Behaviour of flame retardants and other chemicals of concern in fires and their degradation processes

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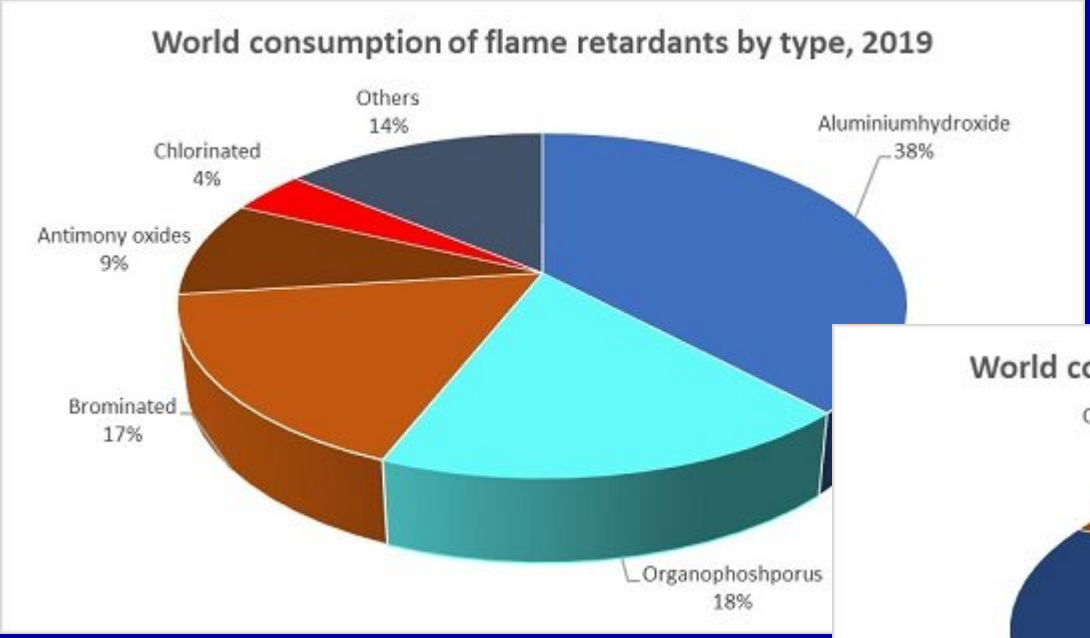
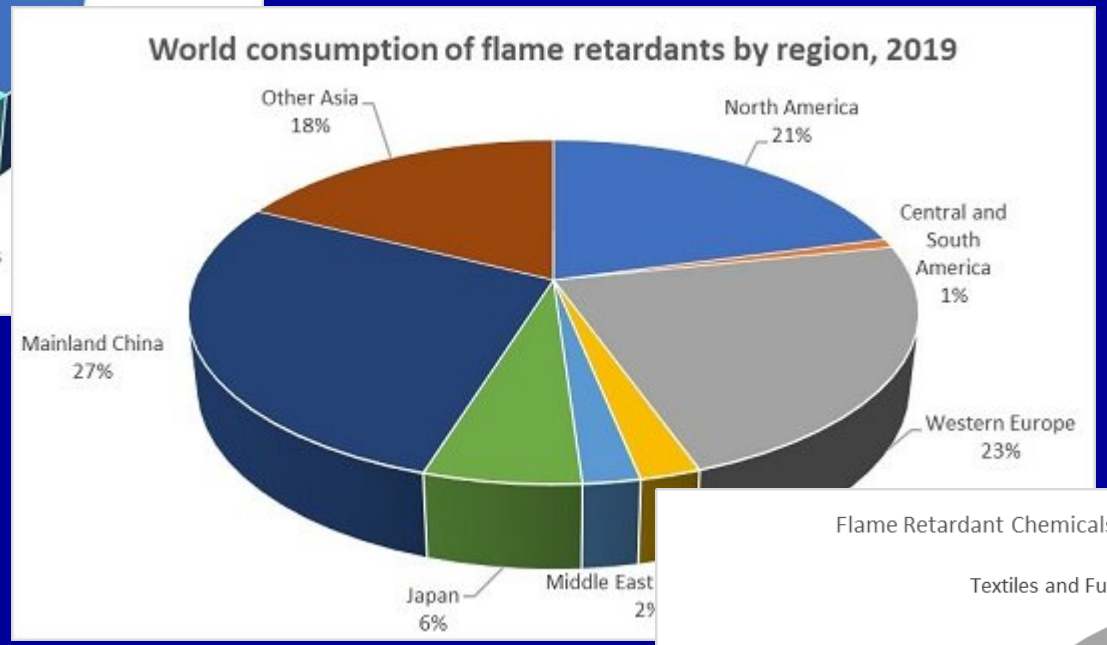
Outline

- Fire retardants are added to combustible materials to pass regulatory tests
- Fire retardants are not all equal!
  - **Gas phase *flame* retardants** have to be volatile or release volatiles to be effective
  - **Char formers** tend not to be volatile and reduce the amount of volatile formation
  - **Mineral fillers** replace up to 70% of combustible material with inorganic hydroxides and carbonates
- Gas phase flame retardants increase the smoke toxicity in three ways:
  - Increasing asphyxiant yields CO and HCN (acute toxicity)
  - Increasing organoirritant and carcinogen yields (acrolein, PAH etc)
  - Increasing smoke and particulate yields (atmospheric particulate deaths)
- All commercially available gas phase flame retardant contain bromine, chlorine, phosphorus or a combination

Most of the concerns over flame retardant toxicity relate to long term exposure to certain *undecomposed* flame retardant molecules.

Flame Retardant Markets



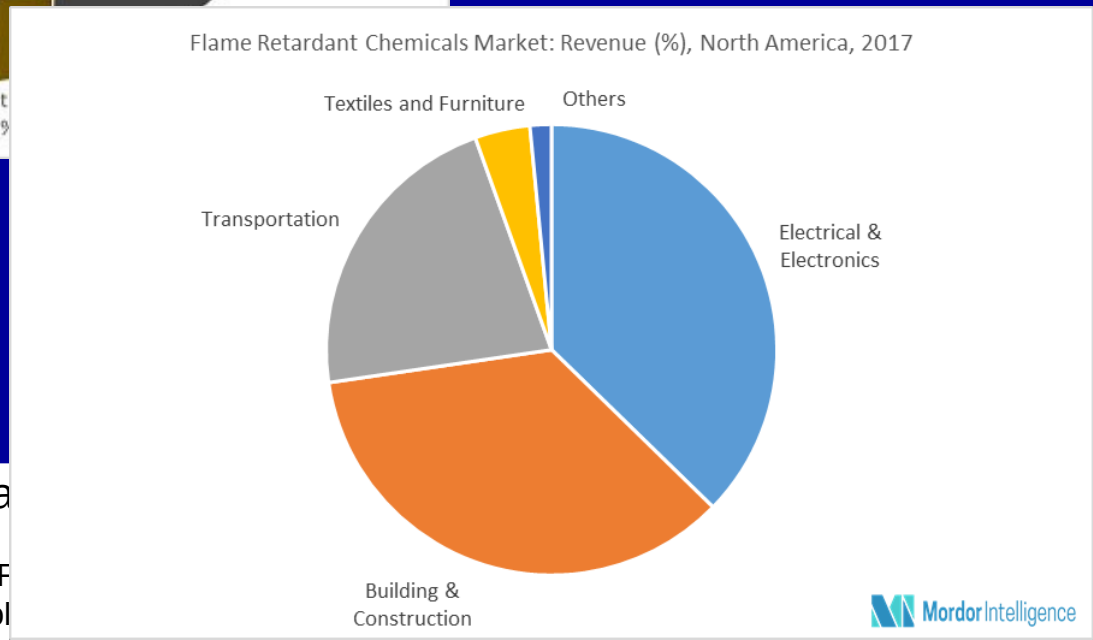


Global flame retardant use 2019

Quantity = 2.9 M tonnes

Value = $7.2 billion

Expected growth 3.6% per year until 2027



https://www.flameretardants-online.com/flame-retardants/market

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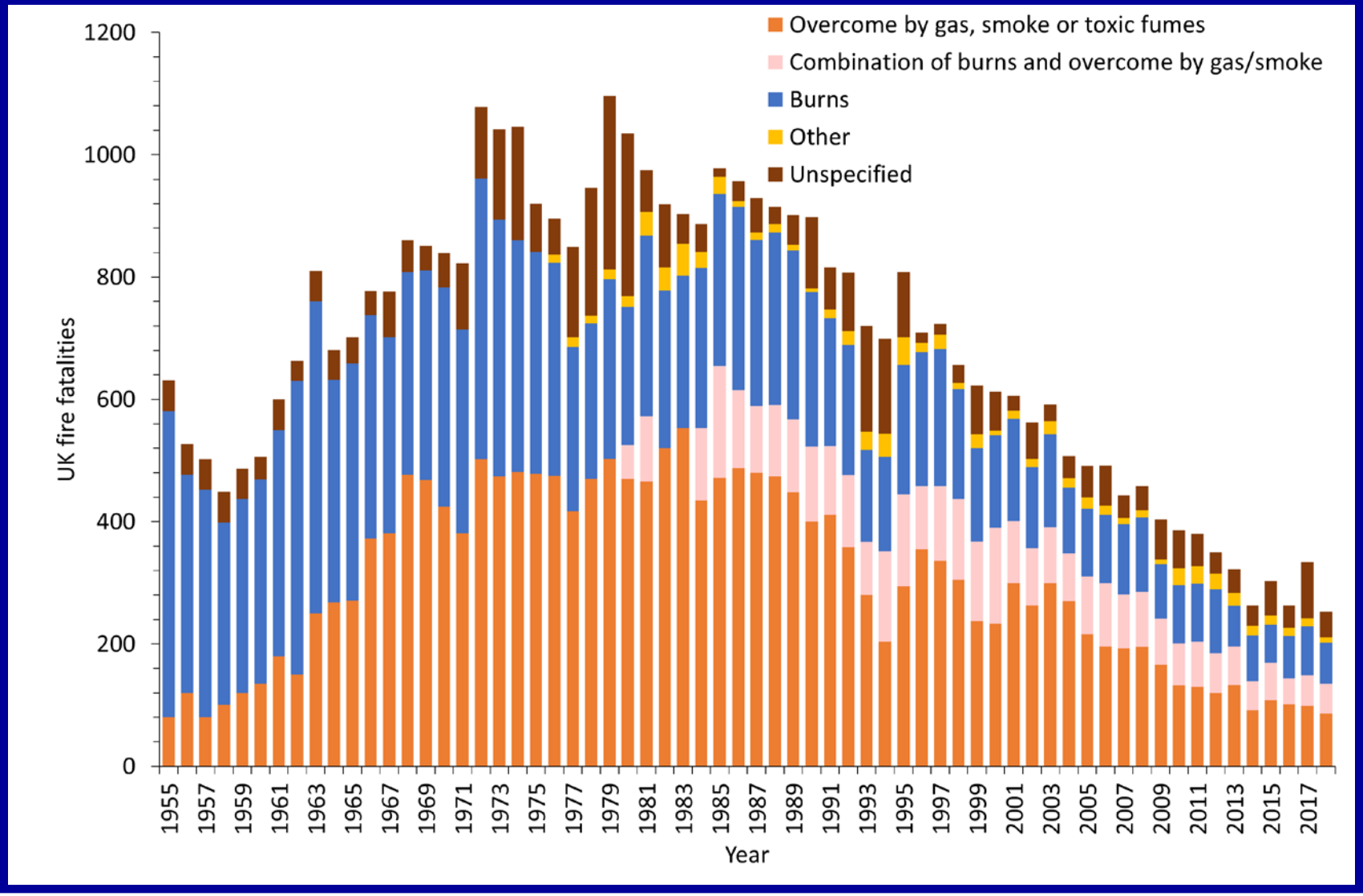
Drivers in Fire Retardant Development

UK Fire Deaths (1955-2018)

Progressive shift from burns to smoke and toxic fumes



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Physical fire retardant action

- ***By cooling*** from endothermic processes such as breakdown of additives.
- ***By formation of a protective layer.***
- ***By dilution*** from additives which evolve inert gases on decomposition

Aluminium hydroxide (ATH)

$$2\,Al(OH)_3\,(s) \xrightarrow{180\text{-}200^\circ C} Al_2O_3(s) + 3\,H_2O(g)$$

$$\Delta H = +1.3\ kJ\ g^{-1}$$

- The same amount of energy would heat 1 gram of polythene ~600°C.
- In addition, aluminium hydroxide is a good conductor of heat, reducing the local hot spots, which are responsible for starting fires.
- Aluminium hydroxide used at about 60% by weight, accounts for 40 % of all the fire retardant additives used.

Alternative Mineral Fillers Fire Retardants

Aluminium hydroxide 180-200°C

$2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O$ $\Delta H = +1.30\ kJ\ g^{-1}$

Boehmite 340-350°C

$AlO(OH) \rightarrow Al_2O_3 + 3\ H_2O$ $\Delta H = +0.56\ kJ\ g^{-1}$

Magnesium hydroxide 300-320°C

$2\ Mg(OH)_2 \rightarrow MgO + H_2O$ $\Delta H = +1.45\ kJ\ g^{-1}$

Hydromagnesite 220-240°C

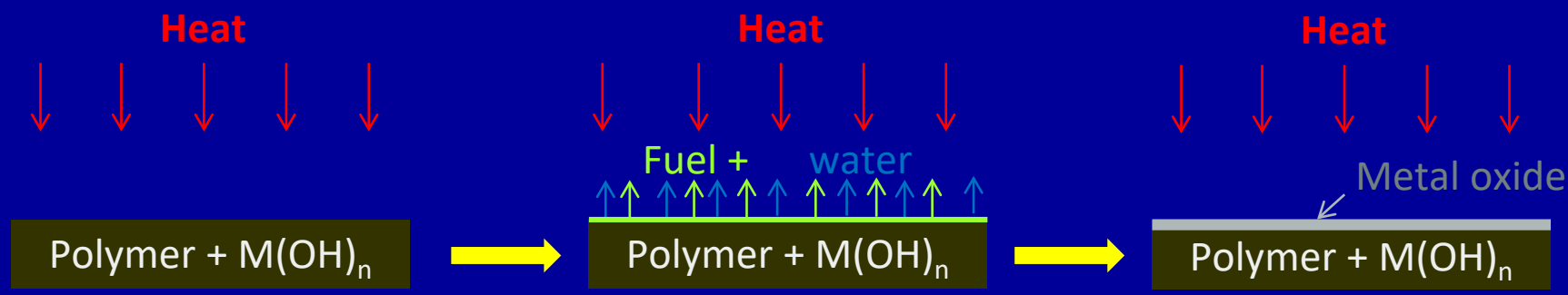
$Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O \rightarrow 5MgO + 4CO_2 + 5H_2O$ $\Delta H = +1.30\ kJ\ g^{-1}$

Huntite 400-600°C

$Mg_3Ca(CO_3)_4 \rightarrow 3MgO + CaO + 4CO_2$ $\Delta H = +0.98\ kJ\ g^{-1}$

Metal Hydroxides and Carbonates

4 modes of action



$M(OH)_n$ absorbs heat

Polymer decomposes to fuel

$M(OH)_n \xrightarrow{heat} MO + H_2O(g)$

- Heat absorbed (endothermic dehydration)
- Water released

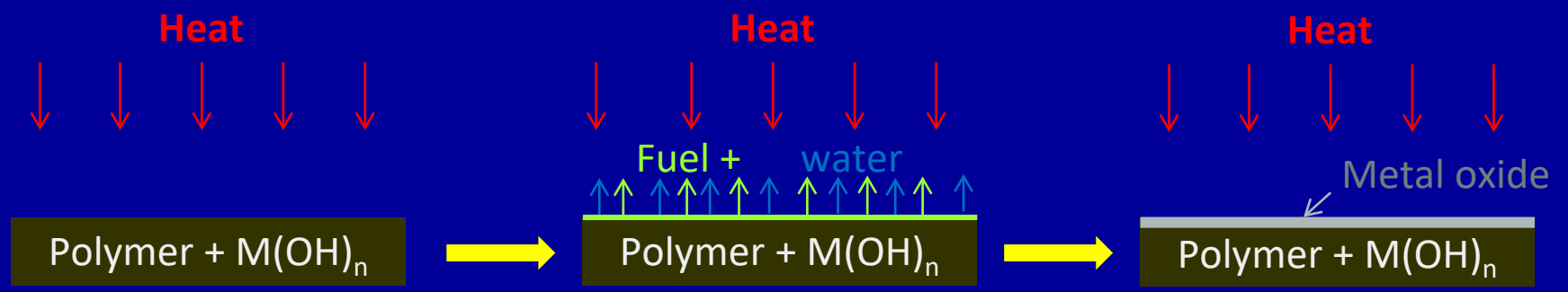
Layer of MO on surface:

- Radiation shield
- Continuous barrier to fuel and oxygen

ll TR, Witkowski A, Hollingbery L., *Fire retardant action of mineral fillers*, Polymer Degradation and Stability (2011), doi: 10.1016/j.polymdegradstab.2011.05.

Metal Hydroxides and Carbonates

4 modes of action



$M(OH)_n$ absorbs heat

Polymer decomposes to fuel

heat

$M(OH)_n \rightarrow MO + H_2O(g)$

- Heat absorbed (endothermic dehydration)
- Water released

Layer of MO on surface:

- Radiation shield
- Acts as barrier to fuel and oxygen

Chemical fire retardant action

- ***Reaction in the gas phase***. Free radical gas phase reactions disrupted by the flame retardant.

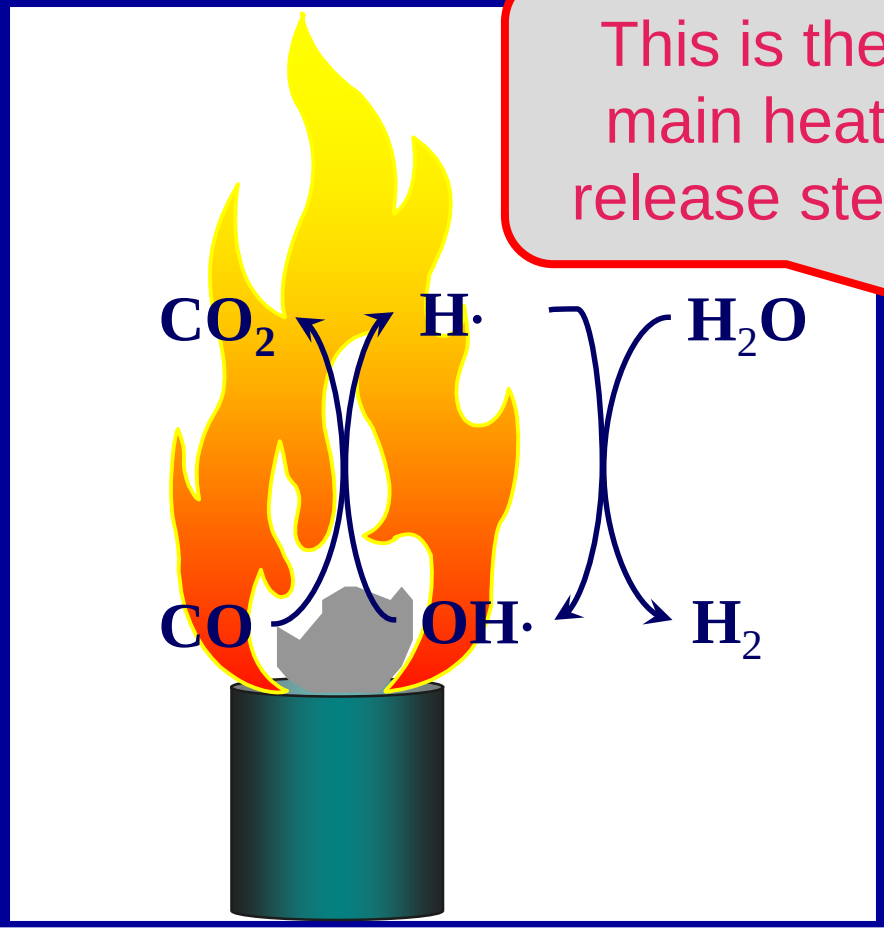
- ***Reaction in the solid phase***.
  - Promoting or inhibiting depolymerisation.
  - Char Formation e.g. by promoting cyclization and cross-linking.
  - Intumescence (swelling to form an insulating layer).

Key applications requiring gas phase flame retardants

- Usually the most difficult materials to fire retard!
- Generally, low thermal inertia ($k\rho c$) materials, with high surface area!
  - eg; Foams, fibres and films
- Particularly, textiles, flexible polyurethane foam (furnishings), polystyrene and rigid polyurethane foam insulation.




Free Radical Reactions in a Flame



$H\cdot + H_2O \rightarrow H_2 + OH\cdot$
$H\cdot + O_2 \rightarrow OH\cdot + \cdot O\cdot$ $\cdot O\cdot + H_2 \rightarrow OH\cdot + H\cdot$ $H_2O + \cdot O\cdot \rightarrow OH\cdot + OH\cdot$
$CO + OH\cdot \rightarrow CO_2 + H\cdot$
$HCHO + OH\cdot \rightarrow HCO\cdot + H_2O$ $HCO\cdot + OH\cdot \rightarrow CO + H_2O$
$CH_3\cdot + O_2 \rightarrow HCHO + OH\cdot$
$CH_4 + OH\cdot \rightarrow CH_3\cdot + H_2O$ $CH_4 + H\cdot \rightarrow CH_3\cdot + H_2$ $CH_4 + O\cdot\cdot \rightarrow CH_3\cdot + OH\cdot$

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Halogen Flame Retardant Action

HX, either HCl or HBr, is released from decomposing flame retardant

HX react with high-energy free radicals:

$$HX + H\cdot \rightarrow H_2 + X\cdot$$

$$HX + OH\cdot \rightarrow H_2O + X\cdot$$

The lower energy of the halogen free radical brings the concentration of active species below a critical level.

This blocks the flame reactions, and preventing the major heat release step:

$$CO + OH\cdot \rightarrow CO_2 + H\cdot$$

Flame Inhibition by phosphorus compounds

PO· is the main radical scavenger

$$H\cdot + PO\cdot + M \rightarrow HPO\cdot + M$$

$$HPO\cdot + H\cdot \rightarrow H_2 + PO\cdot$$

$$HPO\cdot + \cdot OH \rightarrow PO\cdot + H_2$$

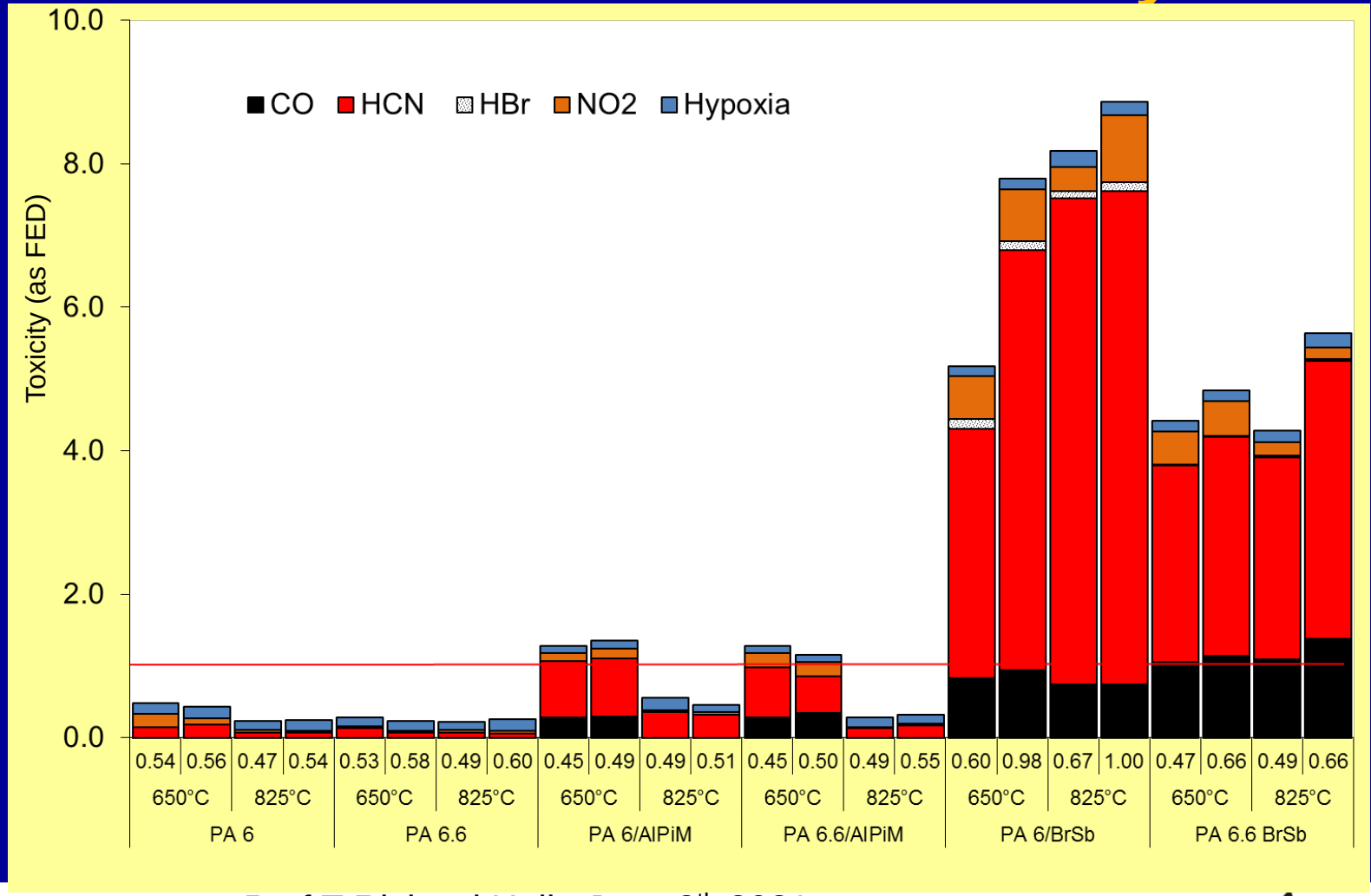
$$PO\cdot + \cdot OH \rightarrow HPO\cdot + \cdot O\cdot$$

$$PO\cdot + H\cdot \rightarrow HPO\cdot + \cdot O\cdot$$

$$PO\cdot + R\text{-}H \rightarrow HPO\cdot + R\cdot$$

Comparison of smoke toxicity for antimony-bromine and phosphorus flame retardants in nylon

Antimony-bromine flame retardant increases yields of both CO and HCN



Molyneux, S., Stec, A.A., Hull, T.R. *The effect of gas phase flame retardants on fire effluent toxicity,* Polymer Degradation and Stability 106, 36-46, (2014).

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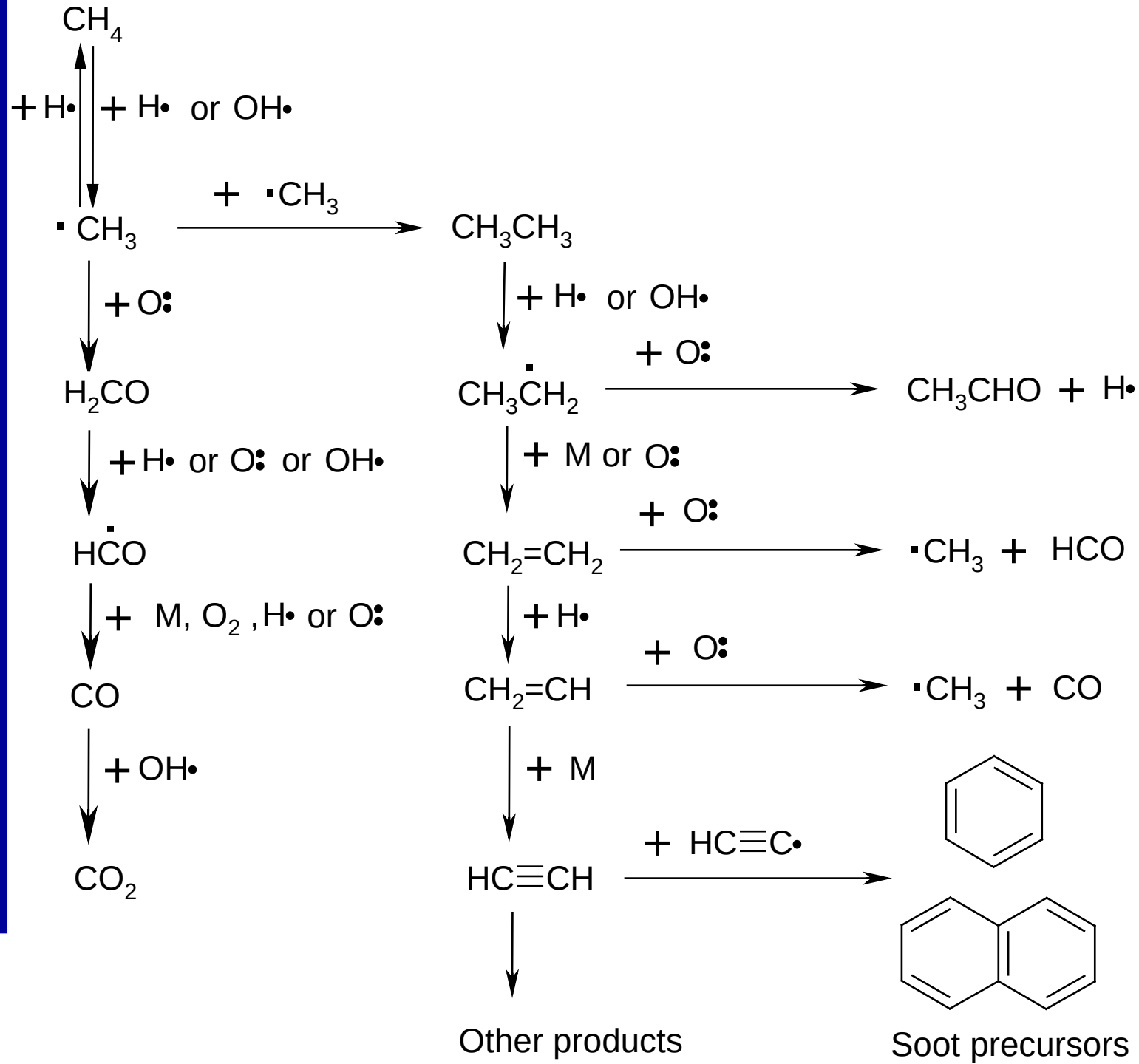
Formation of Products of Incomplete Combustion



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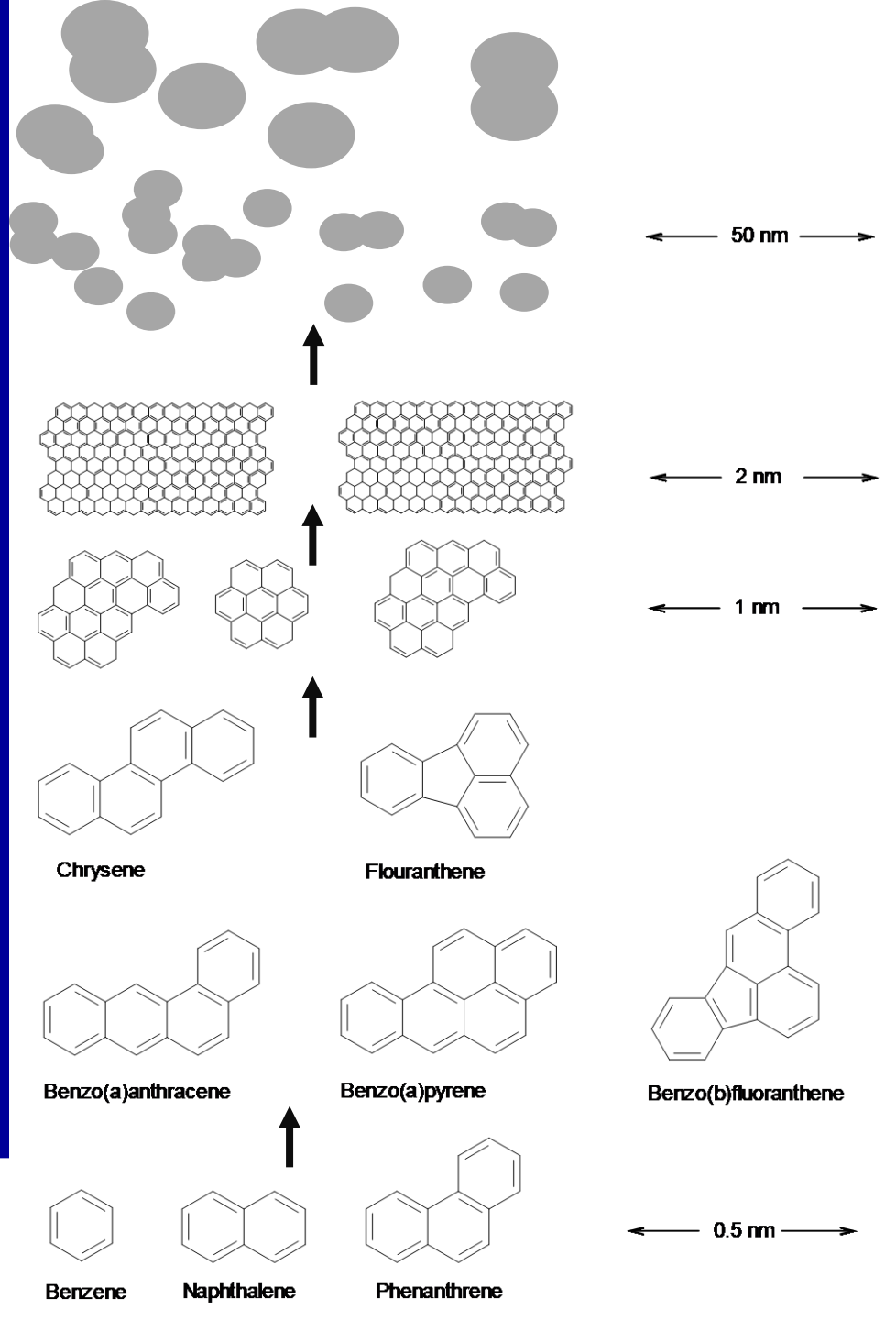
PAH and Soot Formation



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Problems with Halogenated Flame Retardants†

- Easily added to polymers, but easily lost (leaching, evaporation etc).
- Extremely stable, non-polar molecules (= Persistent and Bioaccumulative)*
- Endocrine disruptors (= Toxic)**
- Reduce heat release, but increase smoke, tar and CO and HCN yields.
- Soot increases radiant component of heat transfer – so potentially worse in real fires than fire tests?
- Potential dioxin formation (PBDD/F) in fires, or on incineration or reprocessing

†DiGangi J, Blum A, Bergman Å, de Wit CA, Lucas D, et al. 2010 *San Antonio Statement on Brominated and Chlorinated Flame Retardants*. Environ Health Perspect. 118(12).
*C. A. de Wit, *An overview of brominated flame retardants in the environment,* Chemosphere, 2002, 46, 583.
**Shaw SD, et al, *Halogenated Flame Retardants: Do the Fire Safety Benefits Justify the Risks?* Reviews on Environmental Health 25(4) 261-305 (2011).

Problems with Phosphorus Flame Retardants

- Suspected toxicity, carcinogenicity and reproductive toxicity
- Increased yields of small molecule toxicants
  - CO (LC_{50} = 3500 ppm),
  - HCN (LC_{50} = 165 ppm),
  - and possibly P_2O_5 (LC_{50} = 3500 ppm, vapourises at 600°C)
- Potential neurotoxicity
  - Trimethylolpropane phosphate (TMPP)*
  - Tri o-cresyl phosphate (long-term neurotoxicity)**

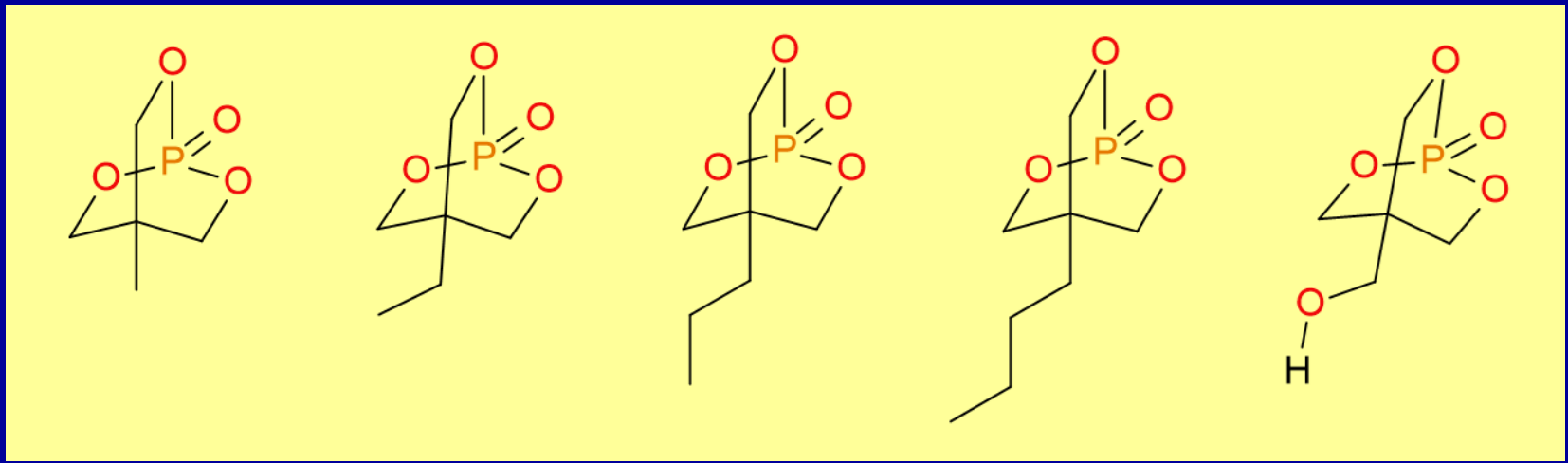
* J H Petajan Science 187, 742-4 (1975)
** M B Abou-Donia, Ann. Rev. Pharmacol.Toxicol. 21, 511-548 (1981)

Trimethylol propane phosphate, and other bicyclic phosphate esters

TMPP formed during burning of PU foam

Trimethylol propane + Phosphate FR -> TMPP
(polyol used to make PUF)

TMPP



LD_{50} /mg/kg	32	1.0	0.18	1.5	>500

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Cross-Linking and Char Formation

The ultimate FR mechanism – turning polymer into protective barrier!

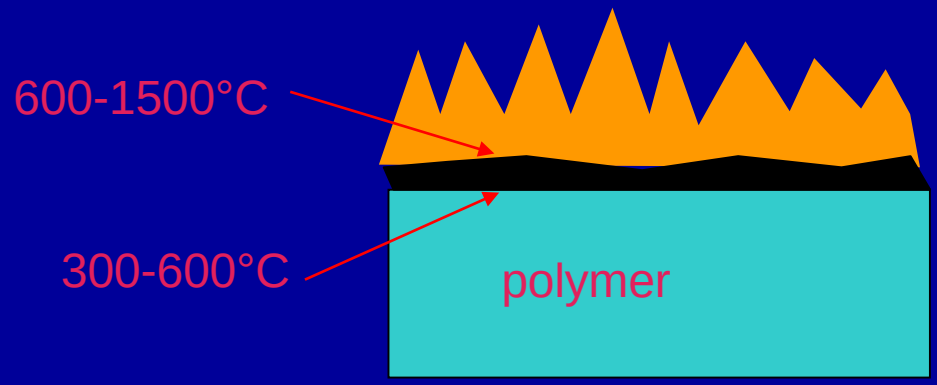
Cross-linked polymers produce *less volatiles and so more char* - provided cross-linkages and polymer chains are resistant to thermal decomposition.

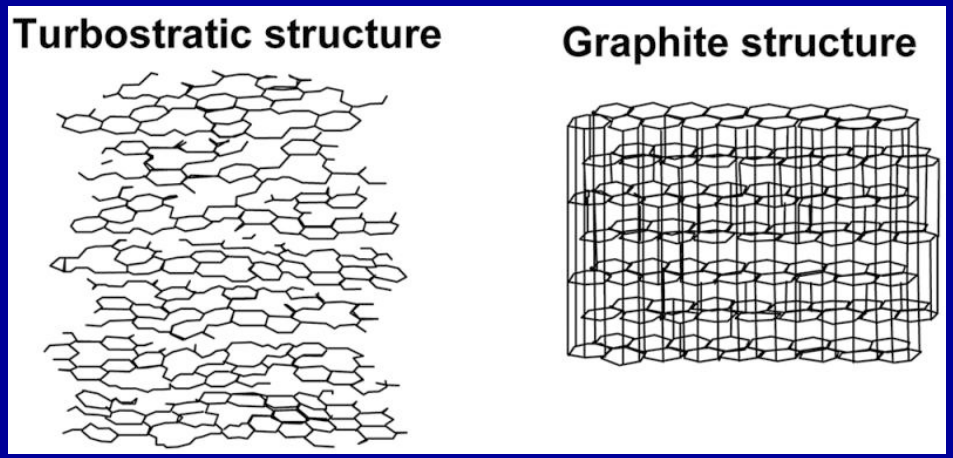
Formation of Char

Polymer passes through several steps

Steps in formation of char:

- cross-linking,
- aromatisation,
- fusion of aromatics,
- turbostratic char formation, and
- graphitisation.

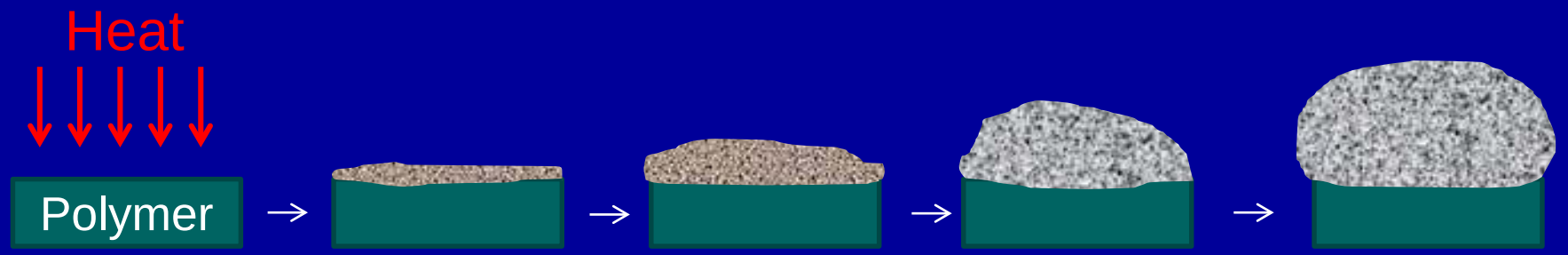




Intumescence

- Intumescent systems, on heating, give a swollen multicellular char, more capable of protecting the underlying material from the action of the flame.

- Polymers of greatest interest are polyethylene (PE), polypropylene (PP), and polystyrene (PS) – difficult to fire retard because they volatilise completely.



Conclusions

- Fire retardants allow combustible materials to be used in place of non-combustible ones.
- Gas phase flame retardants increase
  - smoke toxicity
  - Radiant heat and hence fire spread
  - Particulate emissions
- The toxic effects of smoke are seen in
  - Acute fire deaths (CO and HCN)
  - Firefighter occupational diseases
  - Atmospheric particulate deaths (~10% of total*)

rsson, B., Simonson, M. Fire Emissions into the Atmosphere. *Fire Technology* **34,** 266–279 (1998). https://doi.org/10.1023/A:101535002