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TUR Planner CE Conference

Session D: TUR planning for chemical categories

Liz Harriman, Hayley Hudson, Heather Tenney, Karen Thomas

April 12, 2023

Agenda

- It's all about TUR Planning!
  - Chemical categories overview
- Nanomaterials – Carbon nanotubes and carbon nanofibers (CNTs and CNFs)
- Quaternary Ammonium Compounds (QACs or quats)
- Activity #1
- Flame retardants (FRs)
- Activity #2
- Wrap-up

Overview

- Objective:
  - Learn about hazards and TUR opportunities for 3 chemical categories
- How does this relate to TUR Planning?
  - Heads up on chemical categories that may be listed under TURA
  - Alternative Planning opportunity for 2024 planning cycle!
  - Consider how planning for chemical classes helps avoid regrettable substitutes
  - Incorporating consideration of essential use in planning

Alternative TUR Planning

- Non-TURA listed Chemicals
  - **Non-reportable/Exempt Toxics** alternative/RC planning provisions under TURA

1. **Energy**
2. **Water**
3. **Materials That Contribute to Solid Waste**
4. **Toxic Substances Used Below Threshold**
5. **Chemical Substances Exempt from TURA Reporting**

Planning for Non-reportable and Exempt Chemicals

- Toxics below threshold
- Emerging, unlisted hazards
- Less hazardous substances with substantial resource conservation potential
- Toxics in laboratories
- Toxics in pilot plant production
- Toxics in janitorial uses
- Toxics in products sold
- Toxics in articles used in facility

Chemical Categories and Classes

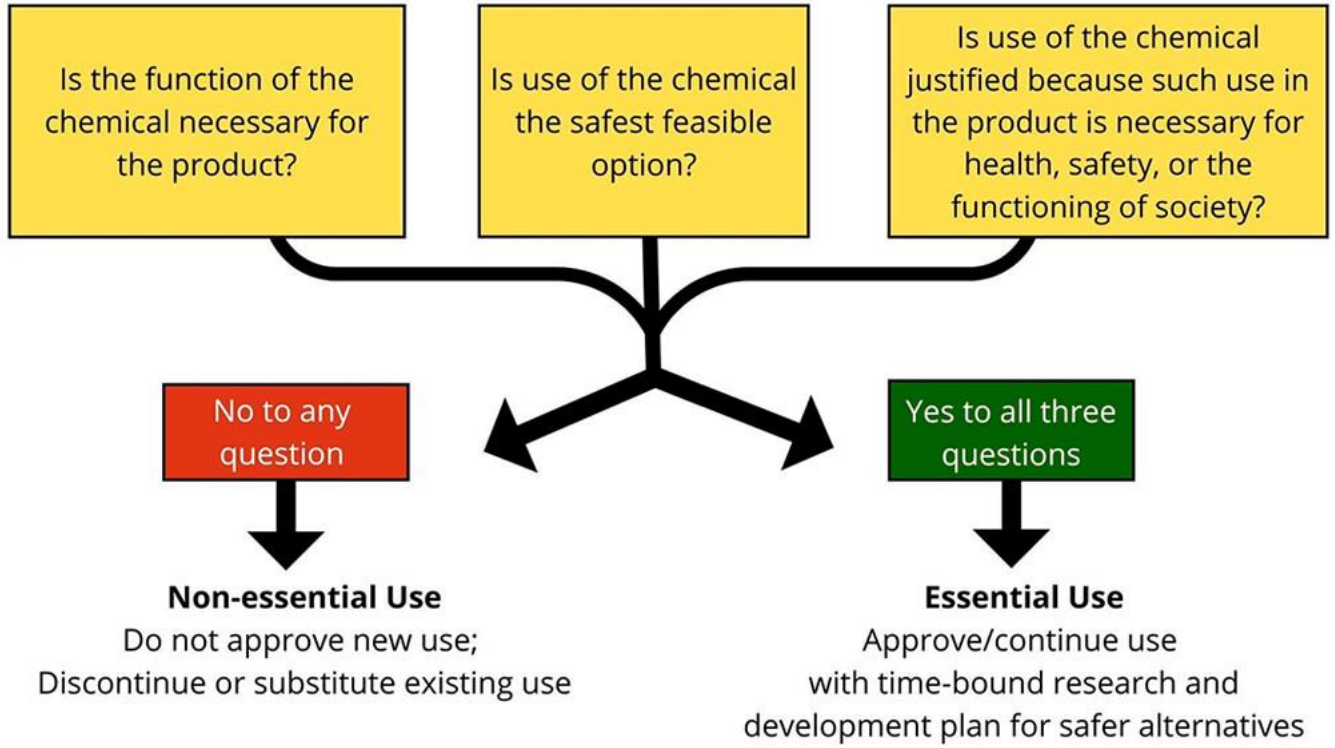
- Chemical Class: groupings that relate chemicals by similar features, including:
  - Structure
  - Uses
  - Physical properties
- Chemical Category under TURA:
  - Useful grouping of chemicals with similar properties - *whose physicochemical and human health and/or ecotoxicological properties and/or environmental fate properties are likely to be similar or follow a regular pattern, usually as a result of structural similarity. (OECD)*

When does it make sense to use Chemical Categories in TUR Planning?

- When it assists with **avoiding regrettable substitutes**
- When chemicals are used in mixtures in commercial products
- When category is known, but specific chemical(s) are not
- When chemicals can be easily modified to create new similar substances with equivalent functionality and hazard, but different CAS numbers.

Essential Use Concept

- TUR Planning – 1st question: "do I need to use this chemical?"
  - Do I need the function this chemical provides?
  - If I do need the function, are there safer alternatives?



Essential-use questions for chemicals of concern.
This figure shows a process for implementing the essential-use approach by triaging decisions about the necessity of chemicals of concern in specific consumer products and industrial processes. Once any question is answered no, the process concludes.

Bălan, et al 2023. Optimizing Chemicals Management in the United States and Canada through the Essential-Use Approach

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Do you think you or your clients are using…

- CNTs, CNFs?
  - Other nanomaterial?
- Quats?
- Flame retardants?

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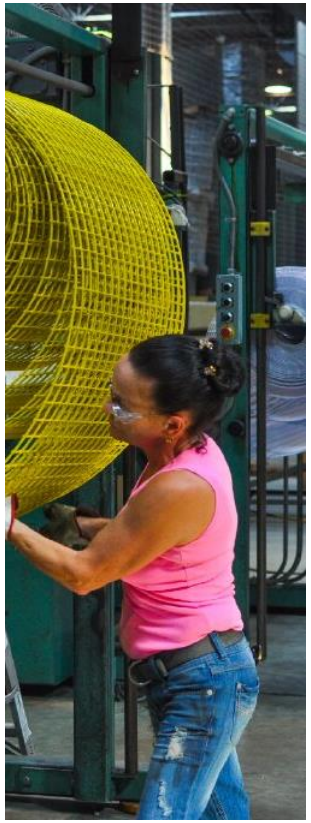


Nanomaterials

Heather Tenney
April 12, 2023

Carbon Nanotube and Fiber Petition 2020

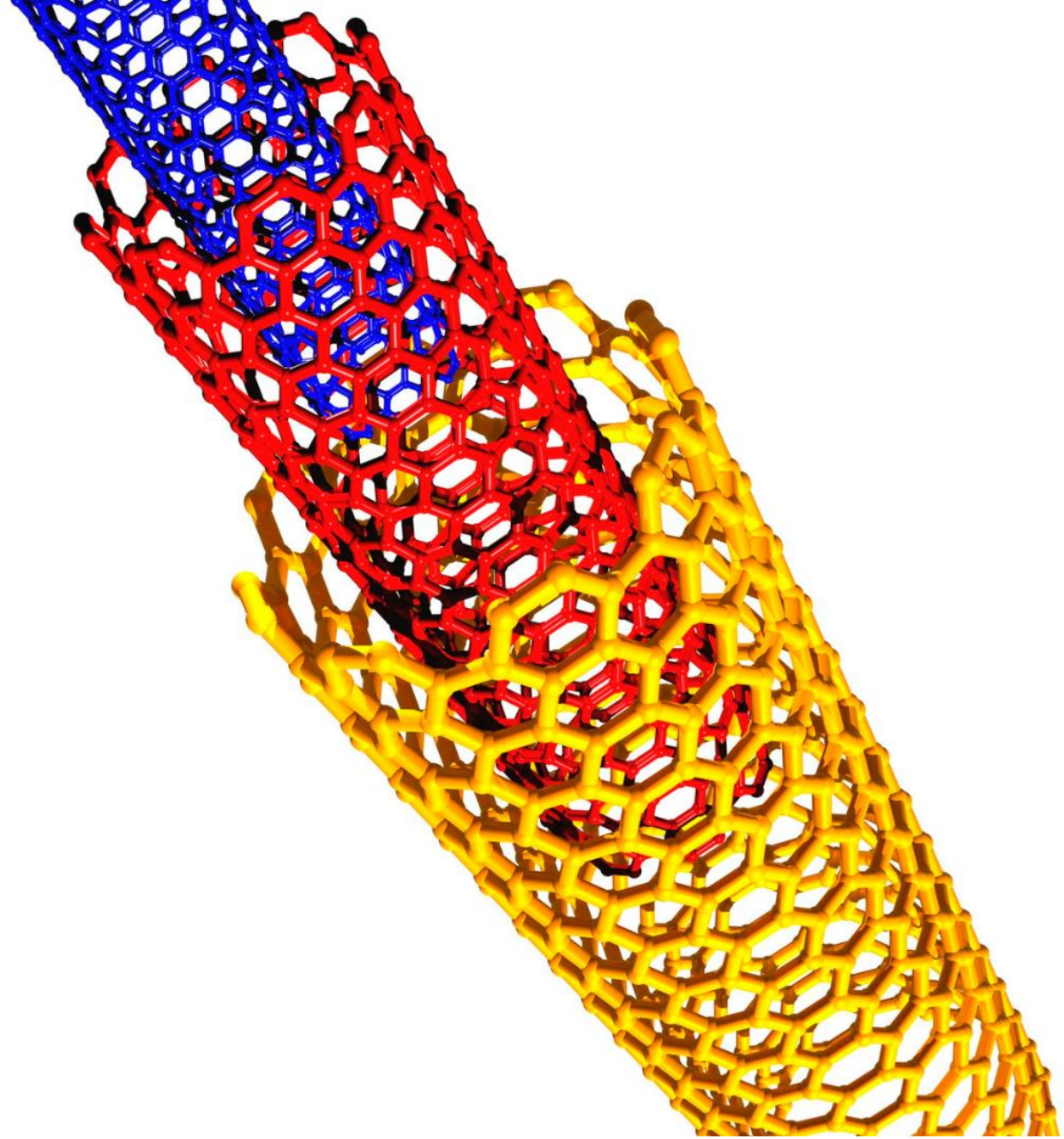
Submitted by Clean Water Action and Public Employees for Environmental Responsibility

Asked to list multi-walled carbon nanotubes, single-walled carbon nanotubes and carbon nanofibers as a group

Asked for HHS designation

Asked for a 100g threshold

Carbon nanotubes may be single-walled , double-walled, or multi-walled, with diameters varying from 1-3 nm (for SWCNT) to 10-100 nm (for MWCNT). Lengths vary widely and are often in the tens of micrometres.



SWCNTs tend to form aggregates or agglomerates by clumping together with other carbon tubes.

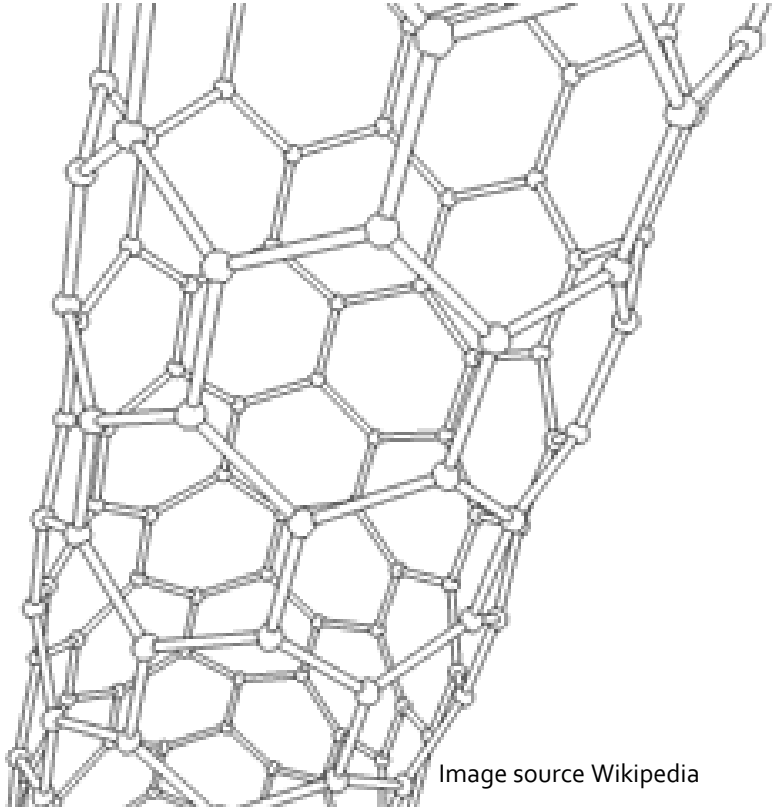
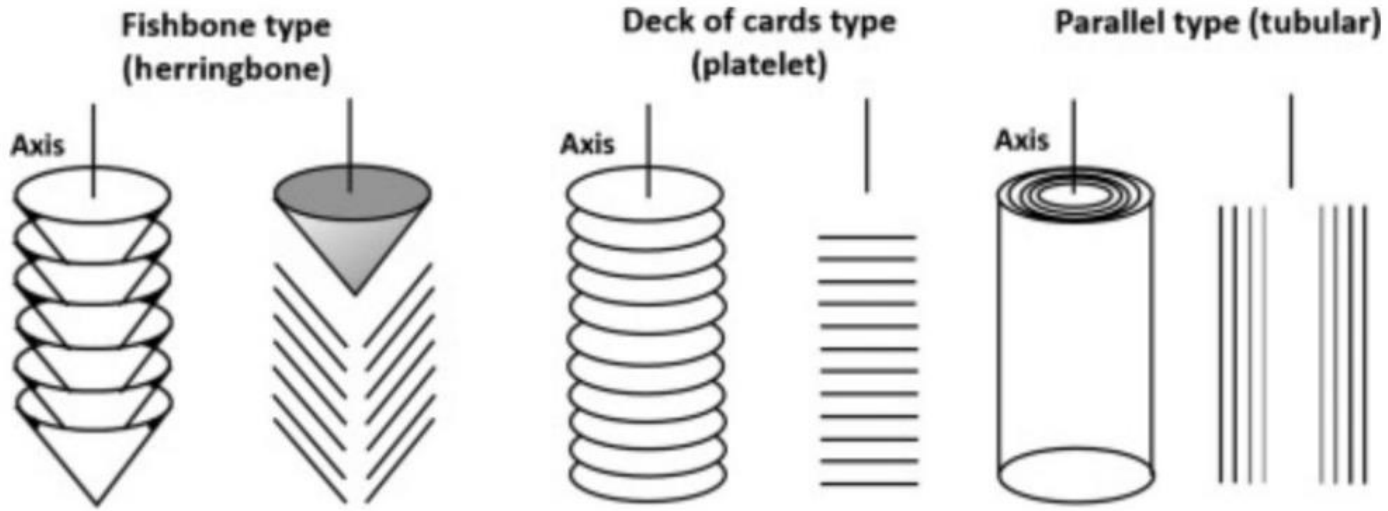


Image source Wikipedia

CNFs have two similar external dimensions in the nanoscale and the third dimension is significantly larger. Nanofibers can be flexible or rigid.



Schematic illustration of three different types of CNFs (Science Direct 2021)

Used for (properties)

Strengthening

Delivery

Flexibility

Conductivity

Used for (products)

Pharmaceuticals

Athletic equipment

Electronics

Construction materials

Authoritative work

NIOSH set a low Recommended Exposure Level (REL) of < **1 µg/m3** for single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) and carbon nanofibers based on pulmonary toxicity concern

IARC classified MWCNT-7, a batch of MWCNTs used in numerous rodent 2 studies, as a Group 2B carcinogen, "possibly carcinogenic" to humans

Multi-walled Carbon Nanotubes

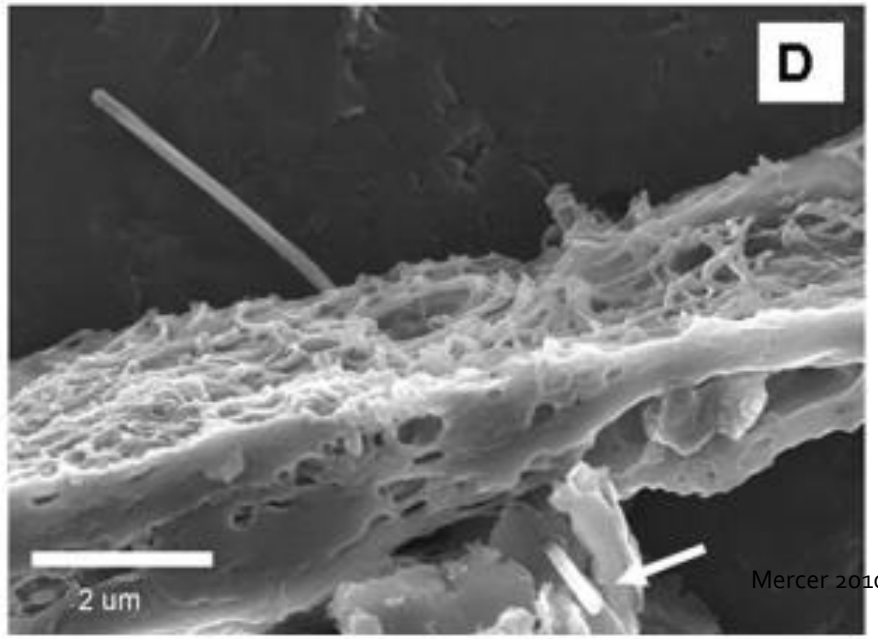
pulmonary toxicity

biopersistence

lung cancer

mesothelioma

environmental persistence



Mercer 2010

Additional concerns for genotoxicity and toxic environmental degradation products

Single Walled Carbon Nanotubes

pulmonary toxicity

environmental persistence

Additional concerns for reactive oxygen species (ROS) production and DNA damage

Carbon Nanofibers

pulmonary toxicity

Lifecycle questions

Nanomaterials may be purchased in emulsions

Consider dry handling at manufacture

Also consider end of life disposal (i.e. incineration)

Next steps

Assess whether CNT or CNF are HHS

TURI writes policy analysis summarizing science, with use and alternative information, other regulations and implications for the TURA program

Present at Advisory Committee and Administrative Council

Additional resources

TURA Science Advisory Board / Councils and Committees / Toxics Use Reduction Act / Policy / Our Work / TURI - TURI - Toxics Use Reduction Institute

CDC Current Intelligence Bulletin 2013 CDC - NIOSH Numbered Publications: Current Intelligence Bulletins (CIB) - Sorted By Date, Descending Order Without Publication Numbers

Greenscreens for MWCNT, SWCNT, CNF

IARC monograph IARC Publications Website - Some Nanomaterials and Some Fibres

TURI Nanomaterial fact sheet Nanomaterials fact sheet - Dec 2017 (turi.org)

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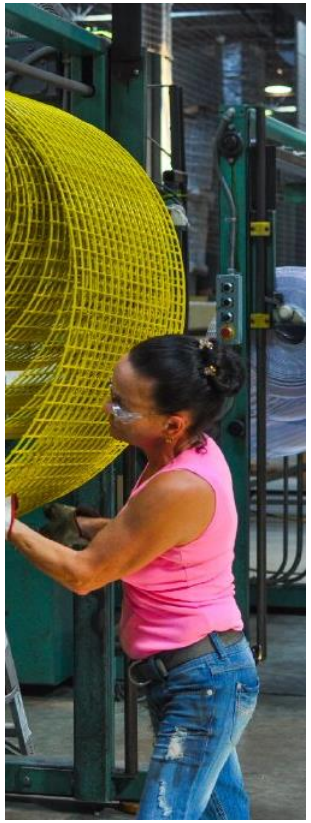


Quaternary Ammonium Compounds (QACs or Quats)

Hayley Hudson
April 12, 2023

What are Quaternary Ammonium Compounds? Quats or QACs

- First discovered in the early 1940s
- Now a broad class of several hundred chemicals
- Commonly found as active ingredients in antimicrobials, disinfectants, and sanitizers.
- Uses beyond disinfection – wood preservatives, herbicides, eye drops, mouthwashes, nasal sprays, detergents and shampoos, wet wipes, algaecides, dryer sheets and fabric softeners.

EPA Quat Clusters

- 1988 EPA issued a notice in which structurally similar QACs were clustered into the 4 groups:
  - ***Group I:*** The alkyl or hydroxyalkyl (straight chain) substituted Quats
  - ***Group II:*** The non-halogenated benzyl substituted Quats (includes hydroxybenzyl, ethyl benzyl, hydroxyethybenzyl, napthylmethyl, dodecyl benzyl, and alkyl benzyl)
  - ***Group III:*** The di- and tri-chlorobenzyl substituted
  - ***Group IV:*** Quats with unusual substituents (charged heterocyclic ammonium compounds)
- SAB focused on commonly used disinfectants in Group I and Group II

Status of Quats in Massachusetts

Science Advisory Board (SAB) recommended to list categories of **Alkyl Dimethyl Benzyl Ammonium Chloride (ADBAC)** and **Didecylmethylammonium Chloride (DDAC)**
5 individual DDAC chemicals
19 individual ADBAC chemicals
Still in review at the Advisory Committee

Quats Recommended to List – DDAC

Individual DDAC Chemicals

CAS Number	Ingredient Name
7173-51-5	Didecyl dimethyl ammonium chloride
32426-11-2	1-Decanaminium, N,N-dimethyl-N-octyl-, chloride
5538-94-3	1-Octanaminium, N,N-dimethyl-N-octyl-, chloride
68607-28-3	Oxydiethylenebis(alkyl*dimethyl ammonium chloride) *(as in fatty acids of coconut oil)
61789-18-2	Alkyl* trimethyl ammonium chloride*(as in fatty acids of coconut oil)

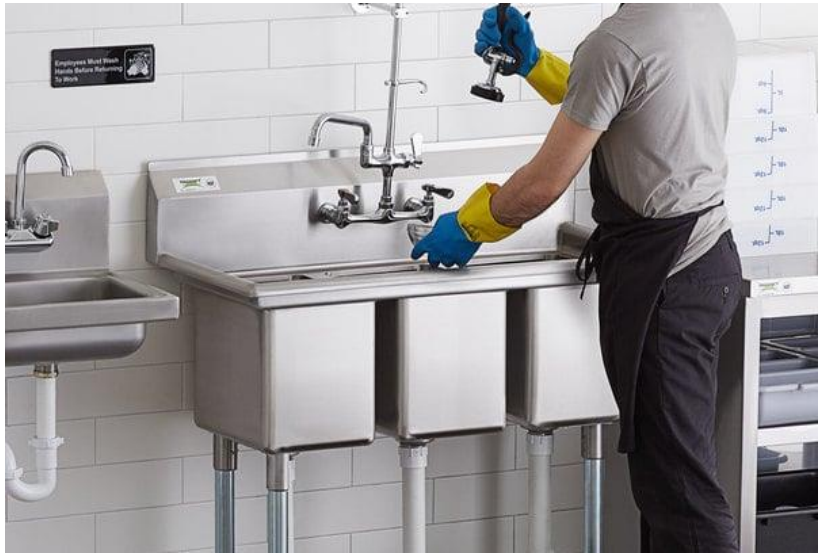
Quats Recommended to List - ADBAC

Individual ADBAC Chemicals

CAS Number	Ingredient Name
53516-76-0	Alkyl (60%C14, 30%C16, 5%C18, 5%C12) dimethyl benzyl ammonium chloride
68424-85-1	Alkyl (50%C14, 40%C12, 10%C16) dimethyl benzyl ammonium chloride
8001-54-5	Alkyl (50%C12, 30%C14, 17%C16, 3%C18) dimethyl benzyl ammonium chloride
139-08-2	Alkyl (100% C14) dimethyl benzyl ammonium chloride
8045-21-4	Alkyl (50%C12, 30%C14, 17%C16, 3%C18) dimethyl ethylbenzyl ammonium chloride
73049-75-9	Dialkyl (60% C14, 30% C16, 5% C18, 5% C12) methyl benzyl ammonium chloride
121-54-0	Benzenemethanaminium, N,N-dimethyl-N-(2-(2-(4 (1,1,3,3tetramethylbutyl)phenoxy)ethoxy)ethyl)-, chloride
1330-85-4	Dodecylbenzyl trimethyl ammonium chloride
68424-85-1	Alkyl (60%C14, 25%C12, 15%C16) dimethyl benzyl ammonium chloride
61789-71-7	Alkyl (61% C12, 23% C14, 11% C16, 2.5% C18, 2.5% C10, traceC8) dimethyl benzyl ammonium chloride
68424-85-1	Alkyl (58%C14, 28%C16, 14%C12) dimethyl benzyl ammonium chloride
85409-23-0	Alkyl (68%C12, 32%C14) dimethyl ethylbenzyl ammonium chloride
68956-79-6	Alkyl (60%C14, 30%C16, 5%C12, 5%C18) dimethyl ethylbenzyl ammonium chloride
68989-01-5	Alkyl (50% C14, 40% C12, 10% C16) dimethyl benzyl ammonium saccharinate
68391-01-5	Alkyl (67%C12, 25%C14, 7%C16, 1%C18) dimethyl benzyl ammonium chloride
68424-85-1	Alkyl (95%C14, 3%C12, 2%C16) dimethyl benzyl ammonium chloride
68391-01-5	Alkyl (41%C14, 28%C12, 19%C18, 12%C16) dimethyl benzyl ammonium chloride
63449-41-2	Alkyl (67%C12, 25%C14, 7%C16, 1%C8, C10, and C18) dimethyl benzyl ammonium chloride
61789-18-2	Alkyl (as in fatty acids of coconut oil) trimethyl ammonium chloride

Where can you find Quats?

- Hospitals
- Restaurants
- Offices
- Our homes
- Several ADBAC and DDAC substances are often found as mixtures in household and commercial disinfectant products.



Hazards of Quats

Respiratory Effects and Asthma

Surveillance studies, case reports, and animal studies indicate that DDAC and ADBAC are associated with respiratory system irritation and inflammation including outcomes consistent with occupational asthma and work-exacerbated asthma.

Hazards of Quats

Dermal Effects

- ADBAC and DDAC are highly irritating to the skin, and long-term exposure may result in skin sensitization or allergic dermatitis.

Irritant

- Eyes, nose, throat, or lung irritation have all been reported among workers exposed to Quats.

Hazards of Quats

Reproductive/Developmental Effects

- Some emerging evidence has suggested that exposure to Quats such as DDAC and ADBAC may affect reproduction and development in animals.

Other Human Health Effects

- A study found concentrations of QACs in the blood of 80% of participants and identified correlations between these levels and biomarkers related to human health.

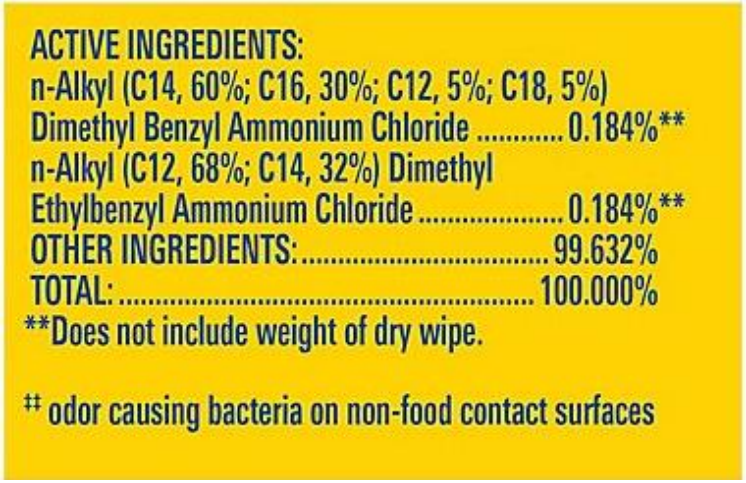
Hazards of Quats

Environmental Fate

- Concerns for microorganisms and aquatic organisms
- QACs can impact wastewater treatment plants
- Found in surface waters, soil, sediments, and wastewater sludge
- Immobile in soil
- Due to their low volatility, they are expected to bind to sediments and soils
- Potential development of antibiotic-resistant bacteria
- QACs have also been detected on surfaces long after being used, and in household dust, meaning they may have the potential to persist in the environment, our workplaces, and our homes.

How do you identify Quats?

- CAS Number
- Substances with "Ammonium Chloride" in the name



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When do you need to disinfect?

- Is disinfecting a part of your daily routine at your job/facility?
- When is it necessary to disinfect?

Safer Alternatives

Caprylic acid or octanoic acid

- Produced by the distillation of coconut or palm kernel oils.
- Corrosive in concentrated form.

Citric Acid

- Extracted from pineapple waste and citrus fruits. Corrosive in concentrated form.

Hydrogen Peroxide

- Readily available in retail stores as a dilute 3% formulation. Note that there is evidence that hydrogen peroxide and peroxyacetic acid together are respiratory sensitizers and may cause asthma, therefore the combination is **not** considered a safer alternative.

L-Lactic Acid

- Naturally occurring organic acid. Concentrated L-Lactic Acid is corrosive and a severe skin and eye irritant.

Safer Alternatives

Alcohols

- Including isopropanol (IPA) and ethanol (ethyl alcohol)
- Concentrated alcohols are flammable, are VOC's and exposure may cause nausea, dizziness, headache, and irritating effects to the skin, eyes, and throat.

Aqueous Ozone

- Typically produced at the point of use in an ozone generator, either portable equipment or handheld spray bottle devices.
- Aqueous ozone has a short shelf life as the ozone readily reverts to oxygen.

Hypochlorous Acid

- Chlorine solution generated by dissolving concentrated sodium dichloroisocyanurate (NaDCC) tablets in water, or by using electrolyzed water systems

Non-Chemical Safer Alternatives

Steam

- Free of chemicals.
- Effective and suitable for many surfaces.
- Caution needed to avoid burns.

UV Light

- Suitable for specific applications, e.g., unoccupied medical rooms, high-tech electronic devices, inside air ducts.
- UV hazards for eyes and skin.

TURI Cleaning and Disinfection Lab

- TURI has a Cleaning Laboratory and a Micro/Disinfection Laboratory.
- Testing the performance and efficacy of cleaning products.
- If you need assistance or have any questions about your cleaning and or disinfection needs, please contact us!

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Activity #1 – CNTs, CNFs, and quats

- For alternative planning, what support/info/services can the program assist with?
- Who else in your organization do you need to include in an alternative planning effort?
- What do you need from your suppliers? Can they help with safer alternatives?

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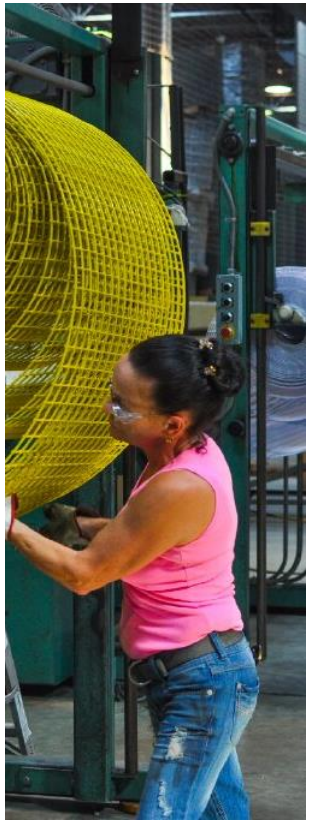
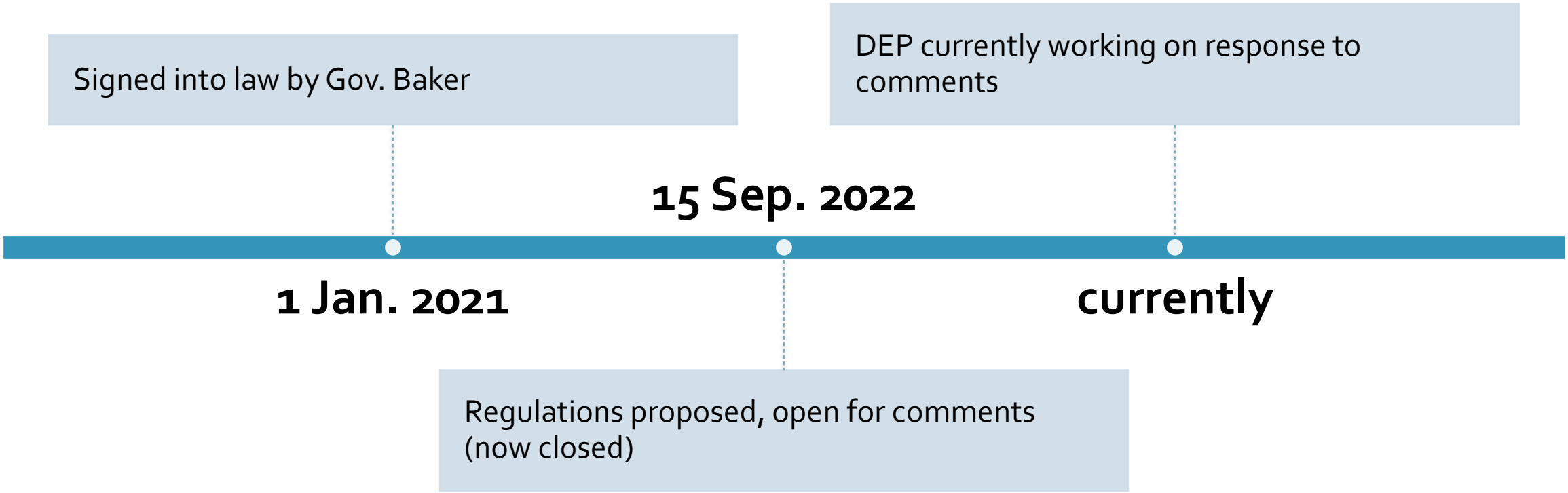


Massachusetts Flame Retardants Law, 2020

An Act to Protect Children,
Families and Firefighters
from Harmful Flame Retardants
Mass. Gen. Laws Ch 21A, Section 28

MA Flame Retardants Law

An Act to Protect Children, Families and Firefighters from Harmful Flame Retardants



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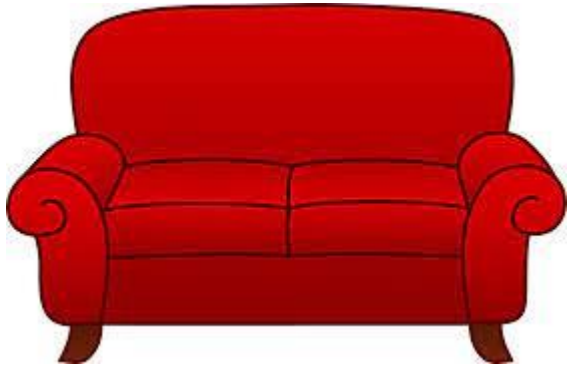



MA Flame Retardants Law

Who:	Manufacturer, Retailer
Cannot:	Sell, manufacture for sale, offer for sale, distribute in commerce, import into Mass.
What:	Product that contains any of the named 11 flame retardants or chemical analogues, the total weight of which is >1000ppm for any component part
In:	Bedding, carpeting, children's products, residential upholstered furniture or window treatments

The 11 chemicals in the MA FR law:

- Tris(1,3-dichloro-2-propyl)phosphate (TDCPP), 13674-87-8
- Tris(2-chloroethyl)phosphate (TCEP), 115-96-8
- Tris (1-chloro-2-propyl) phosphate (TCPP), 13674-84-5
- Pentabromo diphenyl ether (BDE), 32534-81-9
- Octabromo diphenyl ether (BDE), 32536-52-0
- Bis(2-Ethylhexyl)-3,4,5,6- tetrabromophthalate (TBPH), 26040-51-7
- 2-Ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), 183658-27-7
- Hexabromocyclododecane (HBCD), 25637-99-4
- Tetrabromobisphenol A (TBBPA), 79-94-7
- Chlorinated paraffins, C_{10}-C_{13}, 85535-84-8
- Antimony trioxide, 1309-64-4

Differences between TURA and FR law

Provision	MA TURA	MA FR Law
Who does it affect?	Users (manufacturers and distributors) in certain SIC codes, >10 workers	Retailers, importers, and users (manufacturers, distributors)
Which chemicals?	List of over 1500 chemicals, above thresholds	11 chemicals and chemical analogues of the 11, above 1000 ppm for any component
What do they have to do?	Report and plan	This is a ban.
What end products?	All	Bedding, carpeting, children's products, residential upholstered furniture or window treatments

A short history…

- It may have started with Gene Autry chaps
- Rayon fabric, fuzzy fibers
- Federal Flammable Fabrics Act of 1953
- Uncontestable goal to prevent fire injury
- How to comply with the law?
  - Don't make the product?
  - Make the product from a naturally non-flammable fabric?
  - Treat the fabric with chemical, organohalogen, flame retardants?

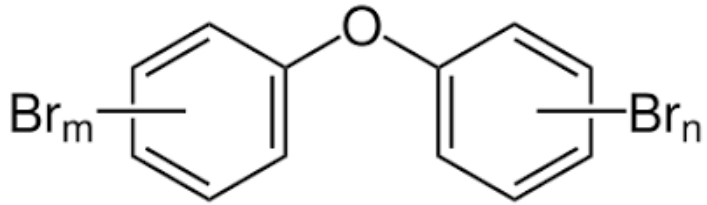
Thus began a "pattern"

- Tragedy/awareness/problem (real or fabricated)
- Government reaction – law, flammability standard/rating
- Often a chemical solution
- Chemical found to be toxic, bioaccumulative, persistent
- Replace with another chemical, often in the same category of chemicals

REGRETTABLE Substitution
example for polyurethane foam products

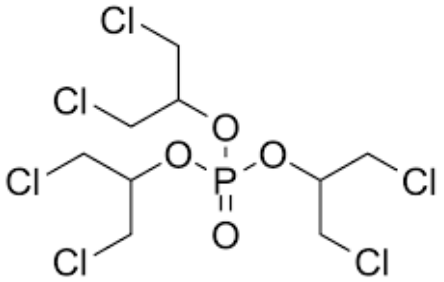
Brominated diphenyl ethers (penta, octa) - 80's-00's

Developmental toxin, aquatic toxin, carcinogen



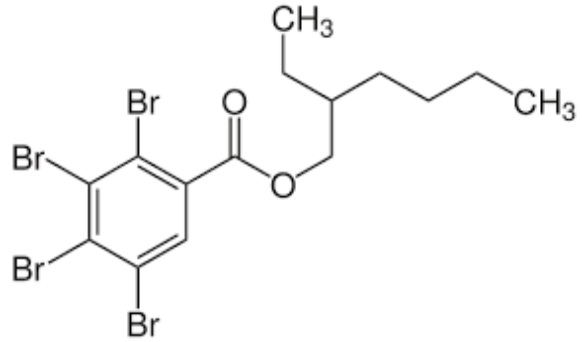
Chlorinated phosphates (Cl tris) - 00's

Mutagen, carcinogen



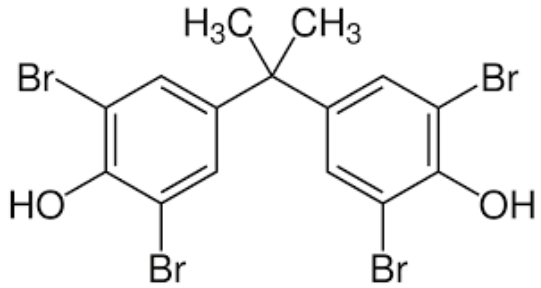
TBB (bromo benzoate),
TBPH (bromo phthalate) - 10's

PBT, birth defects



TBBPA (bromo bisphenol A) - teen's

Carcinogen, repro toxin, PBT, endocrine disruptor



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Common Uses of Chemical Flame Retardants In Manufacturing

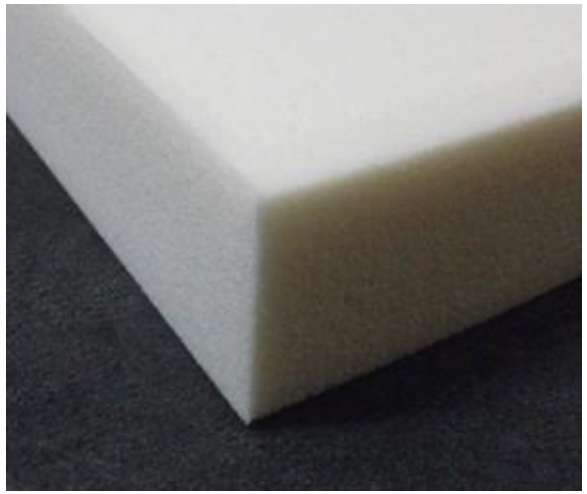
- Electronics - wire and cable, casings
- Polymers & coatings - foams, resins, paints
- Adhesives, sealants
- Building materials - polystyrene and polyurethane insulation
- Textiles - waterproof fabrics, mattresses, curtains
- Transportation - automobiles, aircraft

Credit: westerncanadacoatings.ca/fire-retardant-paint/

Credit: cntraveler.com

Credit: homedepot.com

Credit: gearpatrol.com



Credit: insulationindustries.com.au/product/polyurethane-foam-m2/

Common Uses of Chemical Flame Retardants - In Consumer Products

Photo credit: Ryan Fields on unsplash.com

- children's products - car seats, infant mattresses, toys, nursing pillows
- upholstered furniture - in the polyurethane foam
- gymnasium foam cubes
- mattresses and mattress pads
- carpeting and rebonded carpet padding
- textiles - tents, fabric blinds
- building insulation - polystyrene and polyurethane foam
- paints and coatings
- electronics - casings, wire and cables

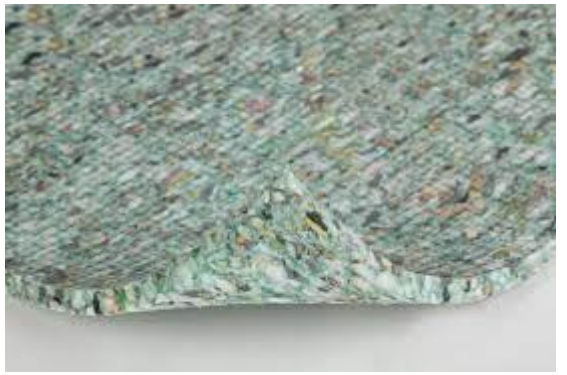


Photo credit: lowes.com

Photo credit: Haley Owens on unsplash.com

Additional Work Environments that may encounter Chemical Flame Retardants

Credit: 3rtechnology.com

Credit: esub.com

- Firefighters
- Day care centers
- Gymnasiums
- Upholsterers
- Electronics recycling facilities
- Construction sites

Credit: childressfabrics.com

Credit: efoam.co.uk

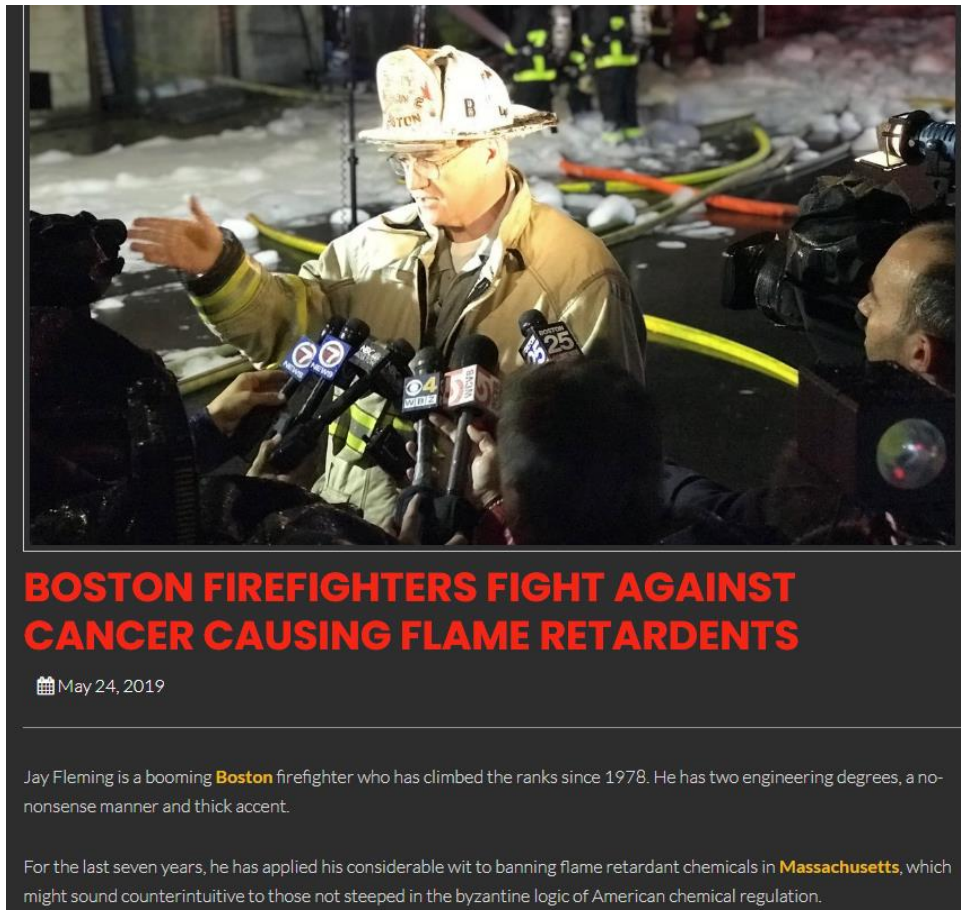
Early 2000s scientists started finding residual "FRs of concern" wherever they looked

- Human breast milk and blood
- Antarctic penguins
- Arctic orcas
- North American kestrels
- Barn owl
- Bird eggs in Spain
- Fish in Canada
- Honey from Brazil, Morocco, Spain and Portugal

Photo credit: Unsplash.com

Photo credit: Jonas Hensel on unsplash.com

Firefighter Health



BOSTON FIREFIGHTERS FIGHT AGAINST CANCER CAUSING FLAME RETARDENTS

May 24, 2019

Jay Fleming is a booming **Boston** firefighter who has climbed the ranks since 1978. He has two engineering degrees, a no-nonsense manner and thick accent.

For the last seven years, he has applied his considerable wit to banning flame retardant chemicals in **Massachusetts**, which might sound counterintuitive to those not steeped in the byzantine logic of American chemical regulation.

Credit: firefighterclosecalls.com

- 2010's Firefighters joined the fight against toxic FRs due to evidence of increased cancer rates
- High levels of OFRs and OFR combustion products (dioxins, furans) in blood of firefighters
- Firefighters were instrumental in changing fire code in MA and advocating for FR law

Essential Use?

Circumstances have changed

- Smoking rates ⇩
- Smoke detectors and sprinklers ⇧
- Fire safety education ⇧
- Use of self-extinguishing cigarettes ⇧
- Technological improvements ⇧

Risk vs. Benefit

- Not all FRs working at intended
- Known hazards of OFRs and some inorganics
- Documented exposure

Drivers for flame retardancy have changed:

- Some flame retardancy "habits" are unnecessary
- Some flammability standards have been or are being updated or should be
- Some flammability standards may still necessitate the addition of a chemical FR

Safer Fire Safety

Credit: valleyinsulationllc.com

Maintaining fire safety without the use of chemical FRs

Textiles – synthetic fibers that resist ignition under prolonged exposure to flame

Foam in upholstered furniture, and mattresses - non-flammable/fire-resistant fabric acts as a barrier on top of the foam.

Building insulation – fiberglass, mineral wool, cellulose

Maintaining fire safety using safer chemical FRs

Electronics wire and cable insulation and jacketing – low-smoke-zero-halogen, usually non-halogenated metal hydroxides

Paints and coatings – intumescent paint which may contain ammonium polyphosphate, pentaerythritol, melamine and titanium dioxide

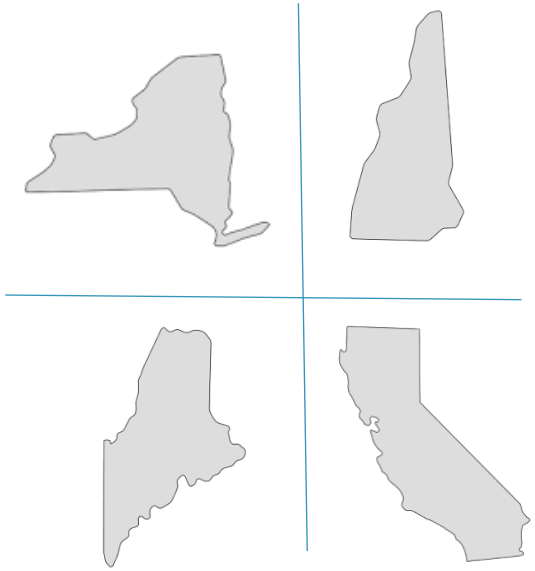
Credit: Quabbin Wire & Cable

"Organohalogen FR" category

2017 Consumer Product Safety Commission recommended that manufacturers of children's products, upholstered furniture sold for use in residences, mattresses (and mattress pads), and plastic casings surrounding electronics refrain from intentionally adding nonpolymeric, organohalogen FRs ("OFRs") to their products.

U. S. Consumer Product Safety Commission

Four states (NY, NH, ME, CA) have passed laws using a version of this broad category



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Additional resources

- TURI's Flame Retardant LibGuide
- Mass Act to Protect Children, Families, and Firefighters from Harmful Flame Retardants (Mass. Gen. Laws ch 21A, section 28 (2020), Regulations at 310 CMR 78.00) and Background Document
- NIH Flame Retardants and Your Health Factsheet
- TURI resources:
  - Gym Creates Healthier and Safer Foam Pits
  - Childcare Guide to Safer Alternatives
  - Clean Water Fund Factsheet: Toxic Flame Retardants
  - Sustainable Routes To Non-halogenated Flame Retardants Based On Phenolic Monomers

The Massachusetts Toxics Use Reduction Institute

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Activity #2 – Considering Essential Use Scenario (optional/additional: use your/client's Company)

- MA manufacturer of roller derby helmets; large customers are public rinks that rent equipment
- Construction: hybrid layered construction
  - layer of epoxy resin modified with 2-5% MWCNTs
  - inner liner of polyurethane foam
    - modified with 2% CNT and fire retardants
  - Instructions for use and cleaning:
    - Use products containing ADBAC

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