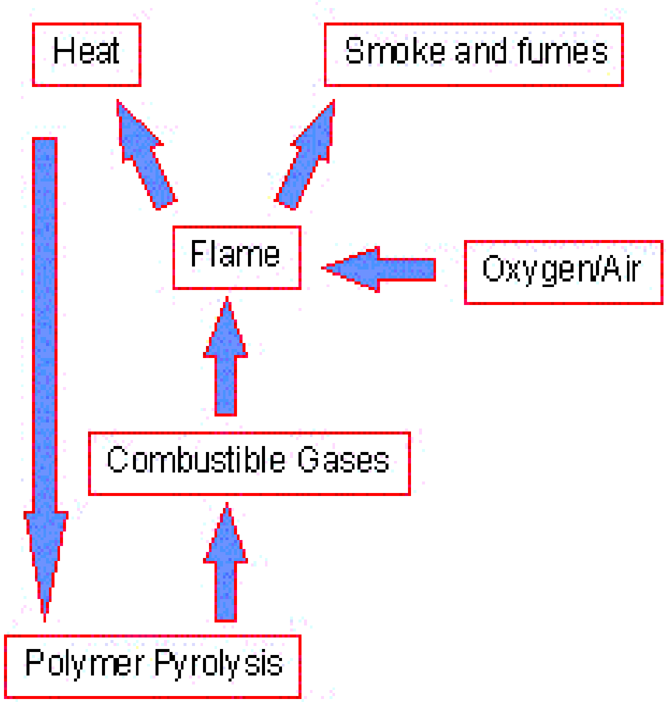
RTP Co.
Imagineering Plastics®

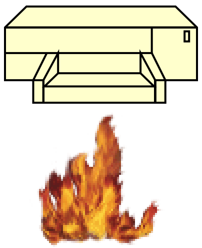
FR Products for the Evolving Global Marketplace

Paul Killian
Global Business Manager, TPE & FR Products

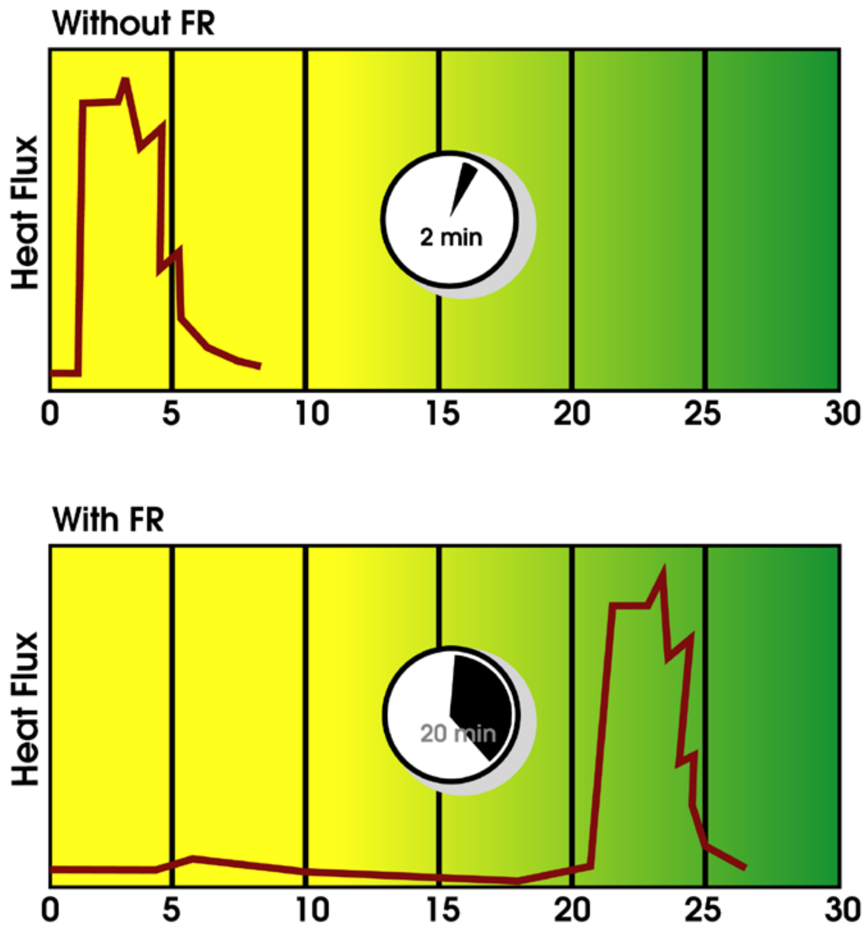
Flame Retardant Thermoplastics

- External heat applied to plastic
- Thermal degradation of polymer (Pyrolysis)
- Gaseous volatiles (FUEL => H* and OH* radicals)
- External heat source + Fuel = HEAT
- Ignition
- Spontaneous Combustion:
  - Heat produced by reaction becomes enough to sustain the combustion





Why use Flame Retardants?



Goals of Flame Retardant Compounds

- Increase Resistance to Ignition.
- Reduce Rate of Flame Spread.
- Reduce Rate of Heat Release.
- Reduce Smoke Emission

  <u>Products are NOT incombustible</u>**
- Meet Customer's Environmental concerns

Regulation Driven

- Independent Certifiers (UL)
- Federal Aviation Association (FAA)
- Military
- Federal/State/City Laws/Local & Country Ordinances
- European Directives
- Building Codes in various countries
- Insurance Underwriters (Factory Mutual)

Flammability of Polymers

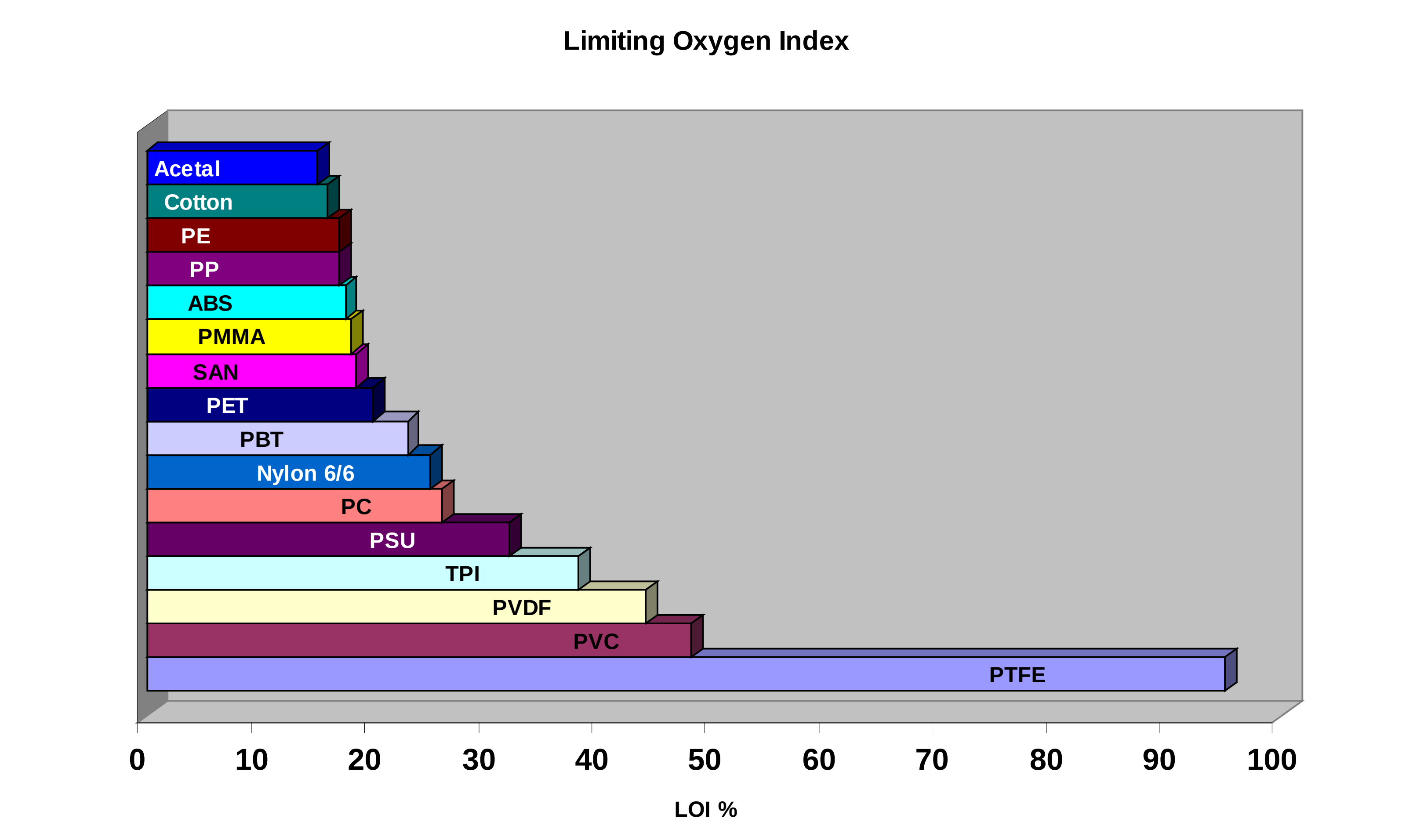
Flammable

- ✓Polyolefins
- ✓Nylons
- ✓Polycarbonate
- ✓Styrenics
- ✓Polyesters
- ✓TPEs

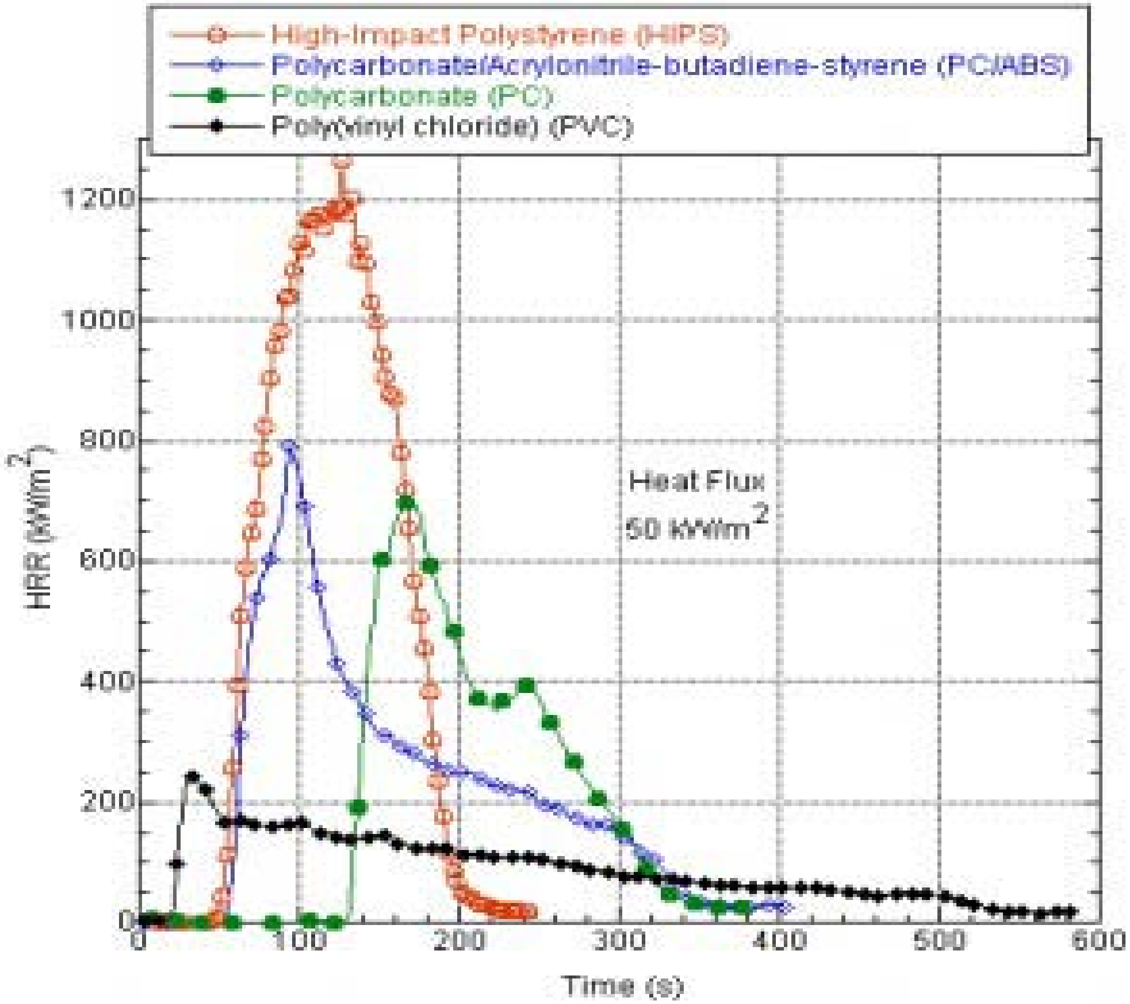
Inherently Flame Resistant

- ✓ Polysulfones
- ✓ Polyphenylene Sulfide
- ✓ Polyetherimide
- ✓ Polyetheretherketone
- ✓ Fluoropolymers
- ✓ TPI
- ✓ PTFE

Comparative LOI Values



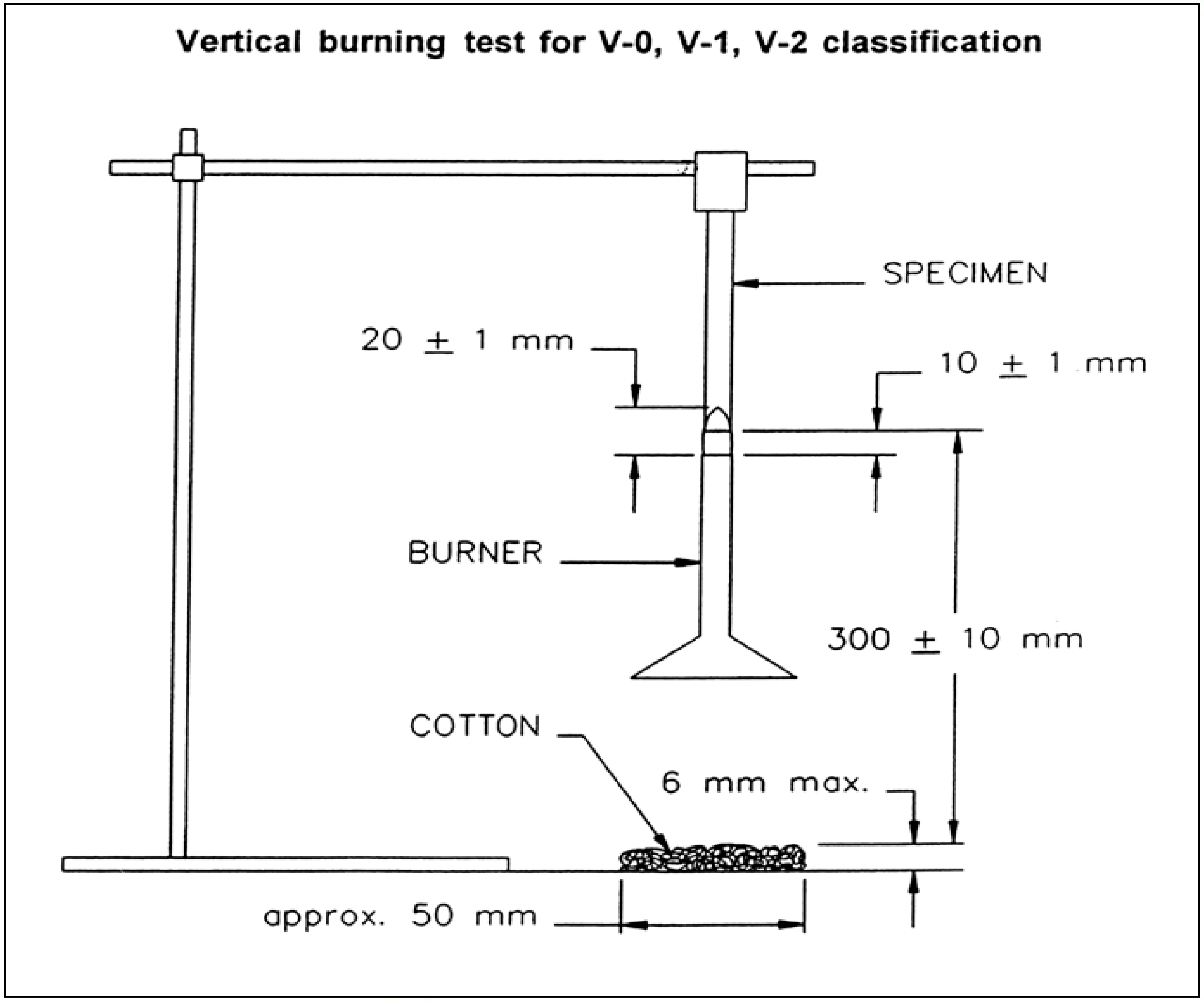
Heat Release Rate



Common Test Methods

- UL 94 – HB, V-2, V-1,V-0, 5-V, VTM
- Glow Wire Ignition – IEC 60695-2
- Limiting Oxygen Index- LOI
- Flame Spread – ASTM E162
- Cone Calorimetry
- Smoke Density
- Various Wire & Cable standards

UL 94 V Test Set Up



Glow Wire Testing

IEC 60695-2 test method

- Glow Wire Flammability Temperature – highest temperature of the incandescent wire at which the material does not ignite
- Glow Wire Flammability Index – highest temperature of the incandescent wire at which the material extinguishes itself

RTP performs this test
at RTP France & RTP HQ

RoHS Directive

- Restriction of Hazardous Substances (RoHS)
  - EU Directive in effect as of July 2006
- Bans use of lead (Pb), mercury (Hg), cadmium (Cd), hexavalent chromium (CrVI), polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE)
  - DOES NOT NEED TO BE HALOGEN FREE
- RTP concern would be pigments and flame retardants.
- Decabrom exemption was annulled (July 2008)
  - RoHS Compliant solutions are in place
  - New UL ratings will be needed on certain RoHS compliant materials
  - RTP can provide official compliance letter

RoHS Directive

Other countries following the EU's lead:

- China RoHS
- Korean RoHS
- Japan RoHS
- RoHS2 – next generation of EU version

Restricted substances are consistent throughout all variations:

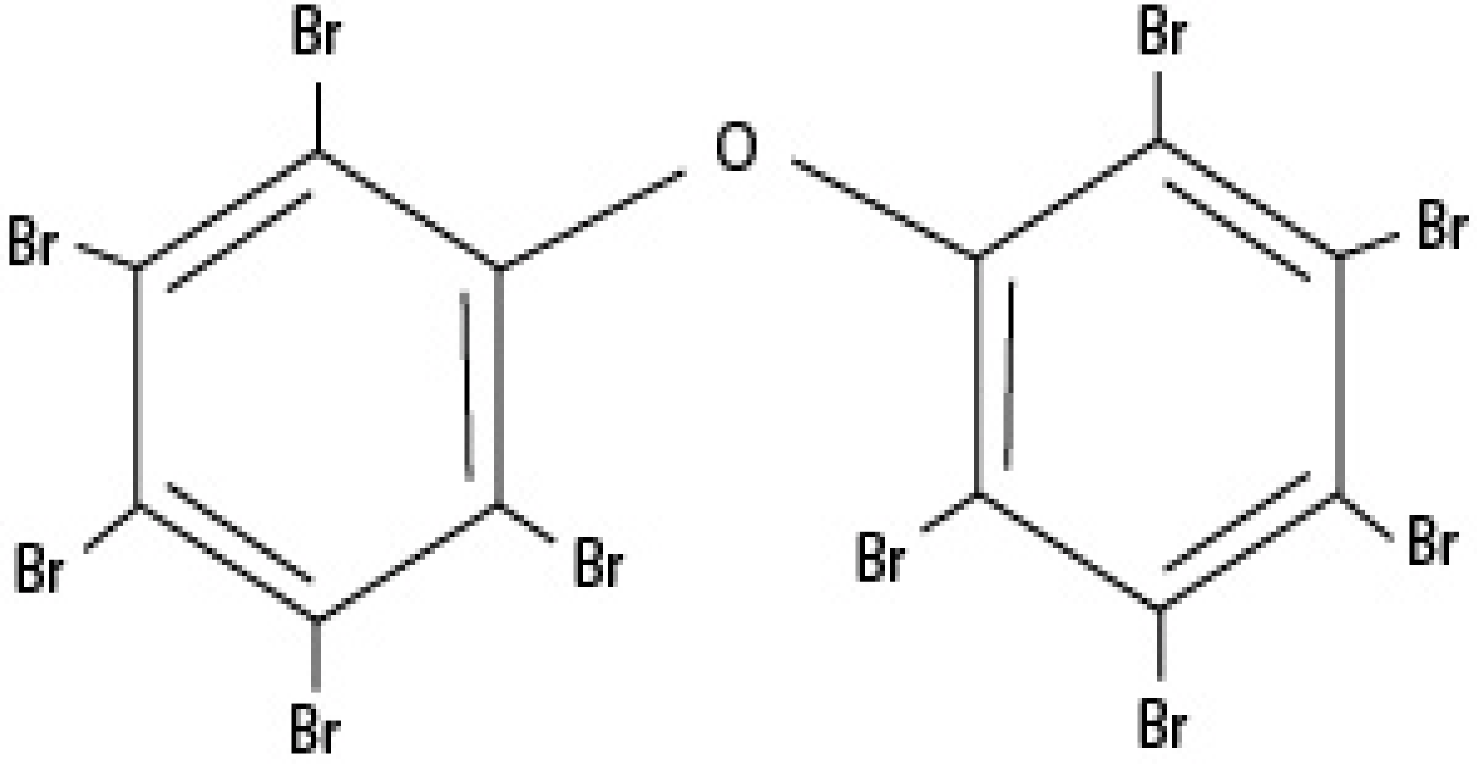
WEEE Directive -

- often linked with the RoHS, affecting electrical and electronic equipment (as opposed to materials).

- WEEE variations to accompany RoHS variations

What is a PBBE?

Decabromodiphenyl ether



EPA Action vs. Decabrom

- Decabrom in the US will be phased out by 2012

- The EPA & the Big 3 supplies of decabrom have come to an negotiated agreement whereby they will stop selling decabrom
  - Albemarle
  - Chemtura
  - ICL
- Importation of foreign manufactured decabrom and goods containing decabrom will also be affected

Eco Labeling

- Currently 328 ecolabels globally in 204 countries and 40 industry segments
- Intended to help consumers make "correct environmental choices"
- In compounding language, this means potential restrictions on FR type, namely halogens
- Each eco-label could have its own unique effect.
- RTP's independence and objectivity in choosing FR technologies provides you the tools to navigate the complicated & changing regulatory world.

Choosing an FR System

How do we decide which FR to use?

- Resin System?
- FR test method?
- Other application performance requirements?
- Fillers/Additives?
- RoHS concerns?
- Halogen concerns

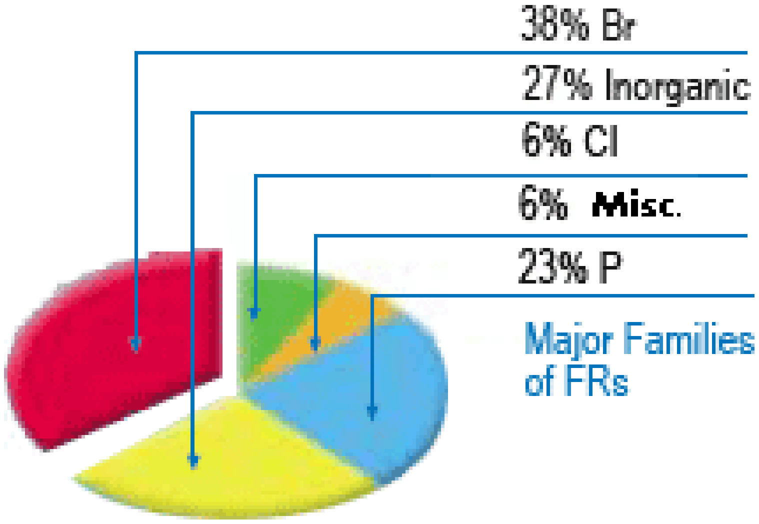
Halogen vs. Non-Halogen

- Halogenated FR – primarily means Br or CL is present
  - Lower Cost
  - Wider processing window
  - Good FR efficiency
  - Good physical properties retention
- Non-Halogenated FR
  - Low Smoke generation
  - Lower Toxicity
  - Less Corrosive in General
  - Not Available in Styrenics

Common Types of FR Additives

- Halogenated FR's **
  - Brominated
  - Chlorinated

**Synergists added



- Non-Halogen FR's
  - Metal hydroxides
  - Phosphorous Based
  - Melamine Based

Flame Retardant Mechanisms

Vapor Phase Inhibition

Halogen radicals affect free radical combustion process

FR additive breaks down

$XBr \rightarrow X + Br\cdot$

Halogen radical reacts with hydrocarbon molecules in the polymer structure

$Br\cdot + RH \rightarrow R + HBr$

Hydrogen Halides interfere with radical chain

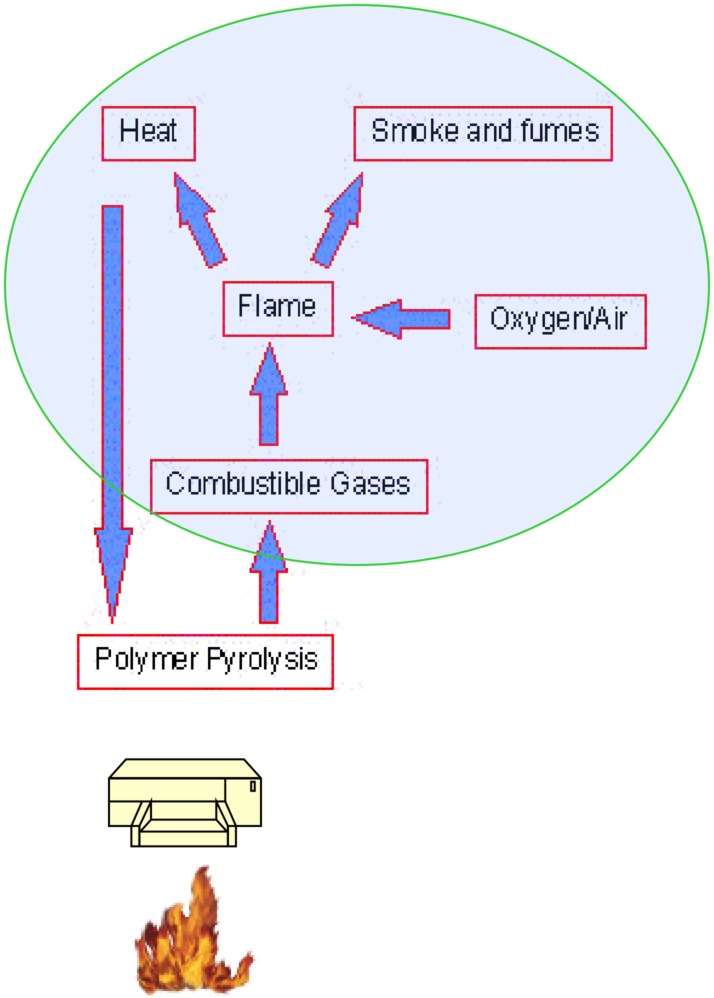
$H\cdot + HBr \rightarrow H_2 + Br\cdot$

$OH\cdot + HBr \rightarrow H_2O + Br\cdot$

Resulting Br· radical is less reactive than the H· and OH· radicals that are responsible for combustion

Lowers energy production & reaction rate

Left over Br· radicals repeat process



Flame Retardant Mechanisms

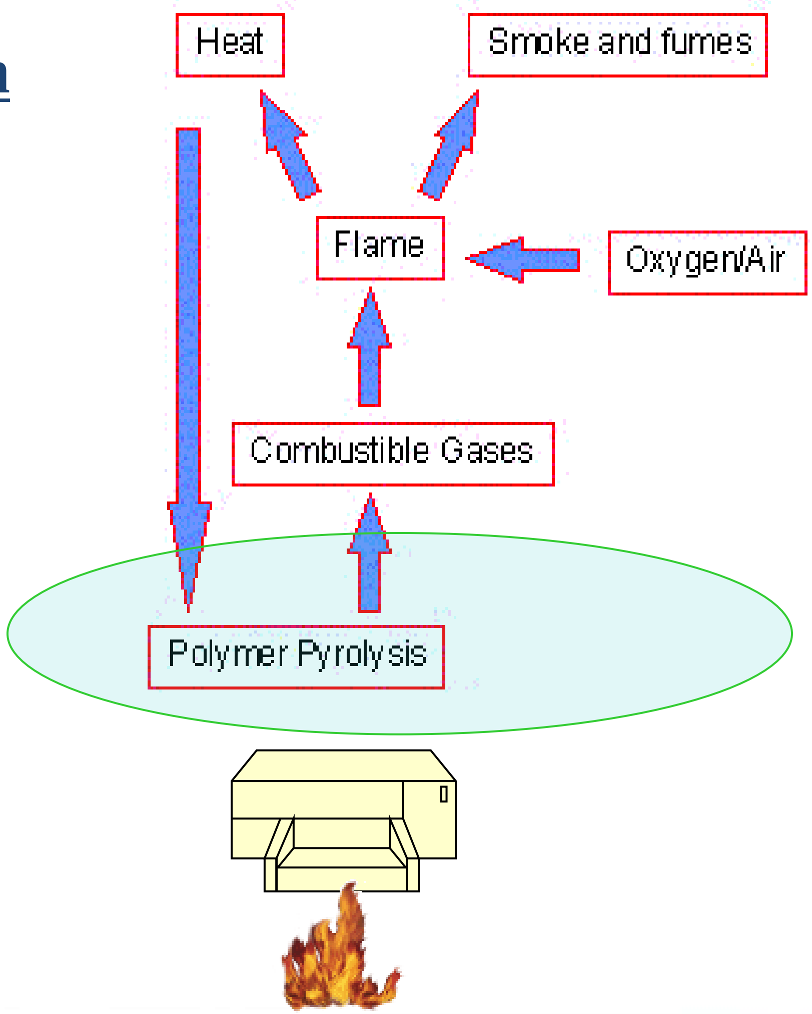
Condensed Phase Char Formation

(Typical of Non-Halogen Systems)

-Melamine Cyanurate
-Metallic Hydrates
-Zinc Borates
-Phosphates
- Metal Phosphinates

Formation of char-layer on surface

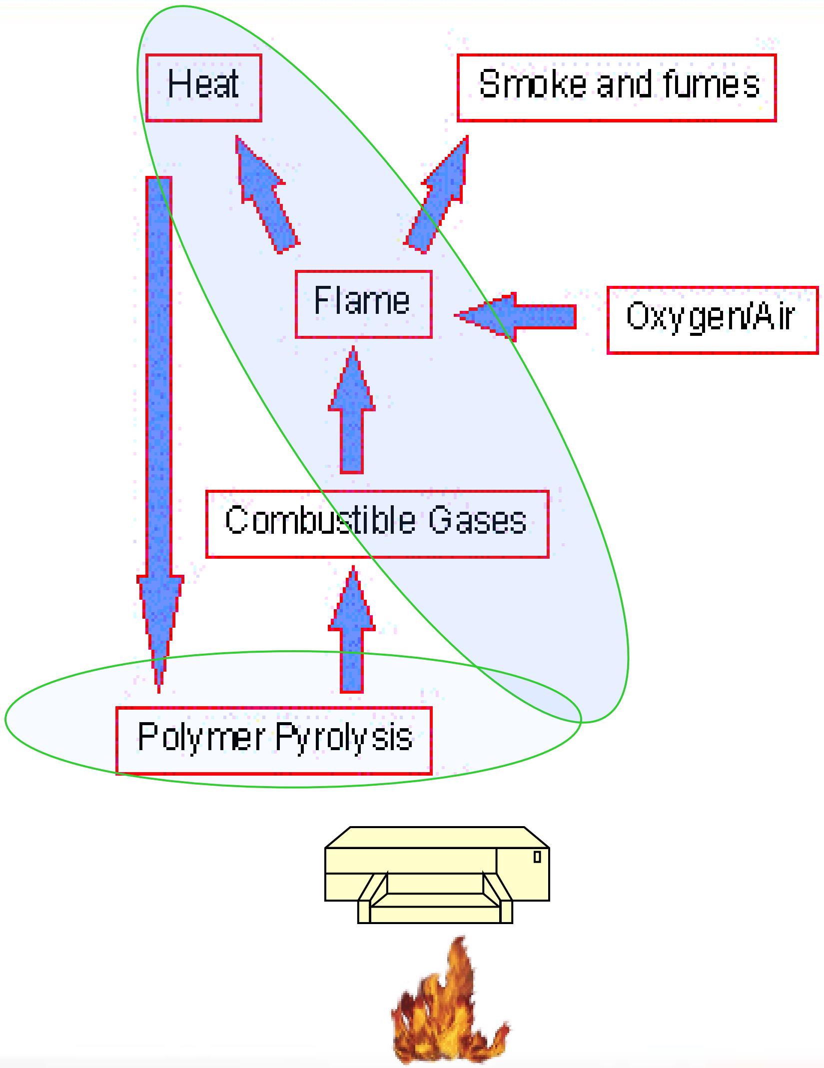
Insulates polymer from heat inhibiting pyrolysis process Creates a fuel barrier hindering the passage of combustible gases



Flame Retardant Mechanisms

Remove/Reflect Heat & Dilute (quench & cool)

- Melamine Cyanurate
  - Decomposes endothermically absorbing heat energy (heat sink)
  - Non-burning drip is created
- Metallic Hydrates
  - Alumina Trihydrate
  - Magnesium Hydroxide
  - Zinc Borate
- Endothermic release of water
  - cools polymer
  - dilutes combustible gases
- Metallic oxide forms a reflective surface barrier
  - Slows polymer degradation & combustion reaction



Halogen Free Chemistry

Phosphorous – in various forms, contributes to the char concept to create a barrier between fuel & flame as well as releases CO_2 to dilute combustible gases

Nitrogen – promotes char formation & works synergistically with phosphorous to make P more effective

Hydrated Minerals – product water during combustion process that quenches the combustion zone, cools the heat of reaction, and dilutes combustible gases

Halogen Free FR types

EDAP & APP (nitrogen/phosphorous)	Olefins, TPEs
Metallic phosphinates	Polyamide, PBT, some TPEs
Hydrated Minerals (ATH, MgOH, ZnB)	Olefinic cable jacketing, specialty compounds
Organo-phosphinates (RDP type)	PC, PC/ABS

Development Trends

Two factors driving push to non-halogen technology

1) Environmental concerns – this the first & traditional concern with halogenated systems

2) volatility in the current FR pricing

- Antimony oxide pricing
- Raw bromine pricing

Development Trends

Halogen Free is the theme

- **Polypropylene** – well established technology for unfilled PP compounds.
- **Glass-filled Polypropylene** – volatile FR market demands this development
- **Nylons** - the available FR technology has expanded and improved over the past 5-10 years
- **PBT** - technology that is an off-shoot of nylon work now available
- **PPA** - improved thermal stability now available for the high temperature nylon resins
- **Polycarbonate** – Glass filled & unfilled compounds show no loss of properties compared to halogenated systems
- **TPEs** - SBCs, TPVs, TPUs, and COPE options

Property Comparison – 30% Glass filled Nylon 6

Physicals:	RTP 205 A FR	Halogen Free Version
FR @ 1.5 mm	V-0	V-0
Tensile Str. (MPa)	138	121
Flex Str. (MPa)	207	192
Flex Mod. (GPa)	9.6	9.1
Notched Izod Impact (J/m)	102	102
Spec. Gravity	1.65	1.39

- Significantly Lower Specific Gravity
- Slightly lower strengths & modulus
- Comparable Impact Strength
- V-0@1.5mm

Property Comparison – 30% Glass Fiber PBT

Physicals:	RTP 1005 FR A	Halogen Free
FR @ .8mm	V-0	V-0
Tensile Str. (MPa)	138	106
Flex Str. (MPa)	228	170
Flex Mod. (GPa))	9.65	10.3
IN (J/m)	87	88
Spec. Gravity	1.65	1.56

- Lower Specific Gravity
- Lower Strength & Modulus
- Maintained impact properties
- V-0@.8mm

Summary of Halogen Free Product Development

- Halogen free FR technology has improved over the past decade
- As a result, more & better compound options are available
  - PPA & high temperature nylons
  - TPE options
  - PBT compounds
  - non red P glass-reinforced nylon compounds
- Development continues as further improvements are necessary
- Economics continue to improve

Conclusion

- Flame Retardant performance remains a critical technology
- Halogen Free technology is dominating the new product development trends
- Combining new FR technologies with other value added technologies will be the development direction of the future

  examples: 1) FR w/ VLF technology
  2) non-hal technology with key additive technologies