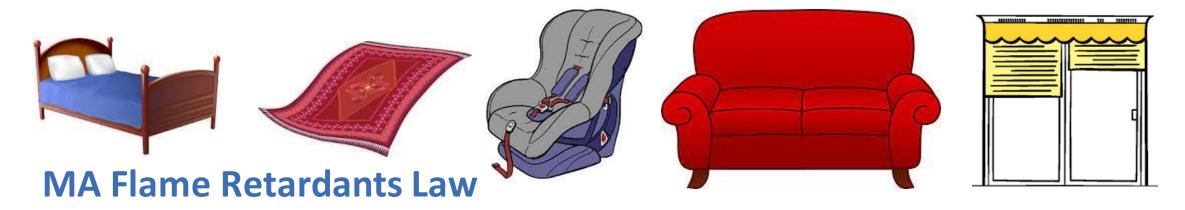


### MA Flame Retardants Law, 2020

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

Mass. Gen. Laws Ch 21A, Section 28





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

### **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

### 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 Polyhalogenated Bisphenol Aliphatics
- Chlorinated paraffins, C10-C13, 85535-84-8 Polyhalogenated Aliphatic Chains
- Antimony trioxide, 1309-64-4

Polyhalogenated Organophosphates

Polyhalogenated Diphenyl Ethers

Polyhalogenated Phthalates, Benzoates, Imides

Polyhalogenated Alicycles

### **SAB Responsibilities – ADVISE DEP**

- Specified in the law
- 3 initial questions CAS, Isomers, Analogues
- Advice can be provided with any qualifiers or explanation necessary. Does not have to be a yes/no vote.
- Broad goal is always (and especially in the case of FRs) to avoid regrettable substitution.

# Q1: When FR chemicals identified in the law are associated with more than one CAS number, should all CAS numbers be included in the regulations?

- Question arose because common CAS numbers for each chemical were specifically identified in the FR law
- This will assist DEP in providing guidance to companies in order to comply
- Additional CAS numbers would be added to regulations
- Consider Q1 through the lens of <u>chemical</u>, <u>structural</u> and <u>functional similarity</u> and <u>sameness of the chemicals</u> and the intent of the law, "to protect children, families and firefighters from harmful flame retardants"

### A few facts about CAS numbers

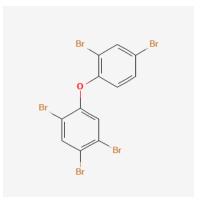
- A CAS Registry Number is a unique and unambiguous identifier for a specific substance
- Isomers may have their own CAS numbers
  - Example: different stereoisomers of a substance may also have different CAS numbers while the same substance with unspecified stereochemistry has its own number.
- Some mixtures have CAS numbers

### Related Q&A about TRI program. Answer provided by EPA

14. We use a toxic chemical with a CAS number not on the list of Section 313 toxic chemicals. There are similar toxic chemicals on the list, but none with the same CAS number. How can I be sure I do not have to report?

 Although CAS numbers are useful, a covered facility should also use the toxic chemical name to determine if a toxic chemical is listed... CAS numbers may be of limited use in the case of mixtures.

### Subclass 2 – Polyhalogenated diphenyl ethers Same name & MF - two CAS numbers



2,2',4,4',5-pentabromodiphenyl	C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O	32534-81-9	Included in MA 310 CMR
ether		(TSCA)	78.00
2,2',4,4',5-pentabromodiphenyl ether	C <sub>12</sub> H <sub>5</sub> Br <sub>5</sub> O		Same name/MF different CAS number

To CAS, these are two different "substances because one of them has a known structure and one of them is registered as an Incomplete Defined Substance (IDS), where its molecular formula is known but for which the complete structure is not known, possibly because it was not fully described in the source for where it was registered from."

### Subclass 2 – Polyhalogenated diphenyl ethers Same name & MF - two CAS numbers

2,2',3,3',4,4',5,5'-	C <sub>12</sub> H <sub>2</sub> Br <sub>8</sub> O	32534-81-9	Included in MA
octabromodiphenyl ether		(TSCA)	310 CMR 78.00
2,2',3,3',4,4',5,5'- octabromodiphenyl ether	C <sub>12</sub> H <sub>2</sub> Br <sub>8</sub> O	85446-17-9	Same name/MF different CAS number

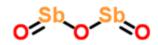
According to CAS: One substance is "incompletely defined" which is why it got its own CAS number.

### Subclass 3 – Polyhalogenated Alicycles Same name & MF - two CAS numbers



1,3,5,7,9,11- Hexabromocyclododecane	HBCD	25637–99–4	Included in MA 310 CMR 78.00
1,3,5,7,9-11- Hexabromocyclododecane		1093632-34-8	Same name different CAS number

### Subclass 6 – Inorganic Same name & MF - four CAS numbers



Chemical name	Common name	CAS Number	Status
Diantimony trioxide	Antimony trioxide	1309-64-4	Included in MA 310 CMR 78.00
Diantimony trioxide	Senarmontite	1327-33-9	Same name different CAS number
Diantimony trioxide	Mineral Valentinite	1317-98-2	Same name different CAS number
Diantimony trioxide	Senarmontite	12412-52-1	Same name different CAS number

### Subclass 5 - Polyhalogenated Aliphatic Chains (Chlorinated paraffins, 85535-84-8) Multiple CAS numbers for mixture

- Listed under TURA as "Polychlorinated alkanes, c10-c13" without CAS numbers
- Chlorinated paraffins (CPs) are complex mixtures of polychlorinated n-alkanes containing thousands of different isomers, enantiomers and diastereomers. CPs are subdivided according to their carbon chain length into short chain chlorinated paraffins (SCCPs, C10-C13), medium chain CPs (MCCPs, C14-C17) and long chain CPs (LCCPs, C>17)
- EPA Action Plan SCCPs and other chlorinated paraffins: "For the purposes of this action plan, SCCPs include the chlorinated paraffins that meet the following definition: CxH(2x-y+2)Cly where x = 10-13; y = 3-12; and the average chlorine content ranges from approximately 40 to 70 percent with the limiting molecular formulas set at C10H19Cl3 and C13Hl6Cl12. Any individual chemical meeting this definition is considered an SCCP and is covered by this action plan....The plan covers any chemical substance or mixture that contains a chemical that meets the definition.

### **Chlorinated Paraffins (c10-c13 range) - CAS Numbers**

Chemical Name	CAS Number	Additional Information, Sources
Alkanes C <sub>10-13</sub> , chloro (40-70%)  **CAS number listed in FR law	85535-84-8	Used by Stockholm Convention for Persistent Organic Pollutant (POP) designation; on European Chemicals Agency (ECHA) Substances of Very High Concern list 2008; DSL (Canadian Domestic Substances List); WA Chem of High Concern
Alkanes, c10-12, chloro (60%)	108171-26-2	National Toxics Program (NTP) 1989 Report on Carcinogens, reasonably anticipated to be carcinogenic to humans; California Prop 65; MN Chem of High Concern; NJ RtK carcinogen; WA Chem of High Concern
Alkanes, C <sub>10-21</sub> , chloro	84082-38-2	DSL; EU CAS registration; MN Chem of High Concern
Alkanes, C <sub>6-18</sub> , chloro	68920-70-7	DSL PBiT; EU carcinogen; MN Chem of High Concern; ME; WA
Alkanes, chloro; chloroparaffins	61788-76-9	DSL; $C_1$ - $C_{15}$ on CAS; $C_{20}$ on PubChem; MN Chem of High Concern; OR High Priority Chem; WA Chem of High Concern to Children
Paraffin waxes, chloro	63449-39-8	DSL PBiT; C10-C16 on CAS Registry; $C_{24}$ , FR use on PubChem; $C_{22-30}$ 70% CI on SDS; $C_{18-28}$ on ECHA; MN Chem of High Concern; OSPAR; WA Chem of High Concern to Children

Does the Board agree that these additional CAS# of the original flame retardants in the law should be included in the regulations?

## Q2: Should isomers of the FRs identified in the law (when used as flame retardants themselves) be included in the regulations?

- The Board should first consider Q2 through the lens of chemical, structural and functional similarity and sameness of the chemicals and the intent of the law, "to protect children, families and firefighters from harmful flame retardants."
- IUPAC Gold Book definition of isomer: One of several species (or molecular entities) that have the same atomic composition (molecular formula) but different line formulae or different stereochemical formulae and hence different physical and/or chemical properties.
  - Same molecular formula - different name

### **ISOMERISM**

#### © Doc Brown

Advanced pre-university school organic chemistry

### Structural Isomerism

#### Carbon chain isomerism

#### Positional isomerism

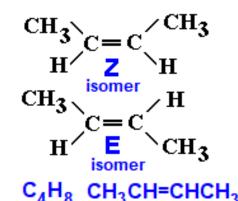
#### Functional group isomerism

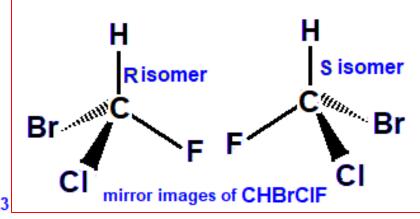
Tautomerism - an isomerisation reaction

$$\begin{array}{cccc} \text{CH}_3 - \text{C} - \text{CH}_3 & \rightleftharpoons & \text{CH}_3 - \text{C} = \text{CH}_2 \\ \text{ketone } \text{O} & \text{C}_3 \text{H}_6 \text{O} & \text{OH enol} \end{array}$$

### Stereoisomerism

### E/Z isomerism R/S isomerism





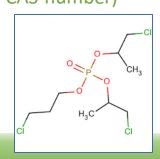
STRUCTURAL ISOMERS have the same molecular formula, but different arrangements of the atoms in the molecule - the componds differ in the order the atoms are connected.

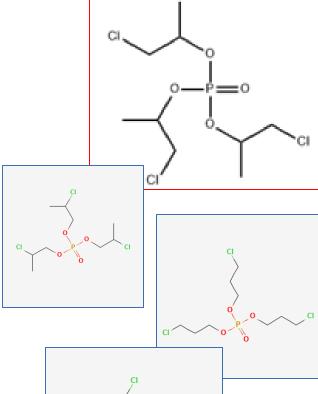
STEREOISOMERS have both the same molecular formula and structural formula (atoms connected in the same way), but differ in the spatial arrangement of the atoms in the molecule.

### Q2: Should isomers of the FRs identified in the law be included in the regulations?

Positional Isomers: Subclass 1 – Polyhalogenated Organophosphates

- Example: Tris (1-chloro-2-propyl) phosphate (TCPP) 13674-84-5
- All  $C_9H_{18}CI_3O_4P$ 
  - Isomer: Tris(2-chloropropyl)phosphate (6145-73-9)
  - Isomer: Tris(3-chloropropyl)phosphate (26248-87-3 and 1067-98-7)
  - Isomer: Bis(2-chloropropyl)(2-chloro-1-methylethyl phosphate) (76649-15-5)
  - Isomer: Bis(2-chloro–1-methylethyl)(2-chloropropyl)phosphate (76025-08-6)
  - Isomer: Bis(2-chloro-1-methylethyl)(3-chloro-1-propyl)phosphate (137909-40-1)
  - Isomer: Bis(3-chloro-1-propyl)(2-chloro-1-methyl)phosphate (no CAS number)





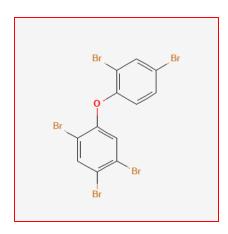
## Q2: Should isomers of the FRs identified in the law be included in the regulations?

Positional Isomers: Subclass 1 – Polyhalogenated Organophosphates

Tris(1,3-dichloro-2-propyl)phosphate (TDCPP)

Tris(2,3-dichloropropyl)phosphate

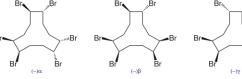
### Positional Isomers: Subclass 2 - Polyhalogenated diphenyl ethers



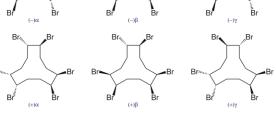
2,2',4,4',5-penta in the law 2,2',4,4',6-penta isomer

Note: Chemicals in red boxes are identified in the FR Law; blue boxes are proposed CAS, isomer, analgue on slides 18+.

Chemical name	Abbr	CAS Number	Status
2,2',4,4',5-pentabromodiphenyl ether	PentaBDE	32534-81-9 (TSCA)	Included in MA 310 CMR 78.00
2,2',4,4',6-pentabromodiphenyl ether	BDE-100	189084-64-8	Isomer
2,2',3,3',4,4',5,5'- octabromodiphenyl ether	OctaBDE; BDE-194	32536-52-0	Included in MA 310 CMR 78.00
2,2',3,3',4,4',6,6'- octabromodiphenyl ether	BDE-197	117964-21-3	Isomer
2,2',3,4,4',5,5',6- octabromodiphenyl ether	BDE-203	337513-72-1	Isomer
2,2',3,3',5,5',6,6'- octabromodiphenyl ether	BDE-202	67797-09-5	Isomer
2,3,3',4,4',5,5',6- octabromodiphenyl ether	BDE-205	446255-56-7	Isomer
2,2',3,3',4,5,5',6- octabromodiphenyl ether	BDE-198	446255-42-1	Isomer
2,2',3,3',4,4',5,6- octabromodiphenyl ether	BDE-195	446255-38-5	Isomer

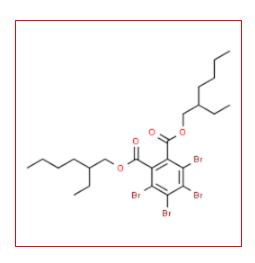


### Stereoisomers: Subclass 3 - Polyhalogenated alicycles

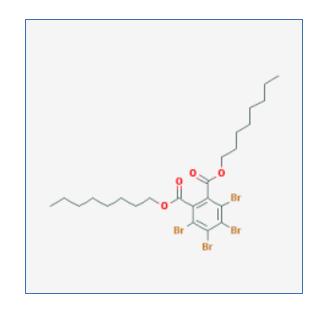


Chemical name	CAS Number	Status
1,3,5,7,9,11-Hexabromocyclododecane	25637–99–4	Included in MA 310 CMR 78.00
1,3,5,7,9-11-Hexabromocyclododecane	1093632-34-8	Same name different CAS number
1,2,5,6,9,10-Hexabromocyclododecane	3194-55-6	Isomer
(alpha)-1,2,5,6,9,10- Hexabromocyclododecane	134237-50-6	Isomer
-(alpha)-1,2,5,6,9,10- Hexabromocyclododecane	678970-15-5	Isomer
(1R,2S,5S,6R,9S,10S)-1,2,5,6,9,10-Hexabromocyclododecane	138257-19-9 (alpha)	Isomer
(beta)-1,2-5,6-9,10- Hexabromocyclododecane	134237-51-7	Isomer
(+)-β-Hexabromocyclododecane	678970-16-6	Isomer
(1R,2R,5R,6S,9R,10S)-1,2,5,6,9,10-Hexabromocyclododecane	138257-18-8 (beta)	Isomer
γ-Hexabromocyclododecane	134237-52-8	Isomer
(+)-γ-Hexabromocyclododecane	678970-17-7	Isomer
(-)-γ-Hexabromocyclododecane	169102-57-2 (gamma)	Isomer
1,1,2,2,3,3-hexabromocyclodecane	25495-98-1	Isomer
1,2,3,4,7,8-Hexabromocyclodecane	10364-34-8	Isomer

# Positional Isomers: Subclass 4 – Polyhalogenated Phthalates/Benzoates/Imides

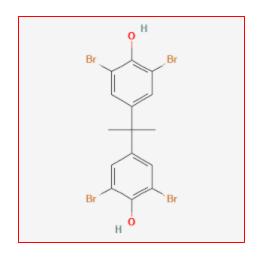


Bis(2-Ethylhexyl)-3,4,5,6- tetrabromophthalate (TBPH) 26040-51-7  $C_{24}H_{34}Br_4O_4$ 



Dioctyl 3,4,5,6-tetrabromobenzene-1,2-dicarboxylate 56720-20-8  $C_{24}H_{34}Br_4O_4$ 

# Positional Isomers: Subclass 5 – Polyhalogenated Bisphenol Aliphatics

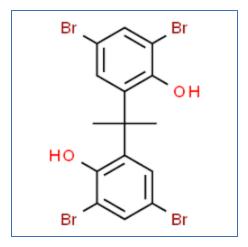


Tetrabromobisphenol A (TBBPA)

<del>79-94-7</del>

 $C_{15}H_{12}Br_4O_2$ 

4,4' TBBPA, 4,4'-(1-methylethylidene)bisphenol tetrabromo deriv. CAS 121839-52-9



2,2'Isopropylidenebis[4,6-dibromophenol], CAS 97890-15-8

Does the Board agree that these isomers of the original flame retardants in the law should be included in the regulations?

### **Analogues**

- Do isomers also satisfy the chemical analogue definition?
- "Product that contains any of the following 11 flame retardants or a chemical analogue" is the language in the law
- Chemical Analogue: A compound having a structure similar to that of another compound, but differing from it in respect to a certain aspect. It can differ in one or more atoms, functional groups, or substructures, which are replaced with other atoms, groups, substructures, or in their arrangement.

Analogue definition from the proposed regulations (developed by DEP, ORS and TURI)

### Do these isomers also fit the analogue definition?

#### Positional Isomers – polyhalogenated diphenyl ethers

2,2',4,4',5-penta in the law 2,2',4,4',6-penta isomer

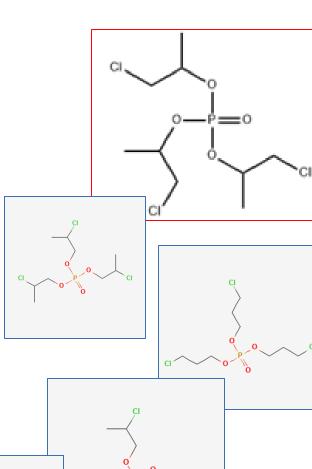
Chemical Analogue: A compound having a structure similar to that of another compound, but differing from it in respect to a certain aspect. It can differ in one or more atoms, functional groups, or substructures, which are replaced with other atoms, groups, substructures, or in their arrangement.

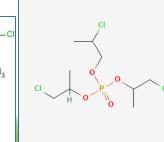
### Do these isomers also fit the analogue definition?

Chemical Analogue: A compound having a structure similar to that of another compound, but differing from it in respect to a certain aspect. It can differ in one or more atoms, functional groups, or substructures, which are replaced with other atoms, groups, substructures, or in their arrangement.

#### **Positional Isomers**

- Example: Tris (1-chloro-2-propyl) phosphate (TCPP) 13674-84-5
- All  $C_9H_{18}Cl_3O_4P$ 
  - Isomer: Tris(2-chloropropyl)phosphate (6145-73-9)
  - Isomer: Tris(3-chloropropyl)phosphate (26248-87-3 and 1067-98-7)
  - Isomer: Bis(2-chloropropyl)(2-chloro-1-methylethyl phosphate) (76649-15-5)
  - Isomer: Bis(2-chloro–1-methylethyl)(2-chloropropyl)phosphate (76025-08-6)
  - Isomer: Bis(2-chloro-1-methylethyl)(3-chloro-1-propyl)phosphate (137909-40-1)
  - Isomer: Bis(3-chloro-1-propyl)(2-chloro-1-methyl)phosphate (no CAS pumber)





### **Analogues**

- Do isomers also satisfy the chemical analogue definition?
- "Product that contains any of the following 11 flame retardants or a chemical analogue" is the language in the law
- Chemical Analogue: A compound having a structure similar to that of another compound, but differing from it in respect to a certain aspect. It can differ in one or more atoms, functional groups, or substructures, which are replaced with other atoms, groups, substructures, or in their arrangement.

Analogue definition from the proposed regulations (developed by DEP, ORS and TURI)

### Q3a: Does each proposed chemical analogue meet the analogue definition?

- TURI/DEP identified possible analogues
- Reviewed reports from more than 30 organizations (universities, NGOs, governments) that have studied FRs, identified a list of approx. 200 chemicals, identified structurally similar chemicals to the 11, considered possible use in the product categories, chose 24 very closely related analogues for SAB consideration

### **Subclass 2 – Polyhalogenated diphenyl ethers**

$$Br_m$$
  $Br_n$ 

Chemical Analogue: A compound having a structure similar to that of another compound, but differing from it in respect to a certain aspect. It can differ in one or more atoms, functional groups, or substructures, which are replaced with other atoms, groups, substructures, or in their arrangement.

Decabromodiphenyl ether Nonabromodiphenyl ether Heptabromodiphenyl ether Hexabromodiphenyl ether Tetrabromodiphenyl ether Dibromodiphenyl ether Monobromodiphenyl ether

### **Subclass 3 – Polyhalogenated alicycles**

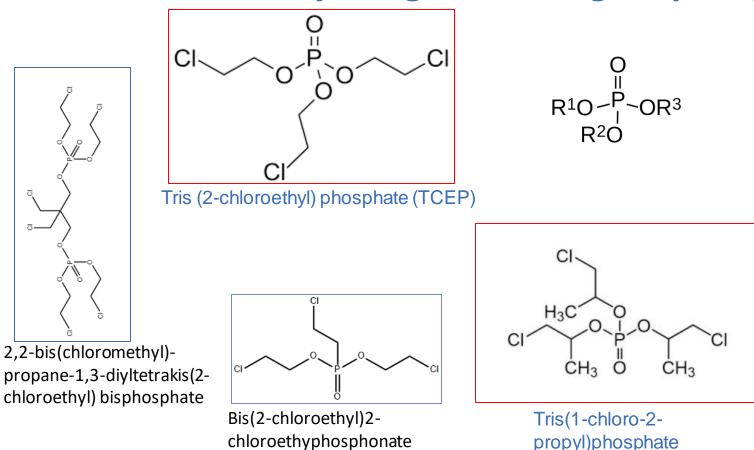
$$H_2$$
CCCCH2

Hexabromocyclodecane C<sub>10</sub>H<sub>14</sub>Br<sub>6</sub>

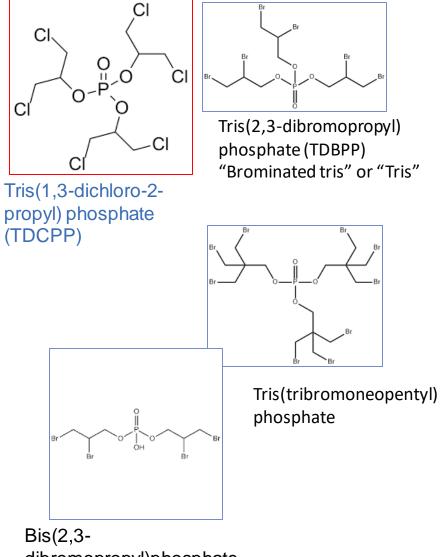
1,2,3,4,5-Pentabromo-6-chlorocyclohexane  $C_6H_6Br_5Cl$ 

### **Subclass 1 – Polyhalogenated Organophosphates**

(TCPP)

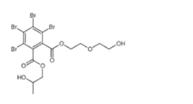


Chemical Analogue: A compound having a structure similar to that of another compound, but differing from it in respect to a certain aspect. It can differ in one or more atoms, functional groups, or substructures, which are replaced with other atoms, groups, substructures, or in their arrangement.

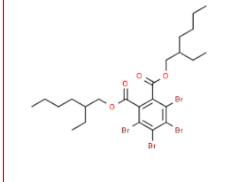


dibromopropyl)phosphate

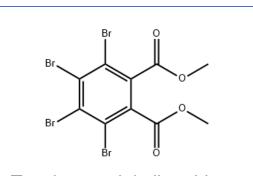
### **Subclass 4 – Polyhalogenated Phthalates, Benzoates, Imides**



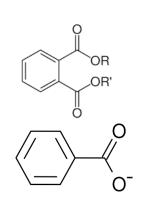
2-(2-hydroxyethoxy)ethyl-2hyroxypropyl-3,4,5,6tetrabromo phthalate

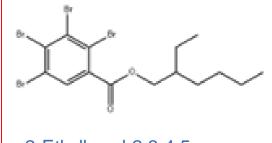


Bis(2-Ethylhexyl)-3,4,5,6tetrabromophthalate (TBPH)

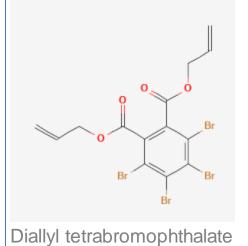


Tetrabromophthalic acid dimethyl ester





2-Ethylhexyl-2,3,4,5-Tetrabromobenzoate (TBB)



Chemical Analogue: A compound having a structure similar to that of another compound, but differing from it in respect to a certain aspect. It can differ in one or more atoms. functional groups, or substructures, which are replaced with other atoms, groups, substructures, or in their arrangement.

2-(2-hydroxyethoxy)ethyl-2-

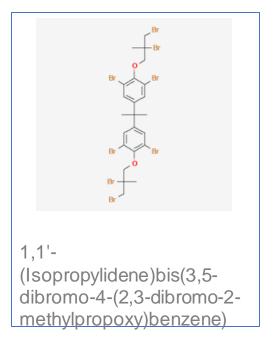
phthalate mixed esters with

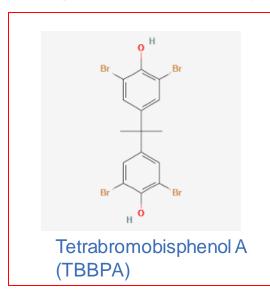
hyroxypropyl-3,4,5,6-tetrabromo

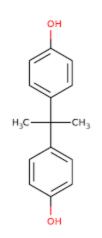
diethylene and propylene glycol

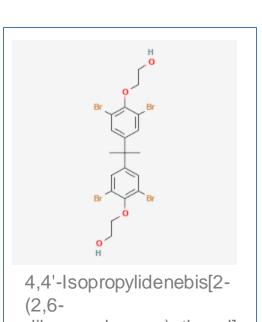
### **Subclass 5 – Polyhalogenated Bisphenol Aliphatics**

Chemical Analogue: A compound having a structure similar to that of another compound, but differing from it in respect to a certain aspect. It can differ in one or more atoms, functional groups, or substructures, which are replaced with other atoms, groups, substructures, or in their arrangement.

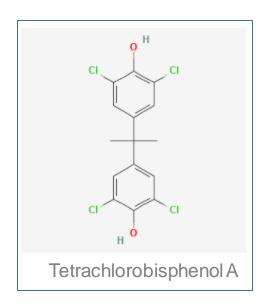


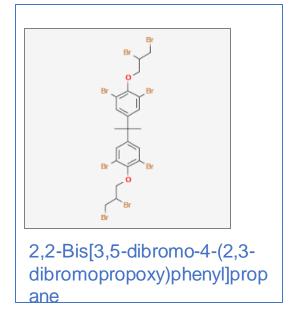




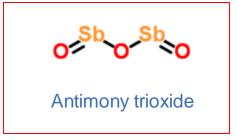


dibromophenoxy)ethanol]

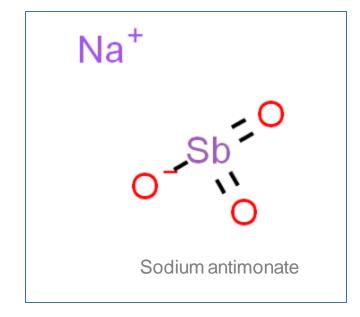


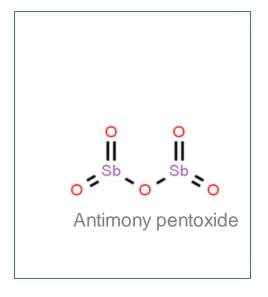


### **Subclass 7 - Inorganics**



Chemical Analogue: A compound having a structure similar to that of another compound, but differing from it in respect to a certain aspect. It can differ in one or more atoms, functional groups, or substructures, which are replaced with other atoms, groups, substructures, or in their arrangement.





### How some other states are categorizing FRs (above certain thresholds)

NY 2022	functional usetoinhibit the spread of fire and chemical isa halogenated (FI, CI, Br, I) organophosphorus, organonitrogen, or nanoscale	Uphol. furn, mattresses, electronic displays
NH 2020	functional use is toinhibit the spread of fire. andhalogenated, phosphorus-based, nitrogen-based and nanoscale flame retardants	Uphol. furn, carpeting, carpet pad
ME 2019	functional use is toinhibit the spread of fire. andhalogenated, phosphorus-based, nitrogen-based and nanoscale flame retardants and any chemical or chemical compound for which "flame retardant" appears on the SDS	Uphol. furn for private use
CA 2020	functional useis to inhibit the spread of fireincludingchemical for which the term "flame retardant" appears on the SDS and one of the following:  (i) halogenated, organophosphorus, organonitrogen, or nanoscale chemical.  (ii) "designated chemical" in Section 105440 of the Health and Safety Code. (CA biomonitoring program and Nat'l Reports on Human Exp to Env Chemicals)  (iii) listed on the Washington State Department of Ecology's list of Chemicals of High Concern to Childrenand identified as a flame retardant to flame retardants in the rationale for inclusion in the list.	Juvenile products, mattresses, uphol furn
Wa DC 2018 2019	Bans TDCPP, TCEP, thenshall not replace the penta/octa/deca mixtures of PBDEs, TDCPP, TCEPwith a chemical that is: (1) known/reasonably anticipated/likely to be a human carcinogen by NTP or EPA or (2) identified by NIH as causing birth defects, hormone disruption, neurotoxicity, or harm to reproduction or development	Children's products, residential uphol furn first then ALL products



### Fall SAB Meeting

Q3b: Is each proposed **analogue** sufficiently similar to at least one chemical identified in the law such that the proposed analogue would be reasonably anticipated to have similar concerns re: toxic hazard, persistence, bioaccumulation?

What would the Board need?