Halogen vs Non-halogen Flame Retardants: Some inconvenient truths!
(with apologies to Al Gore)

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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 polymeric 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 eco-toxicity?

- **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  - Withdrawn: “hexa” (2015)
  - Partially withdrawn/under threat: “deca”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 (NO₂) 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!
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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
Relative effectiveness and concentrations

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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)
Relative effectiveness and concentrations

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Most hydrated inorganics at >55 wt% significantly reduce properties of the polymer matrix.
## Polymer spectrum

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<th>Commodity</th>
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<td>PE</td>
<td>EVA</td>
<td>PA6, PA6.6, etc</td>
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<tr>
<td>PP</td>
<td>PVC-acrylate</td>
<td>HTPA</td>
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**Thermosets:**

- Vinyl & Unsat. polyester
- Epoxy
- Phenolics
Polymer spectrum

Commodity

PE  PP  PS  PVC

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

i. BrFR/synergist (~15%Br for V-0)

ii. P-N FR (25-30% for V-0)

iii. ATH (>60% for V-0)

Engineering

PA6, PA6.6, etc
HTPA
PET
PBT

Thermosets:

Vinyl & Unsat. polyester
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Thermosets:

Vinyl & Unsat polyester
Epoxy
Phenolics

BrFR/synergist, P-N FRs require balance to maintain correct physical properties

ATH or similar often present as an FR component with BrFRs or PFRs
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

Thermosets:
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Polymer spectrum

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Thermosets:

Vinyl & Unsat. polyester
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Engineering

BrFR/synergist effective in all types;
ii. Br-comonomers also effective;
iii. P-N FRs as additives (high levels) reduce resin strength;
iv. P-comonomers for epoxies
“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⁻. And similar radicals are as effective as Br⁻ 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-NFRs function ONLY on 100% cotton if mobilised (ie fluid or volatile) <300°C ($T_{ig} \sim 350^\circ C$); 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 + 2 wt% 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!