Formulating Thermoplastics with Non-Halogen Flame Retardants: An Introduction

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Member of PINFA-NA

Virtual Webinar

Wednesday, February 17, 2021
11:00 AM – 12:30 PM (EST)

Polling Questions: Audience

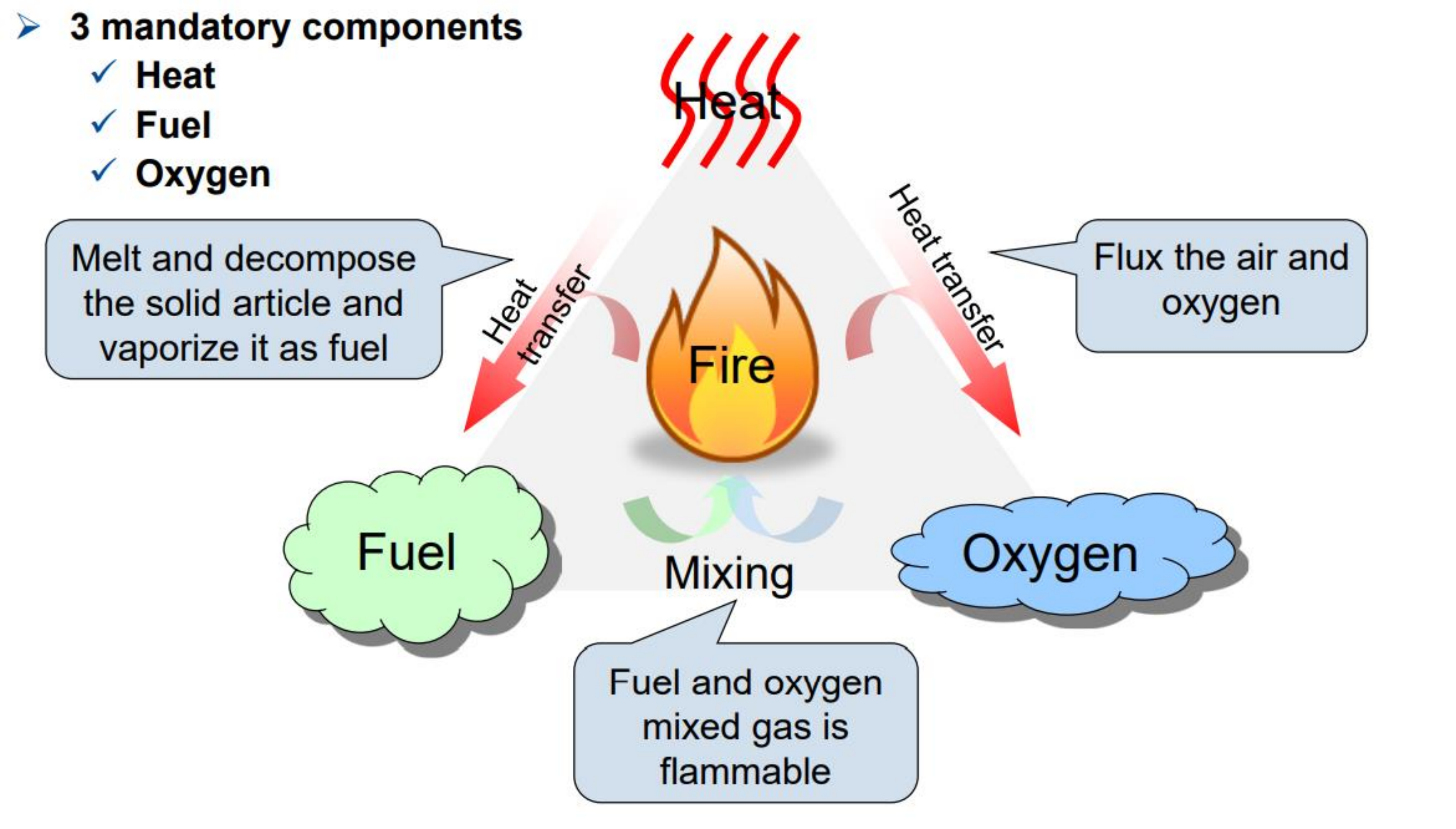
- Are you currently working with/testing flame retardants?
  - Yes
  - No
- Are you currently working/testing with Non-Halogen Flame Retardants?
  - Yes
  - No

Agenda

- Basics of Polymer Flammability and Flame Retardant Mechanisms
- Overview of Most Common Flammability Tests
- Chemistry of Major Non-Halogen Flame Retardants
- Non-Halogen Flame Retardants for Major Thermoplastics
- Introduction to Formulating with Non-Halogen Flame Retardants
- Conclusions
- Relevant Resources/Literature/References
- PINFA/SPE June Webinar Series on NHFRs
- Questions/Contact Information

Basics of Polymer Flammability and Flame Retardant Mechanisms

Fire Triangle

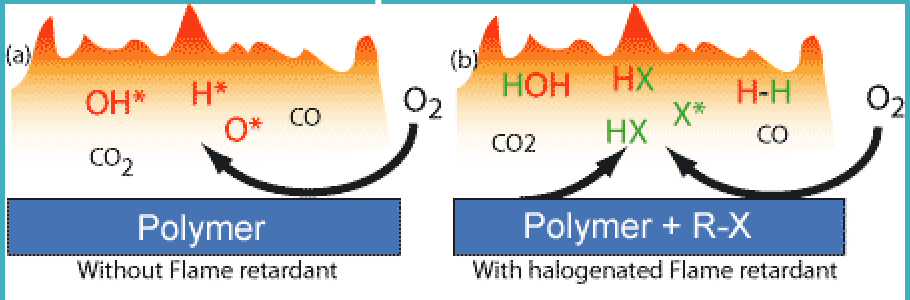


Source: https://www.researchgate.net/publication/316716408_NOR-based_Flame_Retardant_and_Versatile_Synergist

Mechanisms of Flame Retardancy

- Chemical Effect – Gas Phase
  - Halogenated FR - Radical Trap

$$R\text{-}X + P\text{-}H \longrightarrow H\text{-}X + R\text{-}P$$
$$H\text{-}X + H\cdot \longrightarrow H_2 + X\cdot$$
$$H\text{-}X + OH\cdot \longrightarrow H_2O + X\cdot$$



P-H = Polymer
X= Halogen (e.g., Cl or Br)

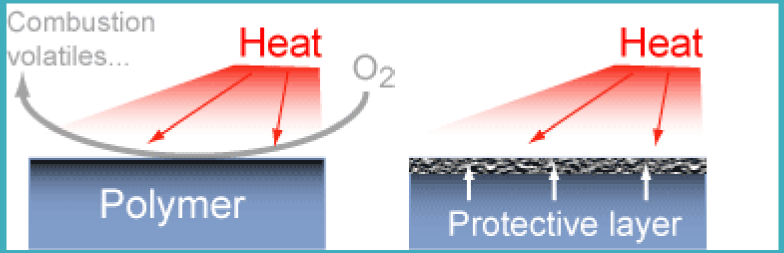
  - Synergism with Antimony Trioxide (Sb_2O_3)

$$Sb_2O_3 + 6\,HX \rightleftharpoons 2\,SbX_3 + 3\,H_20$$
$$SbX_3 + H^* \rightleftharpoons SbX_2 + HX$$
$$SbX_2 + H^* \rightleftharpoons SbX + HX$$
$$SbX + H^* \rightleftharpoons Sb + HX$$
$$Sb + O^* \rightleftharpoons SbO^*$$
$$SbO^* + H^* \rightleftharpoons SbOH$$
$$SbOH + H^* \rightleftharpoons SbO^* + H_2$$

Source: http://www.specialchem4polymers.com/tc/flame-retardants/index.aspx?id=9306

Mechanisms of Flame Retardancy (cont.'d.)

- Physical Effect
  - Formation of a Protective Layer
    - Cooling effect/Endothermic
    - Dilution



formation of protective layer inhibiting, combustion and volatiles

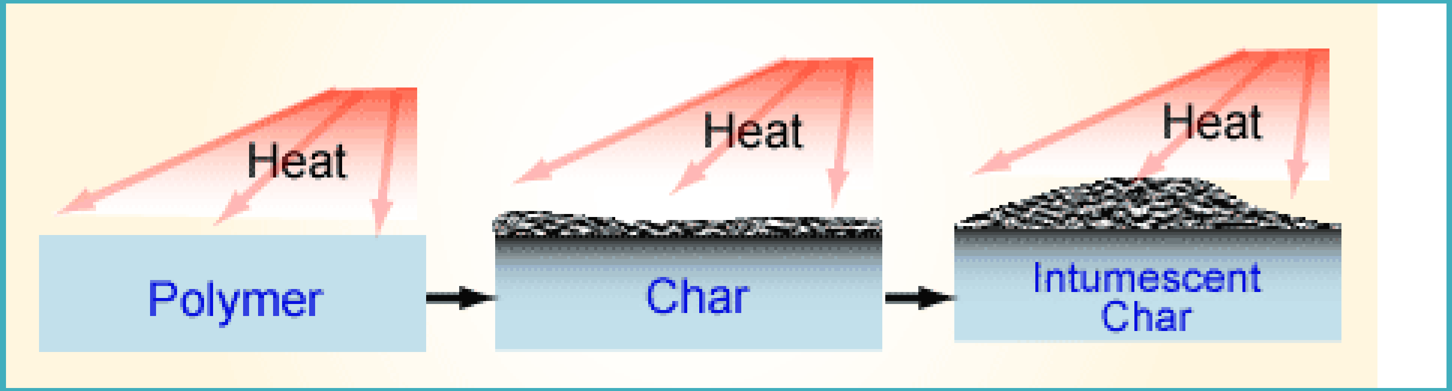
Aluminum Tri Hydrate(ATH):

$$2Al(OH)_3 \xrightarrow[+\ 1050\ kJ/kg]{200°C} Al_2O_3 + 3H_2O$$

Source: http://www.specialchem4polymers.com/tc/flame-retardants/index.aspx?id=9307
http://www.halogenfree-flameretardants.com/HFFR-72.pdf

Mechanisms of Flame Retardancy (Cont'd)

- Chemical Effect Condensed Phase
  - Char forming
  - Intumescent
    - Acid Donor (typically APP)
    - Carbon Source (typically pentaerythritol)
    - Blowing Agent (typically melamine)



Char and intumescence formation

Source: http://www.specialchem4polymers.com/tc/flame-retardants/index.aspx?id=9305

Common Flammability Tests

Limiting Oxygen Index

LIMITING OXYGEN INDEX (LOI)

In this vertical burn test the specimen is mounted in a cylinder which is supplied with an oxygen and nitrogen mixture from the bottom. The LOI value is the lowest oxygen concentration which will sustain burning of the specimen. A pilot flame from the top is used for ignition. In contrast to other vertical tests, the specimen burns downwards. The LOI value gives an approximate indication how well a material burns, e.g. LOI of around 20 (the natural concentration of oxygen in air is 21%) and below indicate easily ignitable materials.

These standards define the LOI method: ASTM D 2863, BS ISO 4589-2, NES 714.

Source: Electrics & Electronics - Pinfa
www.pinfa.eu › applications › electrics-electronics

UL 94

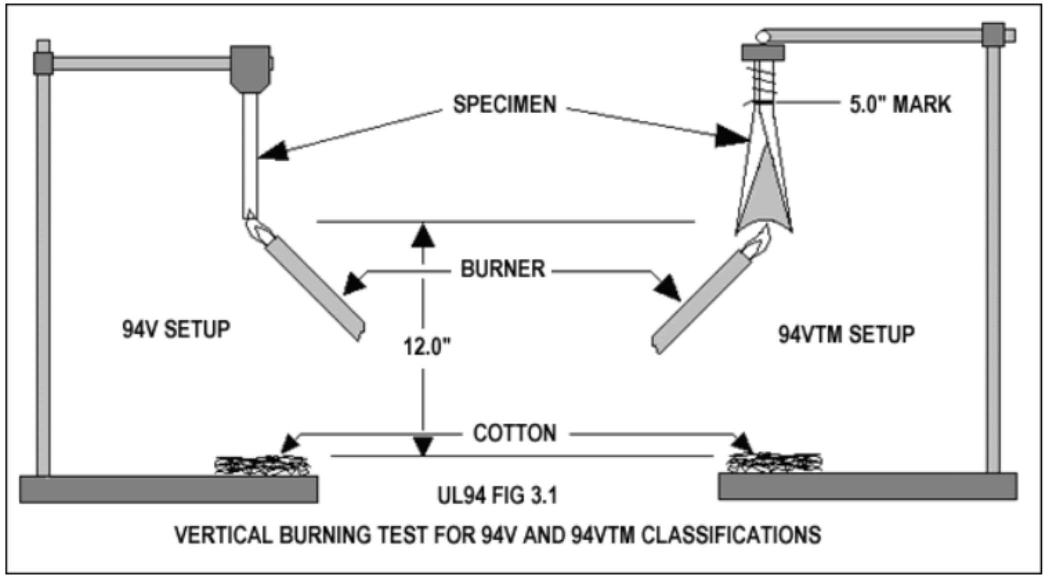
UL 94

The UL 94 test is the most commonly referenced test in the E&E sector. It is a good measure of flammability of materials by a small ignition source like a match, a candle or similar – the pilot flame has an energy output of 50 W. The sample can be oriented horizontally or vertically, the latter being the more challenging test. The classification result depends on how long the specimen continues to burn after removal of the pilot flame and whether a cotton piece below is ignited by flaming droplets.

The test is defined in these standards: Underwriters' Laboratories (UL) 94, ASTM D 3801, IEC 60695-11-10, IEC 60707, ISO 1210.

Source: Electrics & Electronics - Pinfa
www.pinfa.eu › applications › electrics-electronics

UL 94 VTM



UL94 Figure 3.1 -- Vertical Burning Test for 94V and 94VTM Classifications

- The specimen size is 8" x 2").
- The specimen is rolled longitudinally around a ½" dia. mandrel and taped on one end. When the mandrel is removed the specimen forms a cone shape, which provides rigidity to the length of the specimen (see Fig. 3.1)
- The two flame applications have duration of three seconds instead of ten.

Although this test was designed for thinner gauge materials, any material can be tested using 94VTM as long as can be formed around a ½" mandrel. The test is performed in the same manner as 94V with the above mentioned differences. The Material Classification criteria is also the same as 94V (see Table 1.) except that no specimens shall have flaming or glowing combustion up to a mark 5" from the bottom (free end) of the specimen.

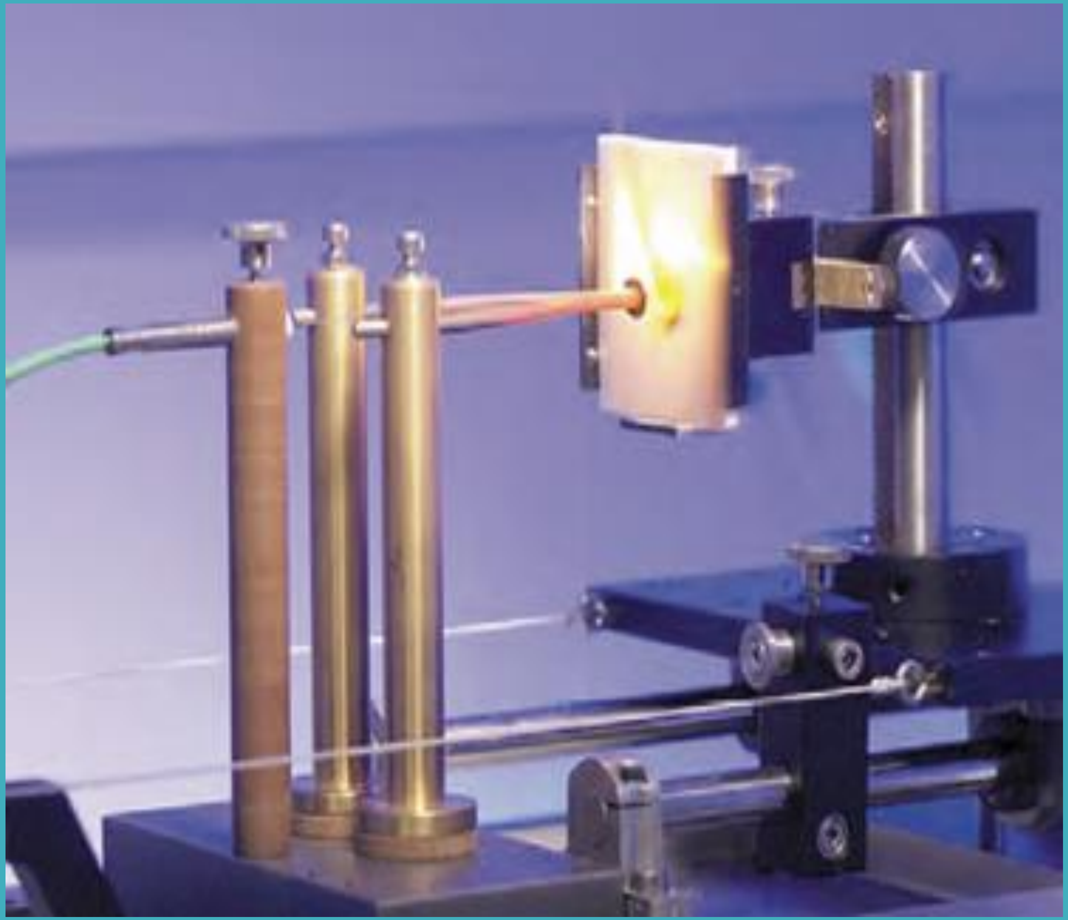
Source: http://fr.polymerinsights.com/testing/flammability/ul94

Glow Wire Test

GWT

The glow wire test (GWT) uses a heated resistance wire which is pressed against the specimen for 30 sec, then withdrawn. For a given glow wire temperature, the test criterion is whether the specimen ignites on contact (or in the 30 sec after withdrawal) and whether droplets can ignite a filter paper below the specimen. The glow wire ignition temperature (GWIT) relates to the ignition of the sample where only a flame of very short duration is permitted (< 5 sec). The glow wire flammability index (GWFI) indicates the temperature where the occurrence of flames is less than 30 sec.

The test is specified in these standards:
IEC 60695-2-10 to 13.



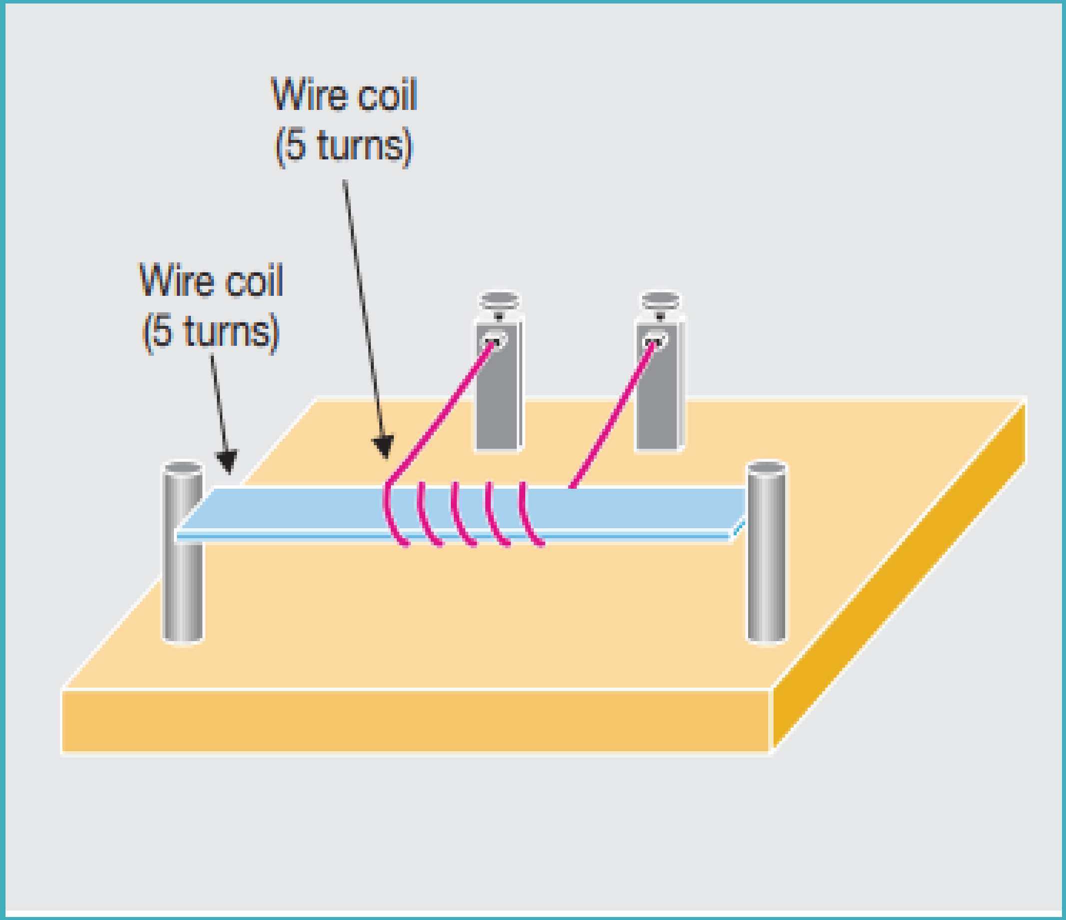
Source: Electrics & Electronics - Pinfa
www.pinfa.eu › applications › electrics-electronics

Hot Wire Index

HOT WIRE INDEX (UL 746C)

The hot-wire ignition performance is expressed as the mean number of seconds needed to either ignite standard specimens or burn through the specimens without ignition. The specimens are wrapped with resistance wire that dissipates a specified level of electrical energy. Performance level categories (PLC) from 0 to 5 are defined depending on the time to ignition (> 120 sec to < 7 sec).

www.ul.com/plastics/746C.html



Source: [Electrics & Electronics - Pinfa](www.pinfa.eu)
www.pinfa.eu › applications › electrics-electronics

FMVSS 302

FMVSS 302 (automotive vehicles: car, bus)

Specimens taken from the passenger compartment are clamped horizontally and subjected to a Bunsen burner flame for 15 s. The rate of flame spread measured over a distance of 254 mm should not exceed 101.6 mm/min for any of the specimens. The specimen thickness must correspond to that of the component and should not exceed 12.7 mm. This test is also used for buses.

The standard is in accordance with DIN 75200 and ISO 3795.

Source: https://www.pinfa.eu/applications/transport/

Cone Calorimeter

ISO 5660-1 Cone calorimeter (rate of heat release)

Time-depending determination of the site-related heat release with the oxygen consumption method.

Heat flux: 25 kW/m^2 or 50 kW/m^2

Duration of examination: 20 min

Specimen dimensions: (100*100* <50) mm

Source: https://www.pinfa.eu/applications/transport/

NBS Smoke Chamber

BS 6401; ASTM E662; NFPA 258 Options: ISO 5659/IMO FTPC Part 2; ATS 1000.001/ABD0031; NES 711

The Smoke Density Chamber has been established for many years and is used widely in all industrial sectors for the determination of smoke generated by solid materials and assemblies mounted in the vertical position within a closed chamber.

This widely-used test instrument measures the specific optical density of smoke generated by materials when an essentially flat specimen, up to 25 mm thick, is exposed vertically to a radiant heat source of 25 kW/m^2, in a closed chamber, with or without the use of a pilot flame.

Source: https://www.fire-testing.com/nbs-smoke-density-chamber/

OSU Test

Heat release

For large parts inside the aeroplane passenger cabin, a heat release test was developed at Ohio State University (OSU).

Specimens:

Three specimens, surface 150 mm*150 mm

Specimen position:

vertical ignition source: 35 kW/m^2 radiant heat attack, pilot flame on lower end of specimen

Test duration:

5 min

Requirements:

Maximum heat release rate (HRR) within 5 min: 65 kW/m^2

Total heat release (HR) during the first 2 min: 65 $kW\ min/m^2$

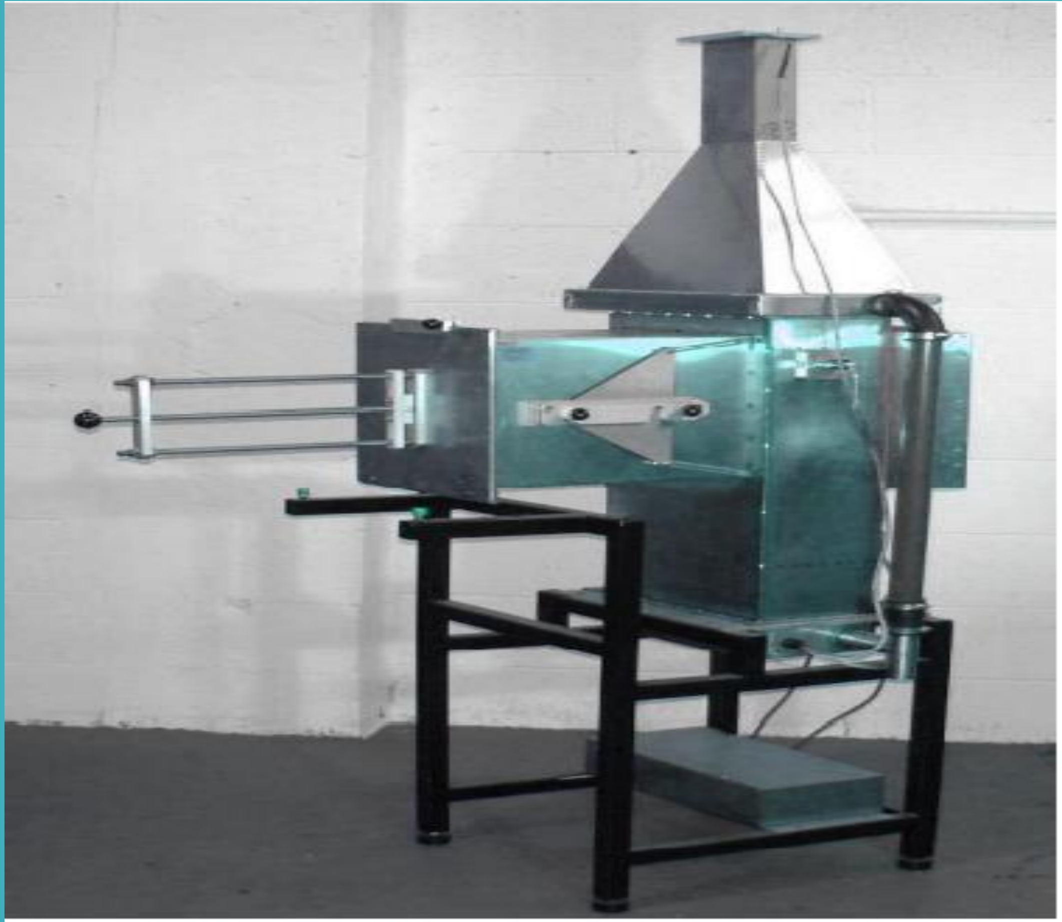


Photo Courtesy The Govmark Organization, Inc.

Source: https://www.pinfa.eu/applications/transport/

Source: DOT/FAA/AR-05/14, Richard E. Lyon and Marc L. Janssens, May 2005

Steiner Tunnel

The test apparatus is a large scale, horizontal furnace chamber into which a 24-feet long by 21-inch wide test specimen is inserted to form the ceiling of the tunnel, facing the floor of the apparatus.

During the ten-minute tests, materials are tested for flame spread when exposed to direct flame impingement from a large gas burner. Air and combustion products are moved through the tunnel by a ventilation system at a controlled velocity. The progress of the flame front across the test material is measured by visual observation through windows built into the tunnel, while the smoke developed from the test assembly is measured downstream from the apparatus, as a calculated product of photocell obscuration.

Source: https://www.element.com/fire/steiner-tunnel-testing

Non-Halogen Flame Retardant Chemistries

Flame Retardant (Chemicals) "Sustainability" Criteria

- "PBT" Profile
  - Persistence
  - Bio-accumulation (related to MW, e.g. low MW molecules vs. oligomerics/polymerics)
  - Toxicity
- Recyclability
- Life Cycle Analysis
  - Green House Gas Generation
  - Water/Electricity Consumption
  - Amount of Waste Products Generated
- Specific Restricted Materials
  - Melamine, BPA, Fluorine Content, nanomaterials, etc.

Chemical Assessment Strategies

- **SAFR® (ICL): Hazard vs. Exposure** https://safrworks.com/
- **GreenScreen®: Hazard Assessment based on various factors** https://www.greenscreenchemicals.org/
- **ECHA (European Chemicals Agency): Hazard Assessment/Exposure Assessment** https://echa.europa.eu/guidance-documents/guidance-on-information-requirements-and-chemical-safety-assessment
- **EPA (Environmental Protection Agency): Risk Assessment as a function of (How much is present, How much Exposure, How Inherently Toxic)** https://www.epa.gov/risk
- **Danish EPA: Use of (Q)SAR as a tool** https://eng.mst.dk/chemicals/chemicals-in-products/

Polymer Pyramid

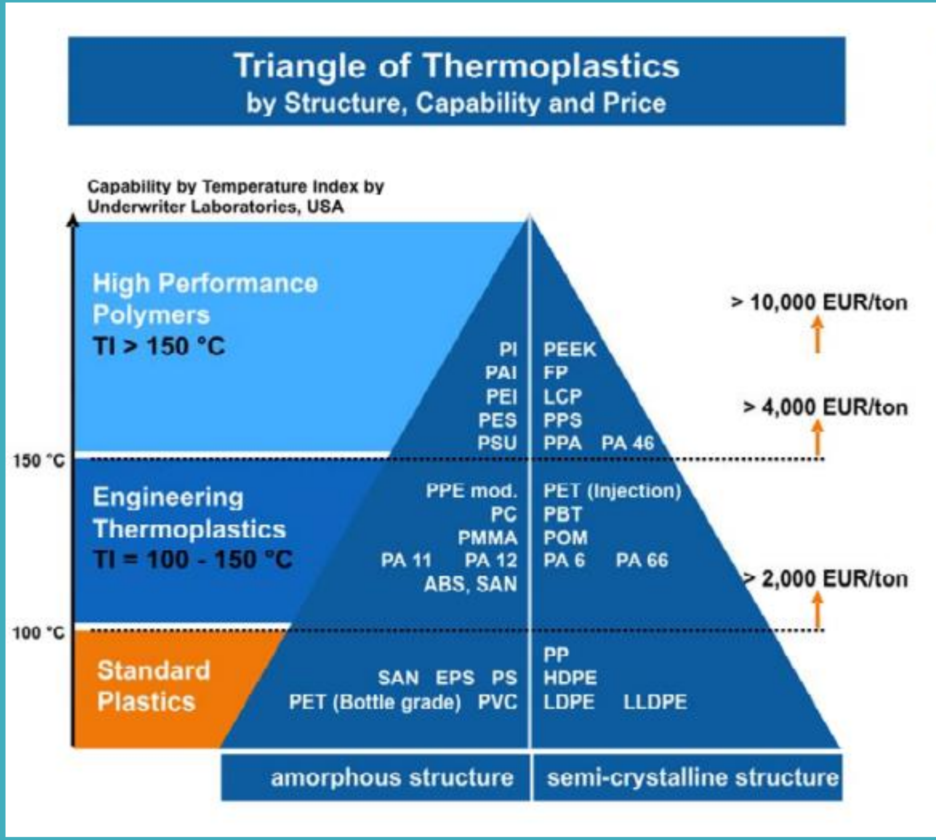


Figure 4: The pyramid or triangle of thermoplastics shows their ranking by capability, structure, and price (source: PlasticsEurope Market Research Group, PEMRG, 2010)

Source: https://www.pinfa.eu/applications/transport/

Almost All of the Standard ("Commodity") Plastics, All of the Engineering Polymers and All the High Performance Nylons Require Flame Retardants to Make Them "Flame Retarded"

POLYMER	LOI, %	UL 94 RATING
PS	18	HB
PVC	45	V0
SAN	18-19.5	HB
HIPS	18	HB
PE	17	HB
PP	17	HB
PMMA	17	HB
ABS	18	HB
CPVC	52	V0
PBT	23	HB
PVDF	44	VO
PA6	24	HB
POM	15	HB
PA11	23	NR
PA12	24	HB
PA66	24	HB
TPU	23.5	HB
COC	n/a	n/a
PC	25	V2
mPPE (Noryl® N110)	19	HB
PET	20	HB
PEN	32	V2
PEI	47	V0
PPS	44	V0
PESU	36	V1
PPSU	38	V0

Sources: DOT/FAA/AR-05/14,Richard E. Lyon and Marc L. Janssens, May 2005
https://omnexus.specialchem.com/polymer-properties/properties/fire-resistance-loi
ww.solvay.com
https://www.researchgate.net/publication/343331325_Flame-Retardant_Polyamide_Powder_for_Laser_Sintering_Powder_Characterization_Processing_Behavior_and_Component_Properties
https://www.researchgate.net/publication/321131295_Para_-Aramid_fiber_modified_by_melamine_polyphosphate_and_its_flame_retardancy_on_thermoplastic_polyurethane_elastomer/figures?lo=1http://www.indochempolymers.com/media/product/1764241773_Noryl_N110.pdf

Use and Cost of Flame Retardants

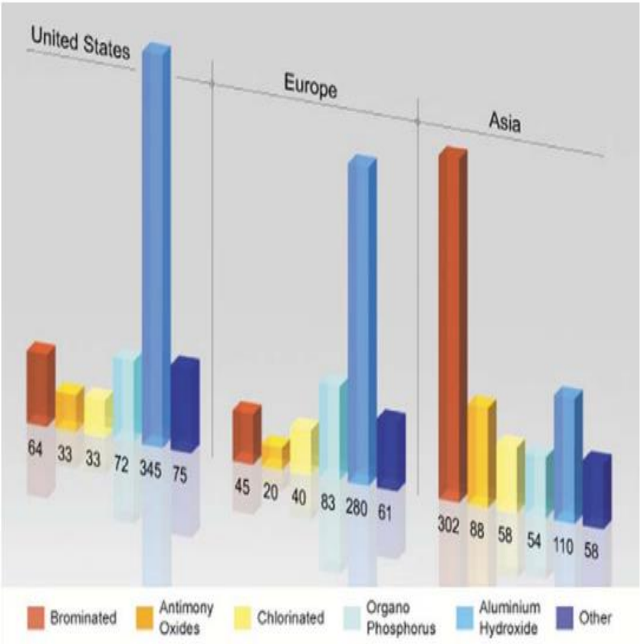


Figure 2: Global consumption of flame retardants by volume, split into regions, which total 1.8 million metric tons (for 2007, source: SRI Consulting, graphics courtesy of www.flameretardants-online.com)

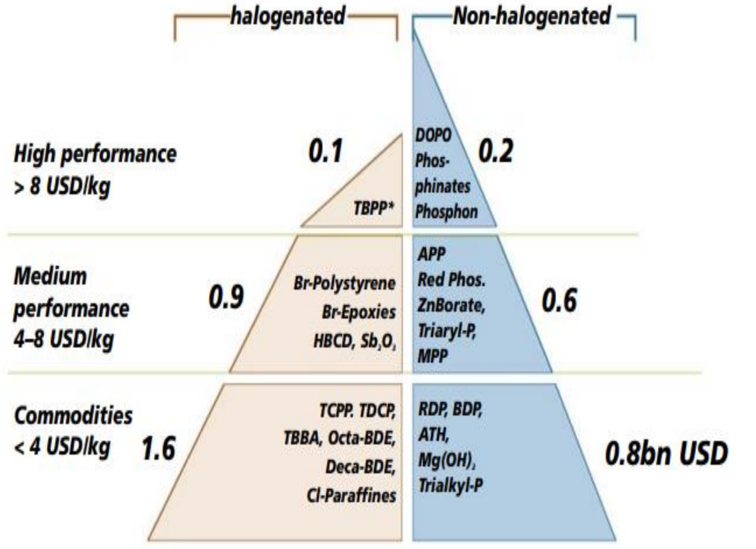


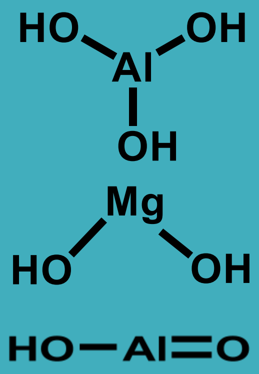
Figure 3: The area of a triangle represents the market share by value, indicated in billion USD. The total FR market size is 4.2 billion USD (2007). For abbreviations see the list of abbreviations.

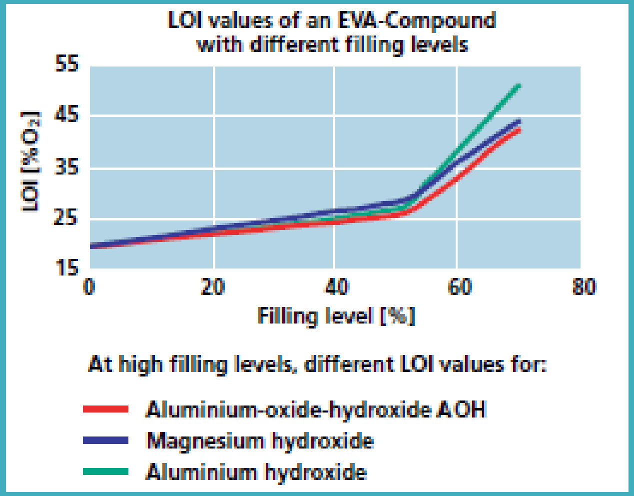
Source: https://www.pinfa.eu/applications/transport/

Non-Halogen FR Chemistries

- **Inorganic Hydrates**
- **Melamine and Derivatives**
- **Phosphorus Compounds**
- **Strong Acids**
- **N-Alkoxy Hindered Amine (NOR HAS)**
- **NHFR “Helpers”**

Inorganic Hydrates





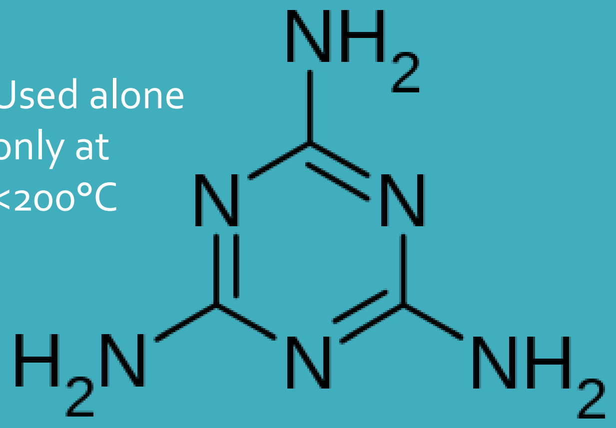
- Aluminum Trihydrate: $Al(OH)_3$
- Magnesium Dihydroxide: $Mg(OH)_2$
- Boehmite: γ-AlO(OH)
- All act as flame retardants by a strongly endothermic reaction which releases water, thus cooling the flame
  - Typically need high loadings in polyolefins and EVA systems, e.g. >>30% and typically ~65%.
- Inorganic hydrates release water at various temperatures; need to be aware during processing
  - ATH, 220º-350ºC
  - Boehmite, 250º-350ºC
  - MDH, 332ºC upwards

Sources:
HTTPs://www.hubermaterials.com/products/flame-retardants-smoke-suppressants/benefits-surface-treated-ath-and-mdh-grades.aspx
https://nabaltec.de/en/products/boehmite/

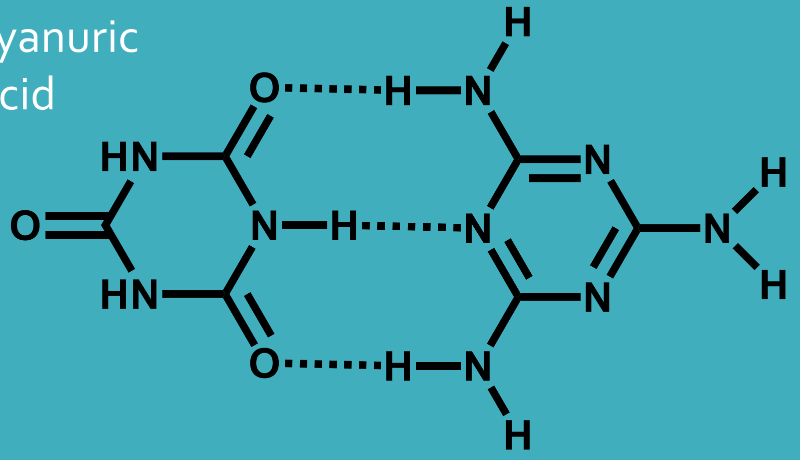
Melamine and Derivatives

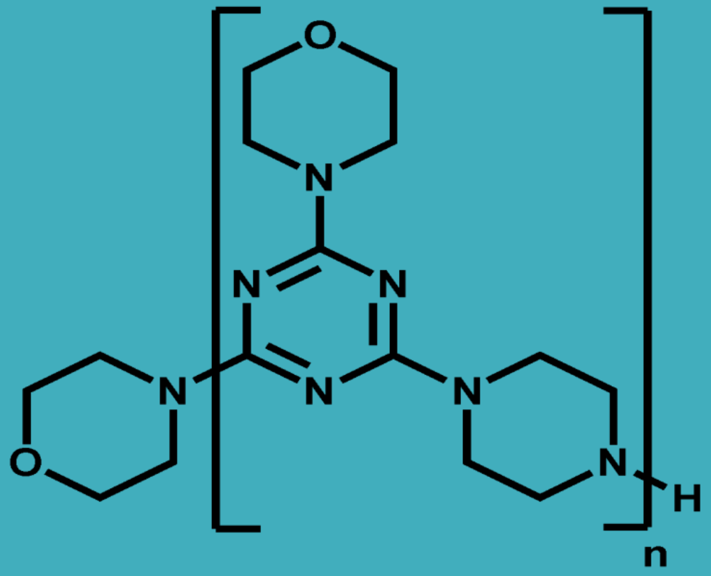
Melamine

Used alone only at <200°C



Cyanuric Acid





Combined with acidic species:

- Boric Acid
- Phosphoric Acid
- Pyro/Polyphosphoric Acids

Typically used in nylon, PE, PP and TPU formulations. Used in conjunction with phosphinate salts.

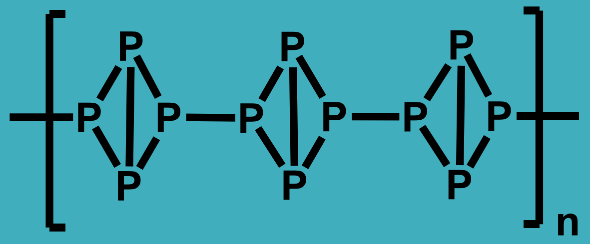
Used with Ammonium Polyphosphate and Inorganic Hydrates in Polyolefins. Polymeric

Sources: https://www.pinfa.eu/applications/transport/
https://www.mcatechnologies.com/products/fire-retardants/index.html

Elemental Red Phosphorus

- **Particularly effective when used with condensation polymers such as polyamides, polyesters, polyurethanes**
- **For polyolefins and polystyrene recommend the combination with synergists**

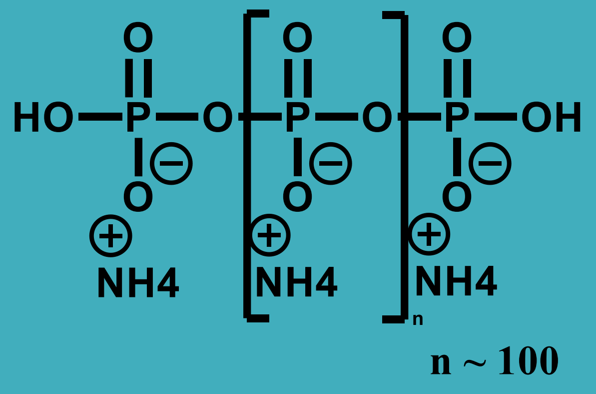
Works very well in Nylons. HOWEVER gives nylon a red color and must be handled carefully (dry!!!) as can form toxic phophine and diphosphane (a.k.a. diphosphine) gases, PH_3 and P_2H_4 respectively.

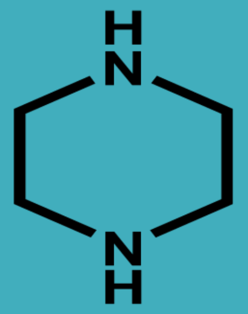


Source: https://www.clariant.com/en/Solutions/Products/2014/03/18/16/31/Exolit-RP-607

Ammonium Polyphosphates

- These materials along with inorganic hydrates are the major NHFRs used in polyolefins. Potential issues are water absorption and the effect of their ionic character on electrical properties, especially in humid/wet environments.
- Ammonium salt can be replaced with other nitrogen bases, e.g. piperazine



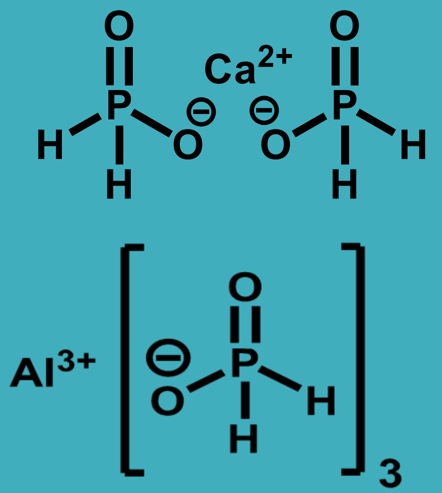


Piperazine

Sources: https://www.jlschemicalusa.com/
https://www.budenheim.com/en/solutions/themen/hffr/
https://www.adeka-pa.eu/specialty-additives/flame-retardants/adk-stab-fp-2500s

Hypophosphites

Also referred to as metal phosphinates



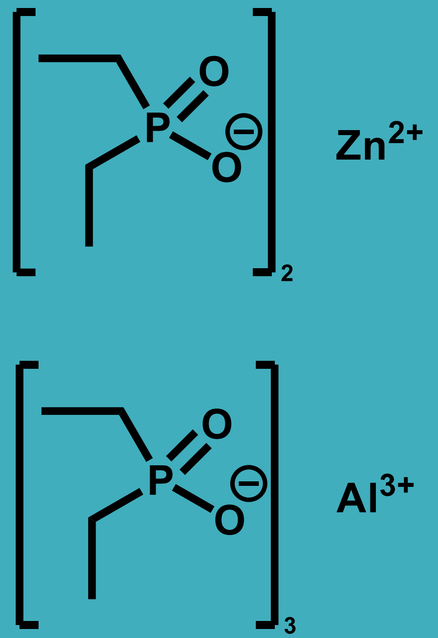
Counter ion is typically Al^{+3} or Ca^{+2}

Use in PBT and reportedly in PC, as well PC/ABS, PS, TPU and some engineering polymers like PBT and PA6 but need to be aware of possible generation of phosphine. Generally used with melamine derivatives.

Source: [Electrics & Electronics - Pinfa](www.pinfa.eu › applications › electrics-electronics)
www.pinfa.eu › applications › electrics-electronics

Phosphinates

Proprietary technology. Generally used with a nitrogen or other synergist. Hydrolytically stable and acts like a filler.
In certain instances neutralizers may be needed.



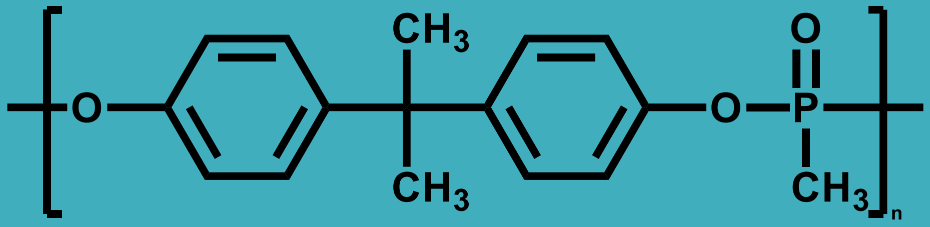
M^{n+} is typically Al^{+3} or Zn^{+2}

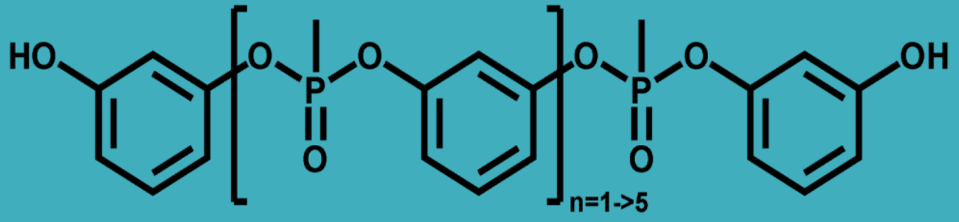
Neat phosphinate salts are reported to work in the gas phase while the synergist melamine derivative works primarily in the condensed phase. Work very well in nylons, TPEs and in polyesters (Zn salt)

Source: www.Clariant.com, “EXOLIT® FLAME RETARDANTS FOR THERMOPLASTICS” Brochure

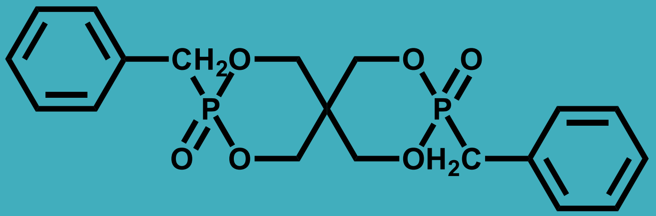
Phosphonates

Polymeric/
Oligomeric

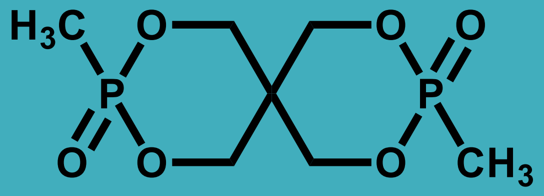




Aryl alkyl



Aliphatic

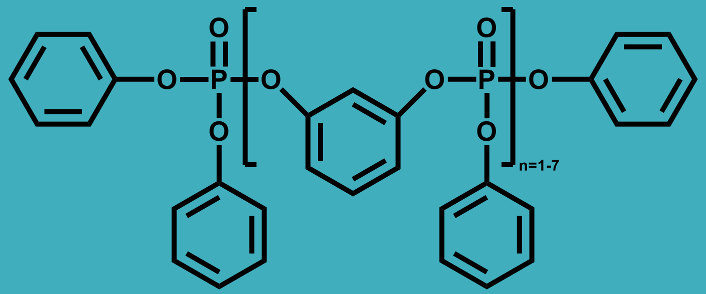


Polymeric versions are moldable polymers in their own right. Copolymers with PC are commercially available. The oligomeric forms are glasses at room temperature. Particularly useful in PC, PC blends, polyesters and TPU
The aliphatic phosphonate being used primarily as a very efficient "booster" in NHFR systems using another primary NHFR flame retardant.

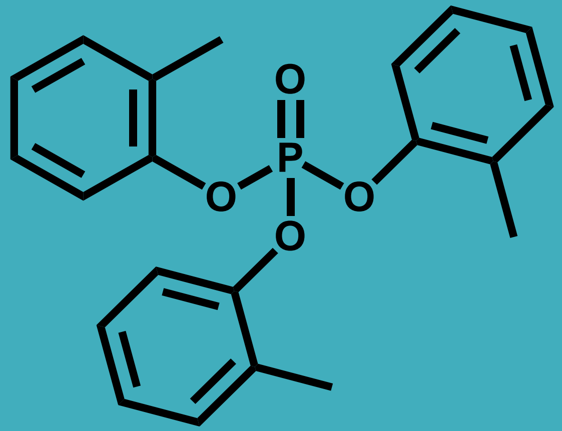
Sources: https://www.frxpolymers.com/nofia-products-1
https://www.thor.com/flameretardantsthermoplastics.html
https://www.teijin.com/products/resin/fg-fcx/

Phosphate Esters

Oligomeric



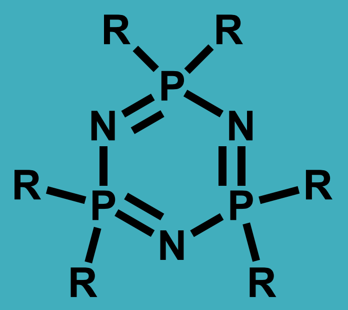
Widely used but can act as a plasticizer reducing Heat Distortion Temperature and Impact. Generally aromatic phosphates are used in Engineering Resins (PC, PC/ABS, ABS, PPE/PS) but aliphatics are used in PVC and other resins.



Monomeric

Source: https://www.adeka.co.jp/en/chemical/products/plastic/pro119c.html

Phosphazenes



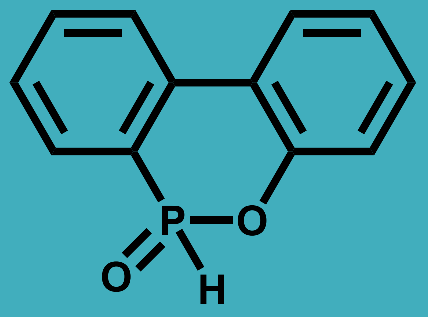
R = -OPh

Extremely hydrolytically stable even against 125ºC steam. Very good thermal stability. Some functionalized derivatives are available on a developmental basis.

Useful in various polymers, e.g. PC, PPE, PET, PBT, HDPE

Sources: https://www.otsukac.co.jp/en/products/flame-retardant/phosphazene/
https://hunan-chem.com/flame-retardant-absorb-burning-heat-plastic-coating-choke-burning-surface/

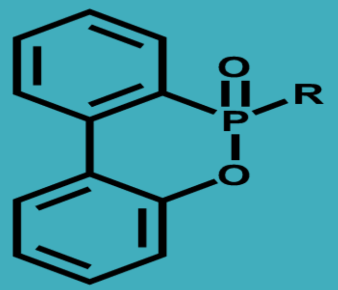
DOPO and Derivatives



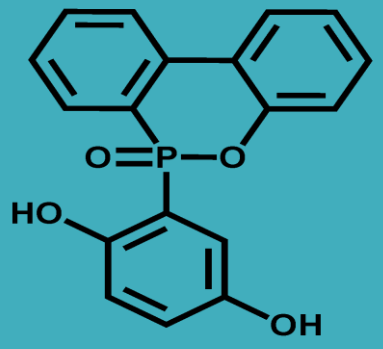
DOPO, a.k.a.
9,10-Dihydro-9-oxa-10-phos phaphenanthrene-10-oxide

Sources: https://hunan-chem.com/
https://greenchemicals.eu/

One of the P-based NHFR additives that does have vapor phase activity.
During combustion DOPO and its derivatives release $PO_2^{\cdot}$ and $PO^{\cdot}$ Radicals
Can be used in ABS, PS, PP, PPE,PC
Reactive NHFR which allows derivatization
Suitable derivatives can be used in polyesters, polyamides, and high temperature polymers



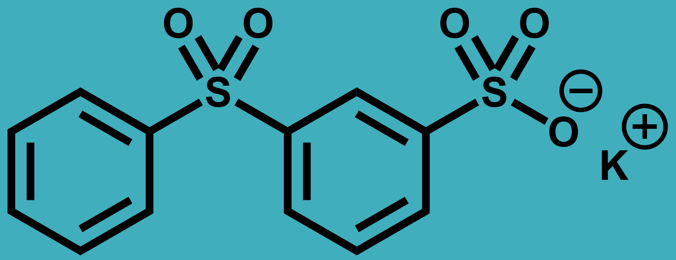
DOPO Derivative



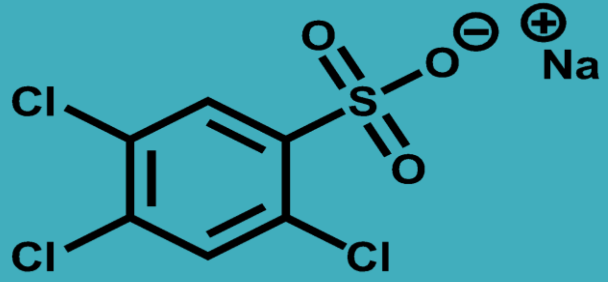
DOPO-HQ

Strong Acids

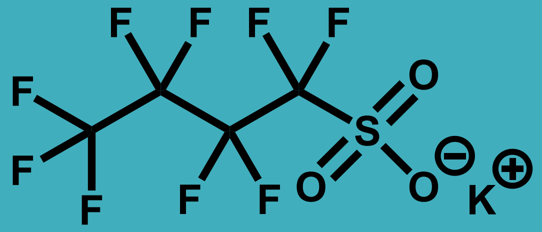
KSS



STB



“Rimar Salt”

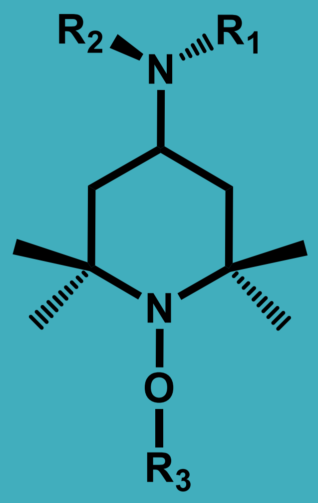


Typically used in PC and PC blends. Must have a critical amount of PC to produce char. Charring mechanism is fairly specific to PC.
At combustion temperatures, salts form strong acids that promote PC dehydration, rearrangement and charring.

Sources: http://www.arichem.com/products/flame-retardants.html
https://www.3m.com/3M/en_US/company-us/all-3m-products/~/3M-Flame-Retardant-Additive-FR-2025/?N=5002385+3292670434&rt=rud

N-Alkoxy Hindered Amine (NOR HAS)

- **Used in polyolefins in thin sections (~200 micron) in films, fibers**
- **Can be used synergistically with P-based NHFRs e.g. phosphate esters, aliphatic phosphonates and ATH**
- **Provides UV and thermal stability as well as flame retardancy**



Sources:
https://www.researchgate.net/publication/316716408_NOR-based_Flame_Retardant_and_Versatile_Synergist
https://www.adeka-pa.eu/specialty-additives/flame-retardants/adk-stab-fp-t80
https://www.clariant.com/en/Solutions/Products/2014/06/17/08/11/Hostavin-NOW-pills-XP

NHFR "Helpers"

- **Borates, e.g. Zinc Borate**
- **Talcs/Nano-clays**
- **Expandable Graphite**
- **Silicones**
- **PTFE/SAN encapsulated PTFE (T-SAN) Drip Suppressants**
- **Molybdate Smoke Suppressants**
- **Tin Additives**
- **Others: CNT, Graphene**

Non-Halogen Flame Retardants for Major Thermoplastics

Sources: Unless specific reference is noted, the references used are the same as used for the NHFR additives

Polyolefins

- PP, HDPE:
  - Inorganic Hydrates:
    - ATH
    - MDH
    - Boehmite
  - Polyphosphates
    - APP
    - Piperazine Derivative
  - N-Alkoxy Hindered Amine (NOR HAS)

Polyesters

- **PBT, PET, PTT, PLA, PCT**
  - **Polyphosphonates: Homo and Copolymer**
  - **Zn Diethyl phosphinate + melamine derivative synergist**
  - **DOPO Derivatives**

Polyamides

- PA6, PA66
  - Red Phosphorus (PA 66)
  - Melamine Derivatives, e.g. Melamine Cyanurate
  - Aluminum Diethyl Phosphinate + melamine synergist
  - Hypophosphites
  - DOPO Derivatives

Polycarbonate

- Homopolymer
  - Strong Acid Salts
    - KSS
    - STB
    - Potassium Perfluoro butane sulfonate
  - Phosphorus Compounds
    - Phosphazene
    - Phosphate esters
    - Polyphosphonates
    - Hypophosphites

Polycarbonate Blends

- PC/ABS
  - Phosphates
  - DOPO
  - Phosphazene
  - Hypophosphites

- PC/Polyesters
  - Polyphosphonates
  - Phosphates
  - DOPO
  - Phosphazene
  - Hypophosphites

PPE Blends

- PPE/HIPS
  - Phosphate Esters
  - Phosphazene
  - DOPO

Polystyrene

- **HIPS/PS**
  - **PPE/Tetraphenyl resorcinol phosphate/nanoclay**
  - **Expandable graphite/resorcinol bis(diphenyl phosphate) or triphenyl phosphate/plus a co-additive, e.g. PC to prevent phosphate migration**
  - **MDH/red P**
  - **Melamine phosphate/expandable graphite**

Sources:
https://www.researchgate.net/publication/249355494_Flame_Retardants_for_Polystyrenes_in_Commercial_Use_or_Development
https://www.sciencedirect.com/science/article/pii/S0141391014001049
https://www.researchgate.net/publication/318965886_Synergistic_effect_of_expandable_graphite_and_melamine_phosphate_on_flame-retardant_polystyrene

Formulating with Non-Halogen Flame Retardants

Flame Retardancy Formulation Criteria

- **What Flammability Test are You Looking to Pass?**
  - **Electronics: UL 94 V?**
  - **Building and Construction: ASTM E-84**
  - **Aircraft Interior: OSU, etc.**
- **What Behaviors of a Fire Are You Interested in Modifying?**
  - **Flame Ignition**
  - **Flame Spread**
  - **Smoke Density**
  - **Toxicity of Evolved Gases**
  - **Dripping**
- **What Material Constraints Do You Have**
  - **Non-Halogen, Halogen-Free? What is Defined as "Halogen-Free"?**
  - **No Red Phosphorus, BPA? Other Customer "Do Not Use" Ingredients?**
  - **Chemical Listing Requirements e.g. TSCA, REACH, etc.**

Flame Retardancy Formulation Criteria

- **How will the Composition Be Processed? Injection Molding, Extrusion, 3D Printing, etc.**
  - **Processing Temperature Considerations**
- **What Ultimate Application Environment Is Expected?**
  - **Outdoor**
  - **Underwater/Humid Environment**
- **What is the Cost Target**
  - **NHFR Formulations are Typically More Expensive than Halogenated Ones**
    - **Lower Volume Specialty Chemicals**
    - **Loading Level is ~2x of Halogenated: Due to Gas Phase vs. Condensed Phase Mechanism**

Flame Retardancy Formulation Criteria

- What Other Considerations, e.g. Color, etc.
- How Will the NHFR Affect Other Required Properties
  - Impact
  - Heat Distortion Temperature
  - Flow
  - Processing
  - Long Term Stability e.g. Thermal Aging, UV Stability, etc.
  - Others
- There Will Be Trade-offs, Need to Identify and Prioritize “Must Haves”

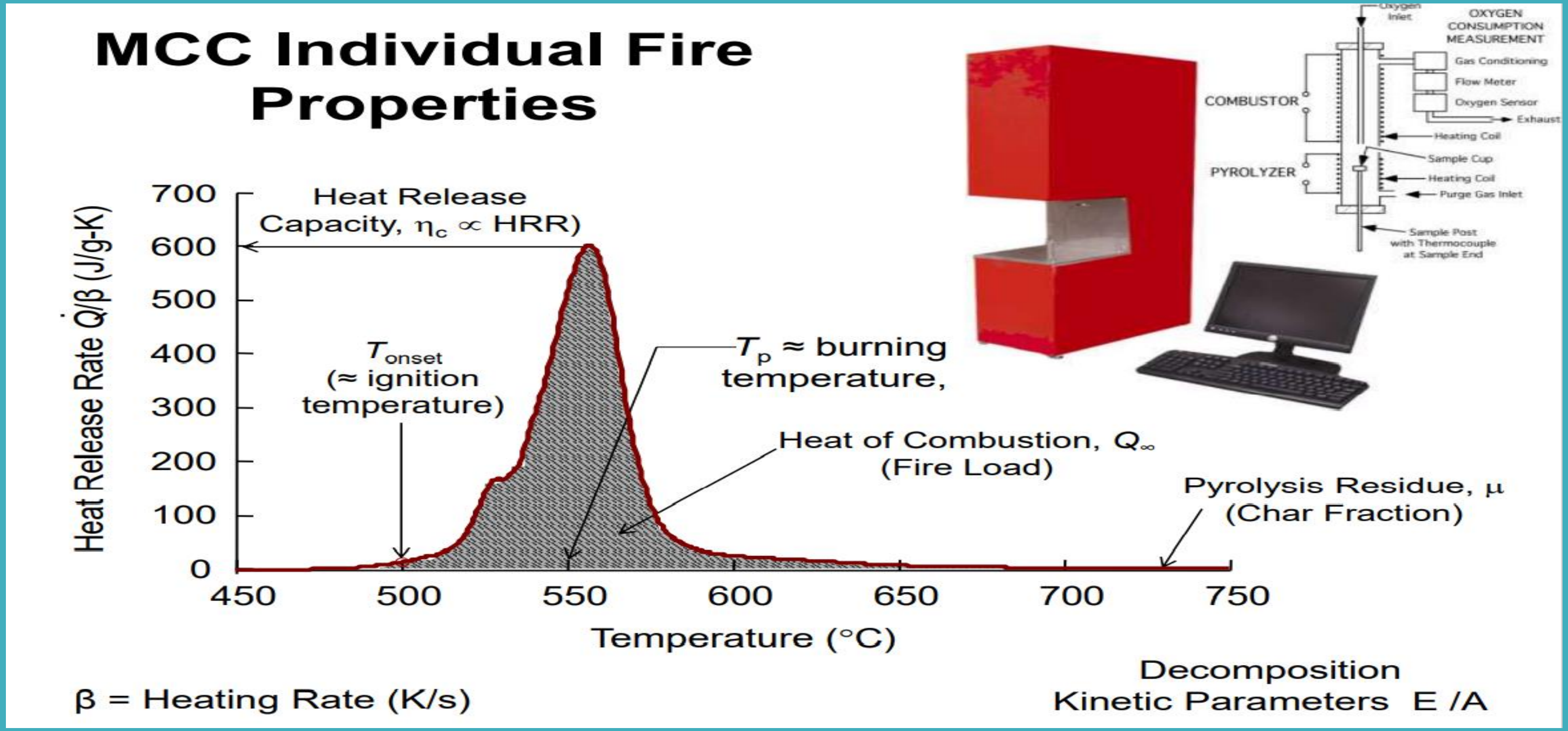
Formulators' Screening Flammability Tests

- Simple Burning of Extruded Strands
  - Use instead of Molded Bars
    - UL 94 HB
    - UL 94 V
    - LOI
  - Allows Quick Screening of Formulations; No Need for Molding
  - Early Screen for Dripping Behavior and Smoke Generation
  - Looking for Overt Effects/Behavior
- Actual LOI/UL 94 Tests
- MCC Microscale Combustion Calorimetry (requires ~3-5 mg pellet sample/test)

Sources: R. Avakian
https://onlinelibrary.wiley.com/doi/abs/10.1002/pen.2087

Formulators' Screening Flammability Tests

- **MCC Microscale Combustion Calorimetry (requires ~3-5 mg pellet sample/test)**

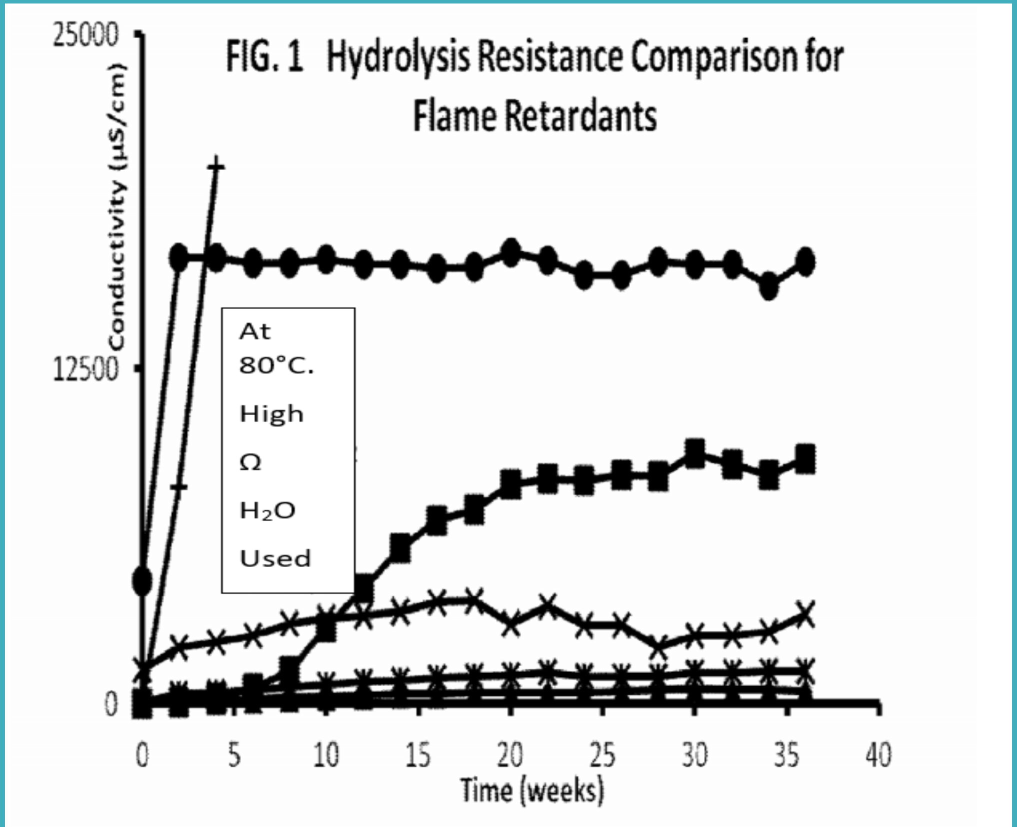


- A large amount of data is obtained with a very small sample
- Several testing labs have this equipment
- Information is valuable to customers
- UL is using as well for monitoring submissions

Formulators' Tips

- **Use the Literature: PINFA Brochures, Suppliers' Information, Publications, Patents, Colleagues, Conferences/Webinars (SPE, PINFA, etc.)**
- **Video tape flammability tests! Don't rely just on the numbers or the rating!**
  - **Seeing the burning behavior accelerates formulation development/optimization**
- **Consider use of multiple flame retardants to modify melting point, gain FR synergy and minimize individual polymer solubility limits**
- **Run a quick "recycle study", e.g. multiple pass extrusions, to see how robust your formulation is (not just for NHFR formulations)**
- **Understand the inherent properties of your NHFR, e.g. gather TGA data, water absorption, effect of water, etc.**

Quick Water Sensitivity Test: “Tea Bag” Test



Test is based on the principle that upon hydrolysis, ionic species are generated that increase the conductivity of the water, thus a high conductivity reading versus time is not desired. The initial reading is most likely due to the inherent ionic content before elevated temperature exposure.

- Place a fixed amount of flame retardant powder (~1-5 g) into filter paper, wrap it with rubber bands.
- Place “tea bag” into a glass jar with a given amount of high conductivity, distilled water. (measure conductivity of water before hand)
- Close jar and weigh.
- Place in 80°C oven
- Place control without FR into same oven
- Measure conductivity with a conductivity meter at regular intervals (measure after 24 and 48 hrs. to determine frequency)
- Make sure same amount of water is present in the jar by weighing

Source: US Patent 9,944,795

Conclusions

- No ONE NHFR additive can work in all applications, polymers and tests
  - Many times several additives are used together along with “helpers” to influence flame behavior, smoke and dripping behavior
- Flammability requirements are becoming more comprehensive with regard to addressing:
  - Heat Generation
  - Flame Spread
  - Smoke Generation
  - Smoke Toxicity
- PBT (Persistence, Bio-accumulation, Toxicity) and LCA (Life Cycle Analysis) are Becoming Key Factors in Choosing NHFR Candidates
- Cost Effectiveness is ALWAYS a Key Consideration

PINFA/SPE June 2021 Webinar Series

Need Formulating Tips?

pinfa North America
Phosphorus, Inorganic & Nitrogen Flame Retardants Association

New Workshop Series from Pinfa-NA
Non-Halogen Flame Retardant Formulator's Workshop

spe

With our specialized workshop series, Pinfa-NA offers insight and knowledge to help with formulating materials for fire safety.

This workshop series provide detailed instruction in Flame Retardant Basics and Test Videos, NHFR Thermoplastics, Emerging NHFRs and TPE/Thermosets.

June 2021

June 1 • June 8 • June 15 • June 21

Suggested Resources/Literature/References

- Pinfa Brochures on Electronics, Building & Construction and Transportation: https://www.pinfa.eu/media-events/brochures-publications/
- Suppliers Literature/TDS/Recommendations
- "Non-Halogenated Flame Retardant Handbook", Alexander B. Morgan and Charles A. Wilkie, Wiley, 2014
- "Polymer Green Flame Retardants", Edited by Constantine D. Papaspyrides and Pantelis Kiliaris, Elsevier, 2014

Polling Questions: Webinar

- Would you recommend this webinar to your colleagues?
  - Yes
  - No
- Do you plan on attending the NHFR Webinar series in June?
  - Yes
  - No

QUESTIONS?

- Contact Information:
  - Roger Avakian, Avakian PolyChem Consulting LLC
  - Email: avakianpolychem@gmail.com