Halogen vs Non-halogen Flame Retardants: ***Some inconvenient truths***!

(with apologies to Al Gore)

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(Broad brush) Costs:

Inorganics (& N-containing) < **Halogen (plus synergist)** < **Organophosphorus**

Eg.

Alumina trihydrate (ATH) (< magnesium hydroxide (MDH))
Zinc borate
APP
Melamine + salts
Intumescents
Zinc stannates

Eg.

Chloro- and bromo- phosphates
Decabromodiphenyl ether (Deca)
Hexabromocyclododecane (Hexa)
Tetrabromobisphenol A (TBBPA)
Bromine-containing polymerics eg
    Brominated polystyrene
    Poly(pentabromobenzyl acrylate)

Eg.

Triaryl phosphates
Resorcinol bis(diphenyl phosphate) (RDP)
Aluminium diethyl phosphinates
THP-derivatives eg Proban
Cellulose reactive phosphonamides eg Pyrovatex

Potential ecotoxicity?

65 ppm in seawater
5000 ppm in the Dead Sea
Sea salt ~2000ppm?

- **Bromine** under the spotlight:
  - Persistent organic pollutants (POPs)
  - Currently banned BrFRs include polybromobiphenyls and octa- and penta-bromodiphenyl ethers (2003-2005)
  - Withdrawn: “hexa” (2015)
  - Partially withdrawn/under threat: “deca”
  - Under scrutiny: Tetrabromo-bisphenol A (TBBPA)
- **Phosphorus**?
  - Essential to life
  - Organophosphate agrochemicals have known H&S issues
  - Nerve agents are based on organophosphorus!
- **Nitrogen?**
  - Basis of protein chemistry
  - Melamine: 2008 - Chinese baby’s milk adulteration!
  - Nox (NO_2) and air pollution (Guardian, 2 April, 2015: 29000 deaths in UK per annum)
- **Carbon??**
  - Carbon monoxide is the main killer in fires!

Relative effectiveness and concentrations

- For acceptable (ie pass “standard” test requirements) FR levels:
  - 5-15 wt% Bromine (requires synergist eg antimony III oxide)
  - 1-2 wt% Nitrogen (usually in combination with phosphorus)
  - 1-3 wt% Phosphorus
  - >55 wt% Aluminium/magnesium hydroxides!

Relative effectiv

Most BrFRs contain 40-80% Br but require ATO with Sb/Br=1/3
Typical “Deca”/ATO combination present at 2:1 mass ratio
Total [BrFR+ATO] levels 10-25 wt% in final polymer.

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Melamine salts rich in nitrogen:
Melamine cyanurate (MC): 49% N
Melamine polyphosphate (MPP); 37.5%N (and ~14%P)
Urea: 47%N

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Most PFRs contain 8-15%P and so 1-3% wt P ~ 5 - >30 wt% in the formulation; additional N-containing species may also be required (eg melamine salt)

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Most hydrated inorganics at >55 wt% significantly reduce properties of the polymer matrix

Polymer spectrum

Commodity

- PE
- PP
- PS
- **PVC**

Copolymerics

- EVA
- PVC-acrylate
- Styrene acrylate
- Synth. rubbers/elastomers
- Styrenics/HIPS
- ABS
- Polyurethanes

Engineering

- PA6, PA6.6, etc
- HTPA
- PET
- PBT

Thermosets:

- Vinyl & Unsat. polyester
- Epoxy
- Phenolics

Polymer spectrum

i. **BrFR**/synergist (~15%Br for V-0)
ii. **P-N FR** (25-30% for V-0)
iii. **ATH** (>60% for V-0)

Comm

PE
PP
PS
PVC

EVA
PVC-acrylate
Styrene acrylate
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Polyurethanes

i. **BrFR**/synergist, **P-N** FRs require balance to maintain correct physical properties
ii. **ATH** or similar often present as an FR component with **BrFRs** or **PFRs**

PA6, PA6.6, etc
HTPA
PET
PBT

Thermosets:

Vinyl & Unsat polyester

Epoxy

Phenolics

i. **BrFR**/synergist, **P-N** FRs require high temperature (>250°C) resistance;
ii. Many non-aromatic FR structures and simple P-compounds eliminated;
iii. Total [FR] ≤ 20 wt% if mechanical/electrical properties to be maintained

Engineering

PA6, PA6.6, etc
HTPA
PET
PBT

PVC

Styrene acrylate
Synth. rubbers/elastomers
Styrenics/HIPS
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Polyurethanes

Thermosets:

Vinyl & Unsat. polyester

Epoxy

Phenolics

Polymer spectrum

Commodity

PE
PP
PS
PVC

E
P
S
S
Styrenic
ABS
Polyurethan

1. **BrFR**/synergist effective in all types;
2. **Br-**comonomers also effective;
3. **P-N FRs** as additives (high levels) reduce resin strength;
4. **P-**comonomers for epoxies

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PA6, PA6.6, etc
HTPA
PET
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Thermosets:

Vinyl & Unsat. polyester
Epoxy
Phenolics

“New/recent” Technologies

- Nanotechnology
  - Nanoparticles alone reduce ignition times, slow down overall burning rate
  - Nanoparticles + FR can reduce total [FR] required;
  - eg EVA/65%ATH ~ EVA/45%ATH/5%nanoclay (Kabelwerk, Belgium)
  - Nanoparticles on surface can create fire protective ceramic layer
- Surface treatments
  - Thermally thin (<4mm): Must still generate high levels of FR required for normal bulk polymer (eg 1-3%P, 5-15%Br, 1-3%N, etc)
  - Plasma
  - Sol gel
  - Layer-by-layer
  - Thermally thick (>4mm), then surface layers can form fire barriers (eg The “fire resistant paint” effect).

Volatile Phosphorus?

- **Hastie & Bonnell (1980):** Volatile P via $HPO^{\cdot}$ And similar radicals are as effective as $Br^{\cdot}$ radicals at terminating flame chemistry radical reactions
- **Horrocks et al, (2008):** Volatile P (as tributyl phosphate or Fyrol 51(oligomeric phosphate-phosphonate)) essential in a textile coating as a potential **BrFR** replacement.
- **DOPO** (dihydro-oxa-phosphaphenanthrene oxide): polyesters, epoxies?
- **Al dialkyl phosphinate:** PA6, PA66, HTPA, PET, PBT

Three Case studies

- Textile back coatings
- Polyolefins
- Engineering polymers

1. Textile backcoatings

- Work at Bolton 1999-2007
  - [BrFR] may be reduced significantly if other FRs (eg, **P-NFRs**, ATH) present
  - **P-NFR**s function ONLY on 100% cotton if mobilised (ie fluid or volatile) <300ºC (T_{ig} ~ 350ºC); APP best of examples tried
  - Addition of heavy metal salts may reduce melting/liquefaction temperature of APP
  - **Best results obtained in a condensed + vapour phase active formulation (*specific to 100% cotton*):**

Pentaerythritol phosphate	+ Fyrol 51	+ Melamine
(Char former)	(Volatile P)	(Volatile nitrogen)

2. Polyolefins (HDPE)

- **BrFR** vs **P-NFR** for V-2 in HDPE
  - >30-35 wt% of proprietary P-N intumescent
  - 10 wt% (~8 wt% Br) DecaBDE + 3.5 wt% ATO

- **BrFR** vs synergist (antimony III oxide vs zinc hydroxy stannate)
  - 17 wt% (~12 wt% Br) BrFR + 2wt% ATO
  - **14 wt%** (~10 wt%Br) BrFR + 4 wt% ZHS

3. Engineering polymers

- Ideally total [FR] ≤ 20 wt%
- Often contain glass fibre (~30 wt%)
- Work at Bolton 2008-2014 for PA6, PA6.6 and HTPA suggests:
  - With **BrFRs** (especially polymeric **BrFRs**), zinc stannate (ZS) often more effective than ATO and so total [**BrFR**] may be reduced;
  - Some evidence that **Sn-P** synergies exist; at present time in PA6 only V-2 achieved with ZS **+ PFR**
  - In HTPA 15wt% **PFR** may be reduced to ~11wt% if ~4wt% ZS present **AND** smoke reduced by ~20%

Conclusions

- Current climate demands that ALL flame retardant presence is reduced in consumer products.
- To attack bromine and promote a total ban on **BrFRs** will divert the attention to the next “easy target”, **P-NFRs**
- FR development should be based on interactive combinations of individual components such that:
  - [total FR] is minimised in any given substrate;
  - Flame retardancy and hence fire safety are maximised
- **There is no “silver bullet” based on a single flame retardant!**