American Chemistry Council | North American Flame Retardant Alliance

NO IGNITION, NO FIRE!

One-Size-Fits-All Policies:

Why Different Products Call for Different Chemical Compounds

Wednesday, September 7, 2022

Introductions & Background

Moderator & Panelists

- **Moderator**
  - Owen Jappen
- **Panelists**
  - Peter Fisk – Principal, Green Chemical Design
  - Ben Gann – Director, American Chemistry Council
  - Ralph Buoniconti – Sr. Regulatory Engineer, SABIC

Agenda

01

EUROPEAN REGULATORY APPROACH

02

NORTH AMERICAN REGULATORY APPROACH

03

PRODUCT DESIGN CONSIDERATIONS

04

QUESTIONS & DISCUSSION

American Chemistry Council

About NAFRA

- **ACC’s North American Flame Retardant Alliance (NAFRA)**
    - Represents leading producers of flame retardants used in industrial and consumer applications
- **Dedicated to improving fire safety in a variety of product applications**
- **Members include Albemarle, LANXESS, and ICL Industrial Products**

Why are flame retardants are used in products?

- Increased use of electronics & electrical equipment in homes
- Polymers/plastics enhance design & optimize performance
- Changing energy sources & output of electronics – and increased use of plastics – increases fire risk
- In 2021, US CPSC recalled over 6.2 million units due to fire/shock risk

Key Factors in FR Selection for Use in Products

- Physical Properties
- Ease of Compounding
- Adequate Thermal Stability
- Corrosivity Issues
- Compatibility
- Health & Environmental Toxicity
- Appearance
- UV Stability
- Electrical Properties
- Combustion Products
- Efficiency/Cost
- Circularity & End of Life

Trend Toward Broader Regulatory Approaches

- ECHA looking at possible approaches for grouping chemistries for assessment
- National (U.S.) PFAS testing strategy
- U.S. states passing legislation regulating chemistries by class
- Raises questions regarding consideration of exposure – and overall risk – in assessment of chemistries

Regulatory Landscape & Product Design

- **Differing regional approaches in regulating flame retardants**
  - Creating additional complexity for product manufacturers
- **Not using a risk-based model can lead to regrettable substitution**
- **Options needed for product manufacturers**
- **Increasing need for input from the value chain**

Why different products require different compounds

Current EU regulatory context for Phosphorus-containing FRs

Peter Fisk, Green Chemical Design

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September 7, 2022

RATIONALE

- Peter Fisk was asked by **pinfa** to review independently whether organophosphorus flame retardants (OPFRs) can be considered for regulatory purposes in one or more groups, based on science. This arose from EU regulatory activities.

- Focus of this talk is that regulation affects choice of substance, and regulation in the EU is always moving.

WIDER CONTEXT

*Some substances eg PFAS and many phthalates really **should** be grouped.*

There are various stakeholders who want to see all FRs put into one ‘box’.

The EU regulators have not set out such a single group but are looking closely at OPFRs.

Some OPFRs do have adverse properties, but not all. They have many different product applications, and different end of life scenarios.

What next? Let’s consider the regulations and the science.

REGULATORY CONTEXT

EU regulation is in principle lead by science then secondarily by socio-economic matters.

The hierarchy of EU regulatory activity

Green Deal >
  Chemicals Strategy for Sustainability >
    Restrictions Roadmap >
      Grouping as a means to speed decision-making compared to one substance at a time

See (for example) Commission Staff Working Document, April 2022
https://ec.europa.eu/docsroom/documents/49734

SCIENTIFIC METHODS

The stepwise methodology used was:

- Collect property data from REACH registration sources or reliable published sources where necessary;
- Examine the possibility of any coherent grouping in structure-based groups; those groups should be consistent with the hazard-related registration data and existing hazard classifications.

WEIGHT OF EVIDENCE

- The OPFRs subject to this study are data-rich in respect of the key requirements of the REACH Regulation
- There are many published papers using non-standard ‘short cut’ methods

➢ **Most weight of evidence should be given to high level regulatory studies**.

CONCLUSION ABOUT A SINGLE GROUP

Key finding #1

OPFRs should not be grouped together in one single group as this cannot be justified by conclusive scientific analysis, mainly due to their different toxicological properties (no extensive patterns can be seen).

ARE THERE ANY STRUCTURAL GROUPS? 1

There are potential structural groups of OPFRs based on **structural features and physicochemical properties.** These structural groups are:

- Trialkylphosphates
- Triarylphosphates
- Monoalkyldiarylphosphates
- Chloroalkylphosphates (already grouped in EU)
- Bisarylphosphates
- Phosphonates

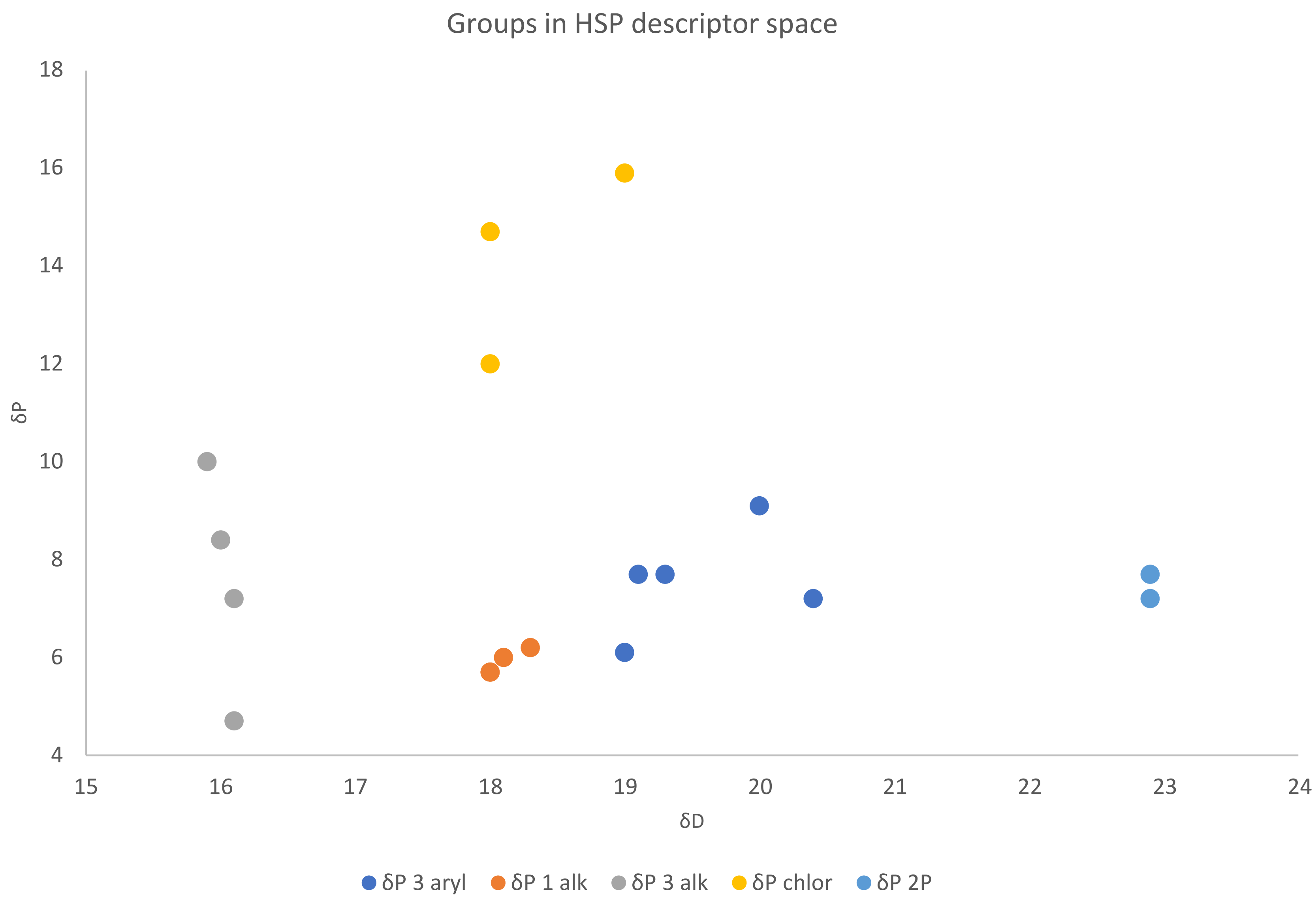
(example structures at the end)

ARE THERE ANY STRUCTURAL GROUPS? 2

The origin of the differences between these groups lies at least in part in the types and energies of fundamental intermolecular forces; these differences are shown well by examination of Hansen Solubility Parameters (HSP).

The figure following shows how for phosphates, the groups are formed in HSP property space (key is at the end).

GROUPING OF PHOSPHATE ESTERS FROM STRUCTURE AND HSP VALUES



ARE THERE ANY STRUCTURAL GROUPS? 3

Key finding#2

In short, the substance groups are fundamentally different!

Phosphonates are also different (figure shown at the end).

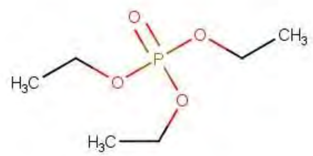
TECHNICAL CONCLUSIONS

- One large group for OPFRs is not sound science
- The structural groups in almost all cases have consistent toxicological hazard profiles;
- A case could be made to work one substance at a time or with the structural groups. This could be useful in respect of discussions with regulators.

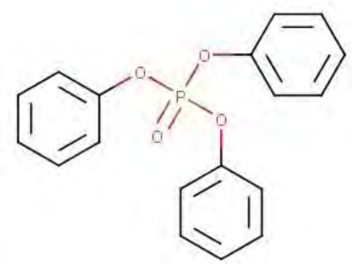
CONCLUSIONS FOR INDUSTRY

- Regulatory developments are a key business context
- Advocacy policy needs to be clear and strong
- In the EU, advocacy **must** be science-based firstly, with socio-economic factors coming second.

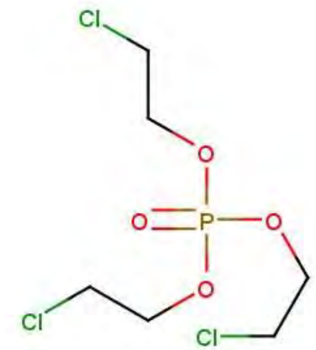
Annex: Examples



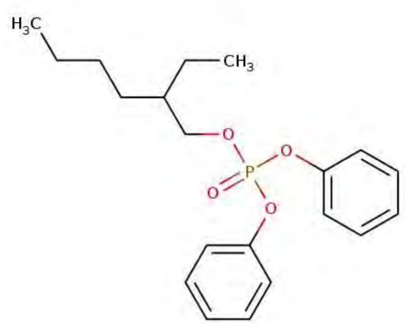
trialkyl phosphate



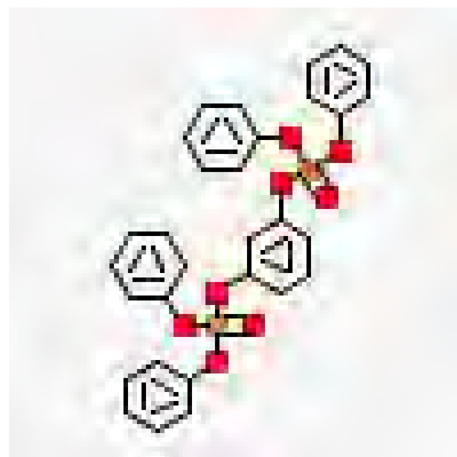
triaryl phosphate



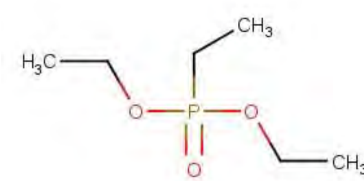
chloroalkyl phosphate



diaryl alkyl phosphate



aryl bisphosphate



phosphonate

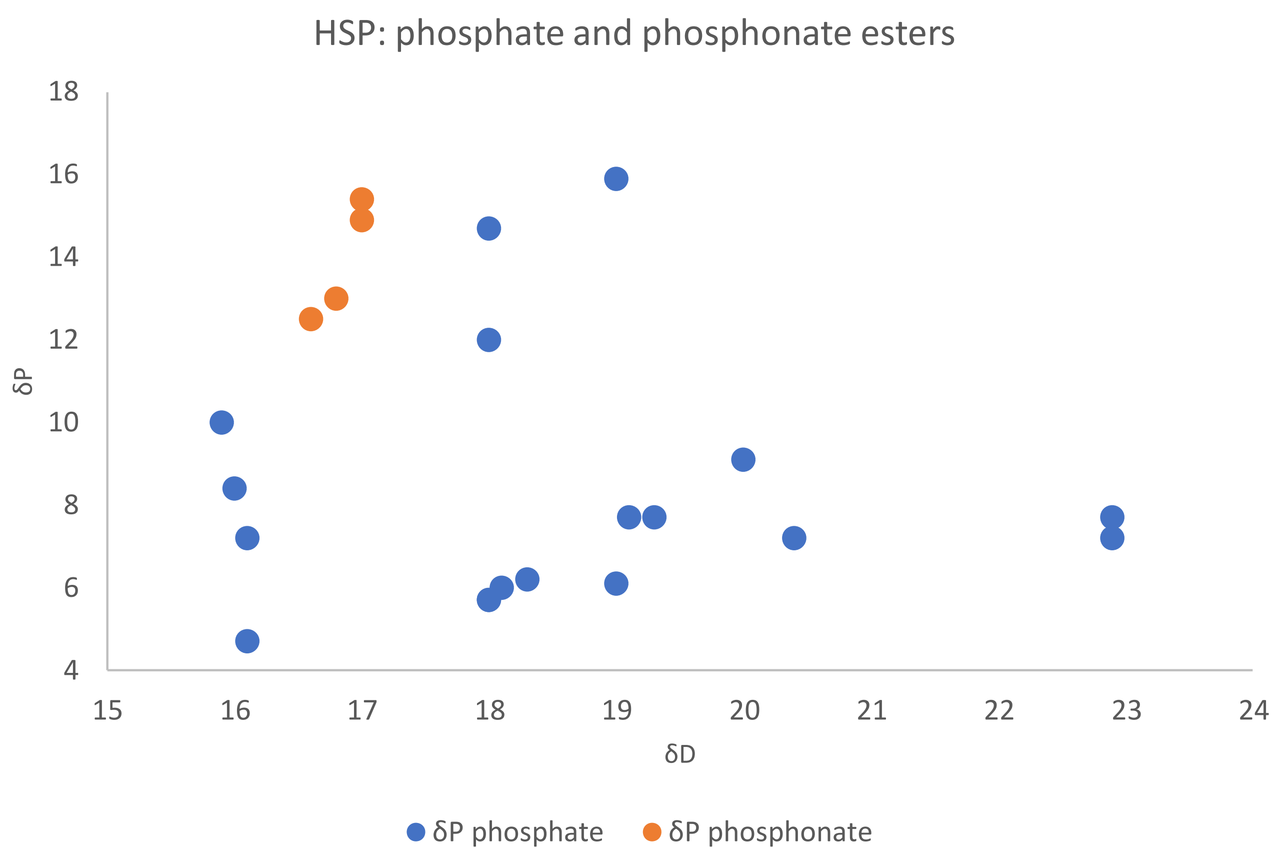
Key to figure

δP values for various structural types are plotted against δD; the structural groups identified were substances with various attachments to the P=O group:

- Three aryl rings - δP 3 aryl in the graph
- Two aryl rings, one alkyl chain - δP 1 alk
- Three alkyl chains - δP 3 alk
- Three chloroalkyl chains - δP chlor
- Two P atoms, various - δP 2P

GROUPING OF PHOSPHATE ESTERS AND PHOSPHONATE ESTERS FROM HSP VALUES

Phosphonate esters form another group, in structure, hazard properties and HSP.



North American Regulatory Approach

One Size Fits All Policies:
Why Different Products Call for Different Chemical Compounds

September 7, 2022

Overview – North America

- **Overall strong science and risk-based system for chemical regulation**
- **Generally, no significant restrictions on flame retardants used in electronics and electrical equipment**
  - In fact, broad recognition that E&E products are unique and typically exempted under existing laws
- **However…we are seeing an increase in policy proposals with implications for E&E**
- **Need for more engagement from downstream users to ensure a continuation of science-based policies**

U.S. Federal Regulation – EPA

- Recent shift to "whole chemical" approach in risk evaluations
- Some FRs are undergoing risk evaluation and in risk management as part of TSCA
- Case study of PIP (3:1) risk management
- Actions prescribed under TSCA intended to align with Unites States-Mexico-Canada Agreement and continued regulatory cooperation between the countries

U.S. Federal Regulation – CPSC

- **Assessing the use of additive, non-polymeric organohalogen flame retardants (OFRs) in casings & enclosures for electronics**
- **NAS recommended sorting OFRs into 14 subgroups for purposes of further assessment**
- **Conducting literature screening on subgroups in partnership with National Toxicology Program (NTP)**
- **Next steps: 1) draft scoping documents & 2) begin work on exposure assessment**

States – New York

- Enacted restrictions on the use of OFRs in stands & enclosures for electronic displays for personal use
- First U.S. state to restrict the use of flame retardants in electronics
- Restrictions take effect in December 2024
- Still unclear on timing of reporting requirement
- Also unclear on the role of Department of Environmental Conservation

States – Washington

- **Rulemaking stage for the use of OFRs in casings and enclosures for electronic & electrical equipment**
- **Preliminary draft rule**
  - Indoor products – 1,000 ppm individual OFR limit; 1,500 ppm combined OFRs limit
  - Outdoor products – Reporting requirement, no *de minimis*
- **Assessing OFRs differently than identified alternatives**
- **Proposal is the farthest reaching of any U.S. state**
- **Need for continued industry engagement and input**

Canada – Proposed Regulation of Some Halogenated Compounds

- **Draft Regulations for 7 halogenated compounds**
  - PFOS, PFOA, LC-PFCAs, HBCD, PBDEs, DP, and DBDPE
  - Screening assessment reports for DBDPE and DP were published at the same time
- **No current restrictions on DBDPE globally**
- **Socioeconomic report noted the lack of DBDPE alternatives**
- **Study finds DBDPE has a long half-life in the environment; and does not at all with the use of UV stabilizers**
- **Current timeline**

Canada – Aryl Organophosphate Group

- **Draft Screening Assessment for 6 organophosphate compounds**
  - PIP (3:1), TPP, BPDP, IDDP, BDMEPPP, and TEP
- **Proposed risk management options**
  - Regulatory measures to minimize the release via wastewater
  - Regulatory actions for PIP (3:1) and TEP
- **Screening Assessment and Risk Management Proposal are expected this fall**
- **Streamlined regulatory process**

Takeaways – North America

- **Changing regulatory landscape with different approaches in different jurisdictions**
- **Influenced by Europe, as well as UN Conventions**
- **Regulators should align with requirements under USMCA**
- **Need for considerations beyond hazard**
  - Considerations for exposure and how it informs risk
  - Product safety, including the threat posed by fire
- **Value chain outreach helpful in articulating lack of alternatives and options for product design**

CHEMISTRY THAT MATTERS™

REACTION-TO-FIRE AND FLAME RETARDANTS

Ralph R. Buoniconti
SABIC
September 7, 2022

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TOPICS

- Additives, in general
- Scale of fire tests, what they measure, and their goals
- Reaction-to-Fire properties
- Small scale test comparison
- Smoke density

THERMOPLASTICS AND ADDITIVES

What can added substances do in thermoplastics? A few examples:

Flammability

- Help extinguish small flames
- Promote char
- Inhibit dripping
- Suppress smoke
- **Compatibility with Resin**

Durability

- Impact modifiers
- UV resistance
- Chemical resistance
- Wear resistance

Appearance

- Colors
- Gloss
- Translucency

Manufacturability

- Mold release
- Stability at molding temperatures

Specialty

- Combination: Electrical insulation & thermally conductive
- EMI/RFI Shielding

Flammability considerations include:

- Fire threat
- Testing requirements from standards and regulations
- Can include risk assessments from actual parts that lead to specific testing scenarios
- Base material’s reaction-to-fire properties.
- Any gaps in performance that need to be addressed?

Flame retardants and additives that help the efficacy of flame retardants are used for safety. What is consider “safe performance” is dependent upon the threat and expected result.

FRS AND ADDITIVES CAN STOP PROGRESSION OF FIRE AT CRITICAL STAGES

Light obscuration due to smoke could possibly affect self-rescue

1 Inch or Less

1 kW or less
- UL94 V Test
- ASTM D635
- cig. Lighter

3-4 Feet

App 40 kW
- waste paper basket
- 35 kW/m2 exposure of FAA's heat release test
- 1st 5 min in NFPA 286

4.5 Feet

88 kW
- Steiner Tunnel (UL 723, ASTM E-84)

8 Feet

App 160 kW
- cushioned office chair
- 10 min in NFPA 286

Prevent catastrophic consequences, such as:

- Loss of life
- Flash-over (1 MW) of room/compartment
- Loss of structure prior to evacuation
- Loss of structure after evacuation
- Loss of vehicle prior to evacuation (plane, train, boat, etc.)
- Loss of vehicle after evacuation

The types of FRs and other additives, along with their respective concentrations, that enable good performance can vary significantly depending upon the threat.

SCALE OF TESTS OFTEN RELATED TO SCENARIOS AND GOALS

Small Flame Exposures (app. 1 kW range)

- Ex: UL 94, FAA vertical and horizontal burn, needle flame test, FMVSS 302, etc.
- Can measure ignitability, dripping, small scale burn rate, extinguishment during test and more
- A goal can be to prevent a small, localized, transient fire from growing out of control (contain, control/extinguish, etc.)
- Context in which the data is used is important to understanding usefulness and limitations.

Intermediate Scale Exposure (totals app. 25-90 kW range, localized 25-50 kW/m2)

- Ex: FAA OSU heat release, ASTM E162, Steiner Tunnel, ASTM E662 (smoke density) 1st 5 min NFPA 256, etc.)
- Can measure reaction to radiant heat and flame, spread-of-flame, heat release rates, smoke production, smoke toxicity/corrosivity
- Goals can be to prevent a developing or established intermediate/larger scale fire from spreading to other objects, to increase escape/reaction times, etc.
- Context can be highly specific to location (plane, train, ship, room, building, etc.)

Larger scale exposures (totals over 100kW, localized 50+ kW/m2

- Ex: 10 min. of NFPA 256, ASTM E119, roof-covering tests, UL 2335, etc.
- Can measure reaction to specific end-use threats, structural integrity, compartmentalization, ability to control fire
- Goals can be to prevent loss of compartment/structure, fire breaching a barrier, macro spread of flame, etc.
- Context is often a specific type of threat against a specific system (wall system, storage systems, roof coverings, etc.)

Common Goals: Prevent Loss of Life, Prevent Injuries, Mitigate Damage to Property

FRS CAN AFFECT IMPORTANT REACTION-TO-FIRE PROPERTIES OF POLYMERS

Base Polymer Performance Examples	Scale of Test/Fire	Examples of FR strategies and/or additives
Lower heat, melts/drip easily, no char, higher heat release (ASTM E1354), burns readily with small flame	Smaller Scale	• If dripping is a negative, drip inhibitors plus an FR to extinguish flame/limit ignitability • If dripping is a positive (ex: some fiber-fill performance), maybe just an FR
	Larger Scale	• Lower heat release through combination of fills, FR (ex. endothermic reaction such as aluminum tri-hydroxide). Maybe FR for gas-phase reactions.
Higher heat, resistant to melt/drip, good char, med.-higher heat release, (ASTM E1354), harder to ignite with small flame	Smaller Scale	• Similar to above, except drip inhibitors can be more effective (possibly needing less FR) because of char and higher heat of materials. • Char promoting FRs such as phosphorous based FRs
	Larger Scale	• Depending upon base resin, maintain integrity through fillers (ex. glass fibers), gas phase FR, and/or char promoting FRs
Very high heat, excellent char, lower heat release (ASTM 1354), hard to ignite and keep burning with small flame	Smaller Scale	• Maybe no additives/FR or very low level of specific type.
	Larger Scale	• Can an additive promote more char and/or stabilize char? Will maintaining integrity (e.g., through glass fiber) be all that is needed?

Differences in a resin’s base performance can lead to differences in amount and type of FR, and amount and type of additives that increase FR performance.

SMALL SCALE FLAMMABILITY – RELATIVE COMPARISON

UL 94 HB	FAA's Horizontal Burn	Materials can burn to completion
V series - V-2, V-1, V-0	FAA's "12 Sec." Vertical Burn	Materials must either a) Not ignite, or b) Main specimen must extinguish during the test Dripping: V-2 can have flaming drips, V-1 and V-0 cannot. FAA's vertical tests can have flaming drips which must extinguish in avg. 5 sec. for 12 sec vertical or 3 sec. for 60 sec. vertical
5V -- 5VB, 5VA	FAA's "60 Sec." Vertical Burn	

Increasing In Severity (generally)

- Designing for highest level of FR performance can lead to a material that has excess FR for lower levels. FRs can have negative effects on other properties (impact, weathering, etc.).

SMOKE DENSITY (OPTICAL) TESTS

- Examples: ASTM E662 and similar tests used in the EU, UL 723/ASTM E-84, ASTM D2843
- These tests do not necessarily correlate with one another
- Some FR/polymer combinations will do worse in some smoke density tests than non-FR polymer
- Suppressing smoke can be its own science and is generally more difficult than suppressing flame. A common example is wet wood - more smoke, less flame.

Generally, there are fewer options overall to suppress smoke than to increase FR performance.

SUMMARY

- Material selection and flame retardant choices (if needed) are often part of a complex balance of written (test) requirements, and practical manufacturing & end-use environment requirements.
- The scale of fire tests and scenarios represented vary widely and can lead to different strategies for FR performance.
- The reaction-to-fire properties of a base material affect the FR strategy used to meet the variety of flammability tests.
- Smoke density mitigation can be more complex than meeting flammability tests.

Differences in polymers, fire threats, and fire tests lead to differences in FR strategies, types, and amounts.

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Key Takeaways

Key Takeaways

- Global regulatory landscape is evolving, and companies should be aware of the challenges
- This shift requires more active input from downstream users
  - Perspectives of those with product design experience and expertise are particularly valuable
- Regulators should consider product design, including the practicality of alternatives, and ensure that there are options for manufacturers

Questions & Discussion

American Chemistry Council

Thank You for Attending