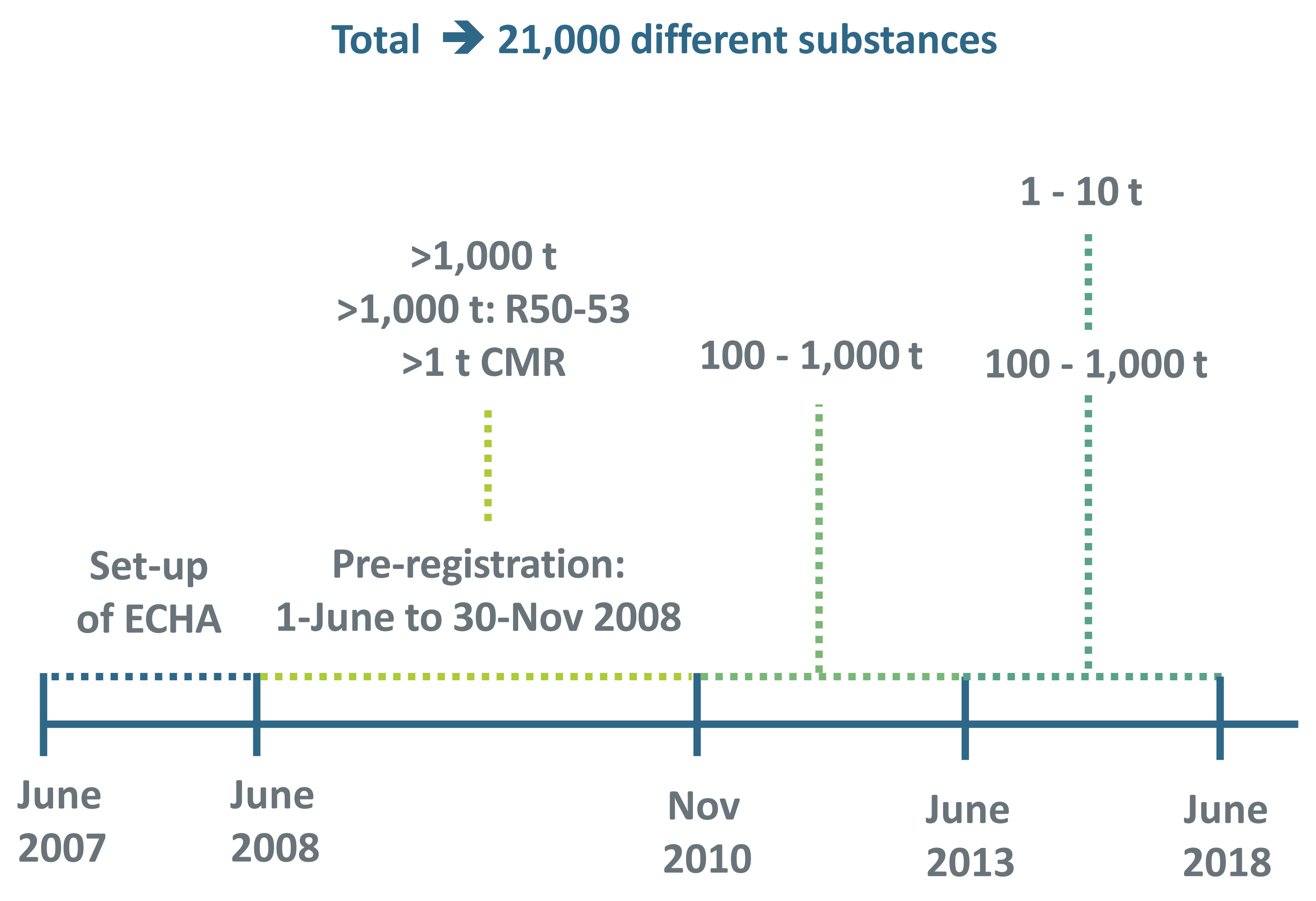
All chemicals sold or used in Europe must be registered under REACH*, with a dossier providing full chemical, environment, health, production and use information.

These dossiers can be consulted on the European Chemical Agency (ECHA) website: http://echa.europa.eu/web/guest/information-on-chemicals/registeredsubstances

In response to a pinfa ATD (access to documents to request), ECHA indicated that around 150 chemicals are indicated for use as flame retardants in REACH dossiers or other public data bases**.

REACH identifies and restricts use of chemicals identified as problematic (Annexes 14 and 17 and CORAP, see following slides).

Total number of all chemicals registered under REACH



*Use of >1 tonne/year. Registration is NOT required for chemicals present in 'articles' manufactured outside Europe and imported
**pinfa notes that these lists include chemicals which are in fact not FRs ammonia - anhydrous, titanium dioxide, coal ashes, hydrogenated castor oil

REACH and Flame Retardants (2)
Restrictions (status 2020-07)

The following flame retardants are "Restricted " under Annex 17 of REACH (that is effectively banned except in specific "authorised" uses):

- Polybrominated diphenyls Penta-, Octa- and DecaBDE*

Additionally, the following are "Restricted for specific uses":

- For skin contact (e.g. textiles): Tris (aziridinyl phosphinoxide, Tris (2,3 dibromopropyl) phosphate (TRIS), Polybromobiphenyls (PBB)
- In cellulose insulation materials: ammonium salts

The following flame retardants have been included in Annex 14 of REACH as "Substances of Very High Concern" (SVHC). These substances will be subject to Restriction, if not already Restricted.

- Penta-, Octa- and DecaBDE (PBT, vPvB)
- HBCD (PBT)
- Short chain chlorinated paraffins = SCCP (PBT, vPvB
- Tris(2-chloroethyl) phosphate (toxic for reproduction)
- Boric acid (toxic for reproduction)

Additionally, Trixylyl phosphate (toxic for reproduction) is under consideration for inclusion in Annex 14.

P = persistent, B = bioacculative, T = toxic, v = very

Photos © ECHA https://echa.europa.eu/fr/image-gallery-echa-chemistry

REACH and Flame Retardants (3)
CoRAP (status 2019-03)

Flame retardants currently on ECHA's **REACH CORAP** (Community Rolling Action Plan) list, that is under evaluation by a Member State for harmonized classification & labelling as well as possible inclusion in REACH Annexes 14 or 17.

Halogenated flame retardants and their synergists	Abbr.	CAS#
Diantimony trioxide		215-175-0
1,1'-(ethane ethane-1,2-diyl)bis[pentabromobenzenepentabromobenzene]	EBP	284-366-9
1,1'-(isopropylidene)bis[3,5-dibromodibromo-4-(2,3-dibromodibromo-2-methylpropoxy)benzene]		306-832-3
1,1'-(isopropylidene)bis[3,5-dibromodibromo-4-(2,3-dibromopropoxy)benzene]	FR720	244-617-5
2,2',6,6'-TetrabromoTetrabromo-4,4'-isopropylidenediphenol, oligomeric reaction products with Propylene oxide and n-butyl glycidyl ether		926-564-6
2,2,6,6-tetrabromo-4,4-isopropylidenediphenol	TBBPA	201-236-9
2,2-dimethylpropan-1-ol, tribromo derivative	TBNPA	253-057-0
2,4,6-tribromophenol	TBrP	204-278-6
Bis(2-ethylhexyl) tetrabromophthalate	TBPH	247-426-5
N,N'-ethylenebis (3,4,5,6-tetrabromophthalimide)	EBTBP	251-118-6
Alkanes, C14-17, chloro (Medium chained chlorinated paraffins)	MCCP	287-477-0
Reaction mass of tris(2-chloropropyl) phosphate and tris(2-chloro-1-methylethyl) phosphate and Phosphoric acid, bis(2-chloro-1-methylethyl) 2-chloropropyl ester and Phosphoric acid, 2-chloro-1-methylethyl bis(2-chloropropyl) ester	TCPP	911-815-4 (237-158-7)
Tris[2-chloro-1-(chloromethyl)ethyl] phosphate	TDCP	237-159-2
Phosphate esters	**Abbr.**	**CAS#**
Tetraphenyl m-phenylene bis(phosphate)	RDP	260-830-6
Tributyl phosphate	TBP	204-800-2
Triphenyl phosphate	TPP	204-112-2
Triphenyl phosphite		202-908-4
Tris(methylphenyl) phosphate		809-930-9
Trixylyl phosphate	TXP	246-677-8

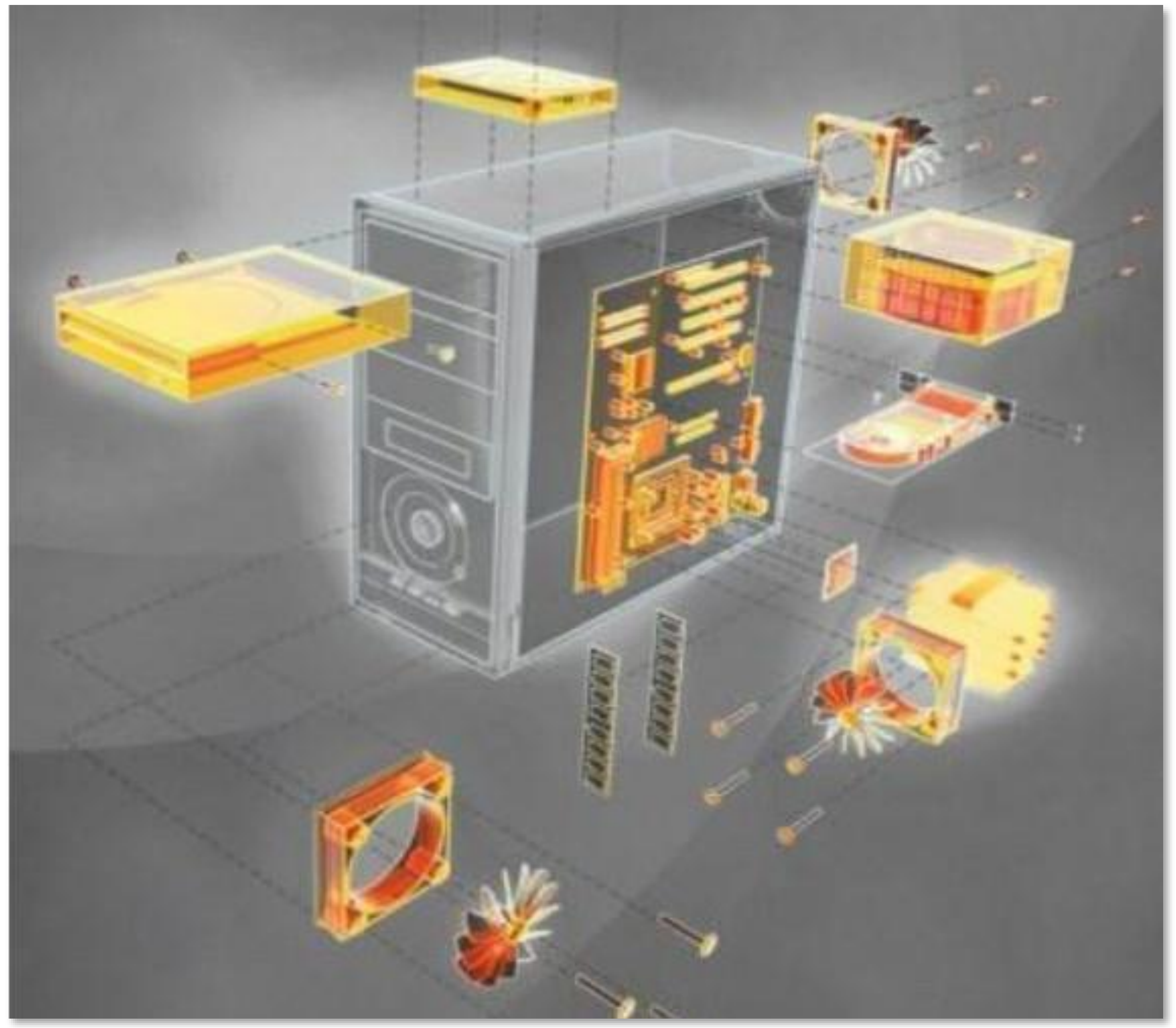
RoHS, WEEE and Flame Retardants

EU Directive on the Restriction of certain Hazardous Substances in Electric and Electronic equipment (RoHS, 2011/65/EU) first published in 2003:

- Bans Cd, Pb, Cr (VI), Hg + PBBs and PBDEs, including DecaBDE (since 2008), in E&E equipment since July 2006
- Directive "recast" as 2011/65/EU - more substance restrictions may come
- 2020 consultation suggested bans on: Tetrabromoisphenol-A (TBBPA, if not used as reactive FR), medium chain-length chlorinated paraffins (MCCP) and antimony trioxide (ATO, review together with BFR suggested)

WEEE Waste Electrical and Electronic Equipment Directive, recast as 2012/19/EU:

- higher recycling quotas and additional product groups covered
- Requires "Selective treatment … have to be removed … plastics containing brominated flame retardants" (Annex VII of the Directive)



picture: CT/tsa medien

EUEcoDesign Directive for Electronic Displays

Regulation (EU) 2019/2021

Annex (4):
The use of halogenated flame retardants is not allowed in the enclosure and stand of electronic displays.*

Annex (2b):
Components containing flame retardants shall additionally be marked with the abbreviated term of the polymer followed by hyphen, then the symbol “FR” followed by the code number of the flame retardant in parentheses. The marking on the enclosure and stand components shall be clearly visible and readable.

Applicable from 1st March 2021

Photo © Shutterstock

* case lodged against the European Commission by BSEF, reference T-113 / 20

Swedish Tax on Electronics and White Goods

Sweden introduced in 2017 an “ecotax” on all electrical and electronic goods.

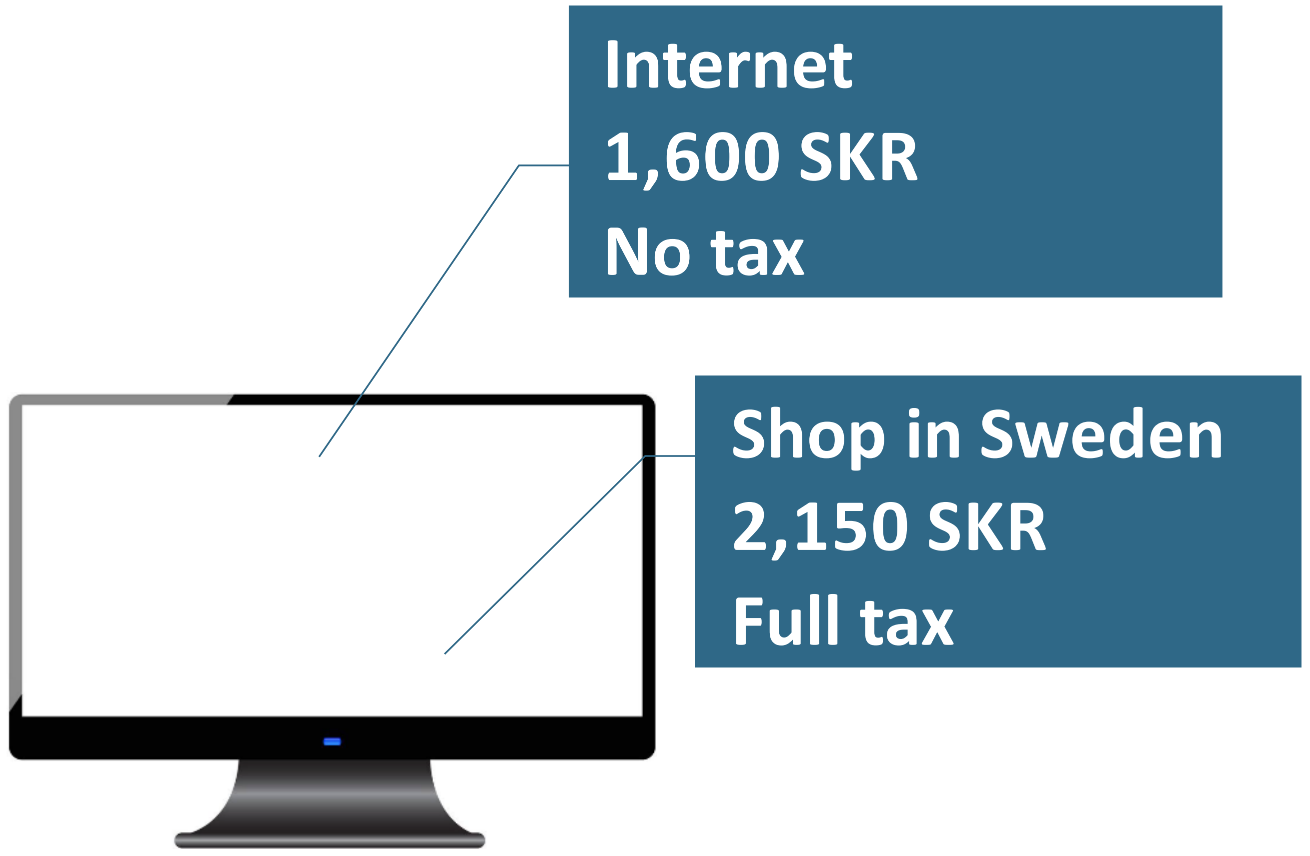
THE TAX CAN REACH
UP TO 40€ PER ITEM

Higher tax levels apply for goods containing any halogenated flame retardant, or additive phosphorus flame retardants.

A MINIMUM 10% TAX
HAS TO BE ALWAYS PAID

The current version of the tax is criticised and is under revision:

- E&E goods purchased from abroad via internet escape the tax
- Safer substitution is not encouraged by hitting all additive phosphorus FRs: the criteria should instead target specific chemicals and properties
- There are no standard testing methods to identify the chemical groups defined in the tax, leading to legal uncertainty
- The tax has not resulted in the fiscal revenue intended by the Government



The environmental NGO ChemSec has criticised the tax because it penalises “some of the preferred alternatives to halogenated flame retardants”. Photo from “The Swedish chemical tax. Do it again and do it right”.
5 minute video: http://www.beard.de/2019-04_pinfa10/2019-09 -17_Swedish_Electronics_Tax.MOV

United-States Federal and State actions on FRs

- Toxic Substances Control Act (1976)
- Frank R. Lautenberg Chemical Safety Act - 21st Century (2016)
- U.S. EPA/Industry agreement voluntary phase-out of FR manufacturing within USA: PentaBDE (2004), OctaBDE (2004) & DecaBDE (2013)
- U.S. EPA Design for Environment Alternative FR Assessment Studies: F-PUR foam (2005), DecaBDE (2014), HBCD(2014), PCBs(2015), F-PUR foam* (2015)
- U.S. EPA workplan - 7 FRs (2012). Planning process risk assess. - 3 clusters - 10 FRs (2015). March 2019 (US EPA): TCEP, TBBPA & TPP - “high priority
- substance” candidate for RA
- U.S. CPSC grants organohalogen petition (2017). NAS study complete (2019)
- U.S. CPSC decision (2019): TB 117-2013 as national STD for upholstered furniture

Local laws on Flame Retardants:

State/District	Law (ref.)
California	HB 53
Hawaii	H 1245, LD 182
Maine	LD 182, HP 138
Maryland	HB 206, SB 447
Massachusetts	H 4900
Michigan	HB 4406
Minnesota	HF 1627
New Hampshire	SB 193
New York	A 3388, S 742
Oregon	SB 596
Rhode Island	H 5082
Vermont	ACT 61
Washington	ESHB 2545
Wash. DC	ESHB 2545
AK, AZ, DE, GA, IA, MA, NJ,TN, VA, WV	**Various legislation under discussion, not signed into law as of June 2020**

Canada Government action on FRs

- Canadian Environmental Protection Act - CEPA (1999)
- Chemical Management Plan - CMP (2006) melamine, tricresyl phosphate (TCP), Dechlorane Plus (DP), TCPP, TDCPP, EBTBP, ATE (BFR), DBDPE, TBB, TBPH, ATO - Sb_2O_3
- PBDE Regulations: pentaBDE/OctaBDE (2008)
- Canada Consumer Product Safety Act - CCPSA (2010), TCEP (foam products - children), TDBPP (textile wearing apparel)
- Prop. Amendments “Prohibition of Certain Toxic Substances” (2018): HBCD, PBDEs(7), Dechlorane Plus & Decabromodiphenyl ethane*

Photo © Shutterstock

*2019 update: Per Canadian authorities - DBDPE may contribute to the formation of persistent, bioaccumulative, and inherently toxic transformation products, such as lower brominated BDPEs, in the environment. A ban on the manufacture, sale or import of the brominated FR DBDPE has been proposed.

Flame Retardant Restrictions in China

Regulation banning or restricting FRs	Halogenated FRs	PIN FRs	Reference
List of Strictly Restricted Toxic Chemicals in China (2020) On the basis of UN Stockholm Convention POPs	HBCD, SCCPs (chlorinated alkanes), PCT (effective from 1st Jan. 2020)	none	*http://www.mee.gov.cn/xxgk2018/xxgk/xxgk01/201912/t20191231_756318.html*
Implementation of the conformity assessment system for restricted use of hazardous substances in electrical and electronic products. AKA China RoHS 2 (6th Jan. 2016)	PBBs, PBDE (effective from 1st July 2016)	none	*https://www.miit.gov.cn/jgsj/jns/qjsc/art/2020/art_0ffb0deb9185404aa94afe3b852dcc6f.html*
Technical requirements for environmental labeling products: small household appliances (Consultation Draft, 30th Sept. 2019)	Green label can only be applied if: • plastic parts ＞25g: no HBCD, TCEP, TCPP, TDCP; • product shells, circuit board substrates and power cord: no SCCPs (Draft for comments, not effective yet)	none	*http://www.mee.gov.cn/xxgk2018/xxgk/xxgk06/201910/t20191016_737822.html*
Technical Requirements for Environmental labelling Products: Microcomputer, Monitor (31st March, 2014)	Green label can only be applied if: • plastic parts > 25 g: no SCCPs, MCCP, HBCD; • Computer main board substrate: no HBCD (1st July 2014)	none	*http://www.mee.gov.cn/gkml/hbb/bgg/201404/t20140403_270117.htm*
Chemicals Subject to Prioritized Control (1st batch, 27th Dec. 2017)	Revision of national mandatory standards to restrict the use of SCCPs, HBCD, PBDE in certain products (27th Dec. 2017)	none	*http://www.mee.gov.cn/gkml/hbb/bgg/201712/t20171229_428832.htm*
Guidelines for use and control of key chemical substances in consumer product (19th Nov. 2020)	Content/Migration control: PBBs, HBCD, PBDES, SCCPs, TCEP, TCP (1st June 2021)	TPP	*GB/T 39498-2020, China national standard (Voluntary)*

Flame Retardant Restrictions in Japan

*PRTR is a system in which business operators themselves understand and report the amount of chemical substances that may be harmful to human health and ecosystems as well as the amount of waste discharged from the business site to the environment (air, water, soil) and the amount of waste transferred out of business to the government once a year. The government aggregates and publishes emissions and movement amounts based on notification data and estimates.

Regulation banning or restricting FRs	Halogenated FRs	PIN FRs	Reference
Banned as Class I Specified Chemical Substances / Act on the Evaluation of Chemical Substances and Regulation of their Manufacture	Hexabromobiphenyl / (April 1, 2010) HBCD / (May 1, 2014) PBDEs including DecaBDE / (April 1, 2018) Dodecachloropentacyclodecane (Mirex) / (September 4, 2002), Polychlorinated normal paraffins (having 10 to 13 carbon atoms and having a chlorine content of more than 48% of the total weight) / (April 1, 2018)	none	Act on the Evaluation of Chemical Substances and Regulation of Their Manufacture, etc. (Article 4 of the Supplementary Provisions unenforced, etc.) https://www.meti.go.jp/policy/chemical_management/kasinhou/files/specified/class1specified_chemicals_list.pdf
Monitored as Surveillance Chemicals / Act on the Evaluation of Chemical Substances and Regulation of their Manufacture	Polybrominated biphenyl (limited to those with 2 to 5 bromine) / (September 22, 2004)	none	https://www.meti.go.jp/policy/chemical_management/kasinhou/files/ippantou/monitoring_chemicals_list.pdf
Monitored as Class I Designated Chemical Substances / Pollutant Release and Transfer Register(PRTR)*	DecaBDE /(March 29, 2000), Polychlorinated normal paraffins / (March 29, 2000) TCEP / (November 21, 2008), please see the attached link about details	none	https://www.meti.go.jp/policy/chemical_management/law/prtr/pdf/engsindai1.pdf
Labelling requirement / the marking for presence of the specific chemical substances for electrical and electronic equipment(J-Moss) JIS C 0950	Polybrominated biphenyl and PBDEs / (July 1, 2006)	none	https://home.jeita.or.jp/eps/epsJmoss.html#no1
Require proper exposure prevention measures in the operation of manufacturing and handling / Industrial Safety and Health Act	[ATO, synergist to brominated FRs, June 1, 2017]	none	https://www.mhlw.go.jp/stf/seisakunitsuite/bunya/0000163262.html http://kankyoanzen.adm.u-tokyo.ac.jp/admin/tokuteikagakubusshitsu_list.pdf

- Taking the decision of POPs in Oct. 2019, METI asked every industries to survey the content of Dechlorane Plus in chemicals/articles in Feb. 2020. After the survey, METI will have detailed survey on Dechlorane Plus regarding usage, content, availability of alternative technologies, alternative costs, etc. planned from Oct. 2020.

Japan: https://www.nite.go.jp/chem/jcheck/list6.action?category=211&request_locale=en

EcoLabels with Requirements on Flame Retardants

- **German Blue Angel**: halogenated FRs are banned or limited except for some exceptions (recycled materials, small parts)
- **EU Flower Ecolabel**: in some product criteria, additive FRs with certain risk phrases are excluded (e.g. R40, 45, 46, 50, 51, 52, 53, 60, 61, 62, 63) and/or certain specified brominated FRs (e.g. PBDEs, PBBs) are excluded. In some cases, FRs are authorised if reactive and if brominated dioxin emissions are limited (effectively excluding brominated FRs)
- **EPEAT** (US EPA Electronic Product Environmental Assessment Tool): criteria for halogen-free, granting optional points
- **TCO**, the health, environment and worker protection label for office and home electronics, specifies a number of PIN FRs on its "safer alternatives" list, including mineral FRs (ATH, MDH), nitrogen FRs (melamine polyphosphate) and phosphorus FRs (based on GreenScreen assessments)
- **Textile ZDHC** (Zero Discharge of Hazardous Chemicals): excludes specified halogenated FRs (TCEP, Deca and other BDEs, TBBPA TDCP, BBMP, BIS and TRIS, HBCDD and SCCPs) and TEPA = Tris(1-aziridinyl)phosphine oxide (which is restricted under REACH for use in textiles with skin contact, Annex XVII)
- **Oeko-Tex 100** (international textile green label): specified halogenated FRs are excluded: TCEP, SCCP, PBBs, TDBP-Tris, HBCD, PBDEs inc. DecaBDE

Third party assessments of PIN Flame Retardants

GreenScreen (Clean Production Action)

- Used by several Ecolabels to verify environmental credentials of FRs: TCO, ZDHC, …
- GreenScreen is a simplified methodology based on chemical hazards only (not exposure)
- “Benchmark” 2 or 3 , use is possible without significant risk

Denmark EPA screening report on phosphorus flame retardants (LOUS October 2016). Concludes that 12 FRs do not pose high risk for any health, environment or accumulation end point (out of 28 P-FRs studied).

The EU-funded project **ENFIRO** concluded (2013) that the following 12 PIN FRs are of low concern: Ammonium polyphosphate (APP), Aluminium diethylphosphinate (Alpi), Aluminium hydroxide (ATH), Melamine polyphosphate (MPP), 9,10Dihydro-9-oxa-10-phosphaphenanthrene (DOPO), Zinc stannate (ZS), Zinc hydroxystannate (ZHS).

The EU-funded **LIFE-FLAREX** project identified non-toxic alternatives to some brominated FRs for textiles: ammonium polyphosphate (APP), poly[phosphonate- cocarbonate], magnesium hydroxide, aluminium hydroxide and aluminium diethylphosphinate (Alpi).

Thank you for your attention.

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