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Comments on the draft rule regarding the use of organohalogen flame retardants

My name is Marcelo Hirschler and I have been an advocate for improved fire safety for many years, by working in the areas of codes and standards at various organizations (see attached recent Curriculum Vitae[1]).

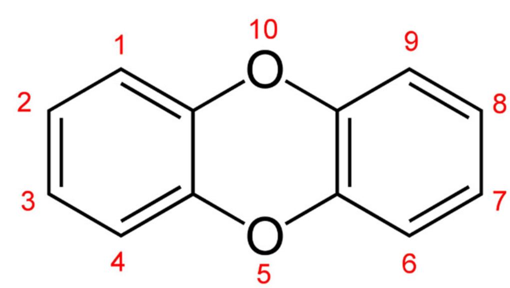
I am concerned about the proposed regulation, "Safer Products for Washington," that would prohibit the use of organohalogen flame retardants in a variety of applications. In particular, this relates to electric and electronic products with plastic external enclosures intended for indoor use. This category includes all types of appliances (large and small) and wires and cables.

My concern relates both to the extreme scope of the proposed regulation and to its implications.

Extreme scope of the proposed regulation: With regard to the extreme scope, let me clarify that I am fully cognizant that some organohalogen flame retardants that had been in use for many years have since been found to be of concern. Those flame retardants (specifically, for example pentabromodiphenyl ether [also known as pentabromodiphenyl oxide or pentaBDE, octabromodiphenyl ether [also known as octabromodiphenyl oxide or octaBDE, and decabromodiphenyl ether [also known as decabromodiphenyl oxide or decaBDE]) are no longer commercial products being manufactured in the US. In place of these materials a variety of alternative flame retardants have been developed by manufacturers and have undergone a plethora of tests to assess their potential toxicity and environmental effects and been found not to be of concern. Therefore, The approach of regulating organohalogen flame retardants as a class does not have the correct scientific basis. There is much scientific rigor if every individual flame retardant of concern is identified by its individual chemical structure (and/or its CAS registry number) instead of an inappropriate broad brush approach covering every single organohalogen flame retardant irrespective of whether it is or is not of concern, particularly since most of them have been identified, as a result of all the testing, as not being of concern.

Similar structure is not sufficient to classify generically: It has been shown repeatedly that the vast majority of the properties of a specific material can be very significantly different in terms of their properties from those of materials with very similar chemical composition. I will provide three examples.

<u>The first example</u> of this are the "polychlorinated dibenzodioxins", often simply known as "dioxins" or "PCDDs". In PCDDs, chlorine atoms are attached to a structure of two benzene rings joined by two oxygen bridges at any of 8 different places on the molecule, at positions 1–4 and 6–9, as shown below. They are named based on at which position the chlorine atom is attached.



[1] Curriculum Vitae of Dr. Marcelo M. Hirschler, dated January 2023.

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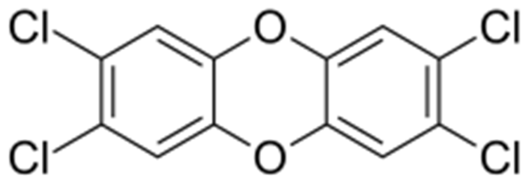
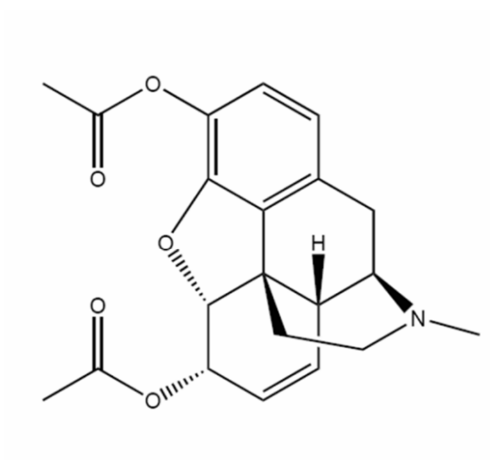
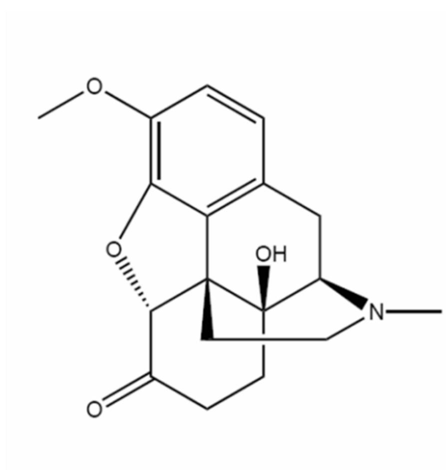
There are a total of 75 different PCDD congeners. The most widely known PCDD. the 2, 3,7, 8 tetrachlorodibenzodioxin, shown below, is often incorrectly labeled simply as "dioxin":



The relative toxic equivalency factor of the vast majority of these PCDDs[2], when compared to the base one (2, 3, 7, 8 tetrachlorodibenzodioxin) is virtually negligible (meaning that they are virtually nontoxic), except for one that is about equally toxic (1,2,3,7,8-PeCDD), three that are 10 times less toxic, one that is 100 times less toxic and one that is 3,000 times less toxic. In spite of this scientific finding, all "dioxins" are treated as the same, when only a few of them are actually toxic. Obviously, I am not proposing that any PCDDs be allowed for use in any way. Moreover, I am not claiming that the proposed ban on the use of organohalogen flame retardants is in any way related to dioxins. However, the above is an example as to why it is important to identify materials specifically rather than dealing with them as a class.

The second example showing the fallacy of regulating all materials with similar chemical structure the same way can be found in the field of medicine. Let's use the example of the opioids to illustrate this point. Below is shown the chemical structure of heroin (a dangerous illicit street drug; right) and of oxycodone (a prescription pain reliever medication; left). It is clear that these two drugs have very similar structures. However, one of them is dangerously toxic (and potentially lethal) while the other one is used as an effective painkiller.





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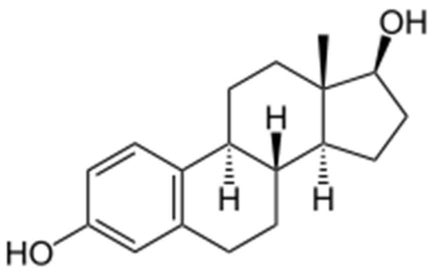
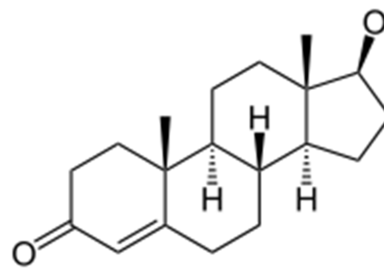
[2] "The 2005 World Health Organization Re-evaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-like Compounds", by Martin van den Berg, Linda S. Birnbaum, Michael Denison, Mike De Vito, William Farland, Mark Feeley, Heidelore Fiedler, Helen Hakansson, Annika Hanberg, Laurie Haws, Martin Rose, Stephen Safe, Dieter Schrenk, Chiharu Tohyama, Angelika Tritscher, Jouko Tuomisto, Mats Tysklind, Nigel Walker, and Richard E. Peterson, published in Toxicological Science 2006 Oct; 93(2): 223–241.

The third example is of two substances with very similar chemical structure but very different function. In this example there is the case of estradiol (which is a female sex hormone, on the left) and testosterone (which is a male sex hormone, on the right). They have a similar structure but very different activity.





Not all organohalogen flame retardants are similar: Many of the newer organohalogen flame retardants are polymeric (and not monomeric) flame retardants, with very high molecular weight, meaning that the probability of their volatilization to become airborne and cause respiratory effects is very low. Many other newer organohalogen flame retardants are reactive, and not additive, meaning that they are incorporated into the substrate (the plastic material) by covalently reacting with the plastic (or polymeric) material when the plastic material is being created. The finished material thus contains a built-in flame retardant that cannot easily migrate out (volatilize, or bloom to the surface) like the less strongly bound additive flame retardants. It is essential that any regulation of flame retardant use must take into account the difference between polymeric, oligomeric, and monomeric flame retardants and between additive and reactive flame retardants. It is also essential that the opportunity for innovation must be provided, which is not available when a full class of materials (including some that have not yet been developed) is being banned, thereby declaring as unsafe potential materials that do not yet exist.

Also, a standard has relatively recently been approved by ASTM, as ASTM D8280-20a (Standard Test Method for Determination of the Blooming of Brominated Flame Retardants onto the Surface of Plastic Materials by Ion Chromatography), which allows the quantitative determination of the bromine originating from any flame retardant that has bloomed onto the surface of the plastic after aging under specified conditions. With this test, based on the known structure of the flame retardant used, the amount of the flame retardant that bloomed can also be calculated. More importantly, the test can be used as a pass/fail assessment to determine whether or not the flame retardant actually escapes onto the surface of the material into which it has been incorporated. The use of this technique as a regulatory tool would allow brominated flame retardants that "pass" the test to be used instead of just all brominated flame retardants being lumped together .

The proposed regulation has the potential to lower fire safety.

Flame retardants improve fire safety and halogenated flame retardants are very efficient

The proposed regulation implies that any flame retardant can simply be substituted for an alternate one. There is abundant evidence that this is not a valid assumption. In particular, this will be, at least partially, of the mechanism of action of the flame retardants in question. It has been shown that brominated flame retardants (for example) act primarily in the gas phase while many phosphorus-containing flame

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retardants act primarily in the condensed phase (I attach a study of mine from back in 1982[3], with information that was "recent" at the time). Therefore, it is clear that replacing a brominated flame retardant by a phosphorus-containing one will not be a simple one-to-one replacement.

A few years ago (initially in 2005, and updated in 2015), for example, the US Environmental Protection Agency[4] conducted a study looking at replacing a halogenated flame retardant (pentabromodiphenyl ether) that was found to be undesirable and had been used to protect flexible polyurethane foam. As stated earlier, the US manufacture of pentabromodiphenyl ether has long since been discontinued. However, the reason the study is important to note is that it found that there were no easy replacements that were equally efficient in providing the needed fire performance.

Another example of the fact that direct replacement is often not possible to achieve with the same result is the case of plenum cables. In the US all electrical and optical fiber cables intended for use in plenums (which are the spaces above the dropped ceiling where the air distribution system is located, meaning heating and air conditioning) are required by the National Electrical Code and all building codes to meet a very severe flammability requirement. In spite of over 30 years of research and development it has been found that only systems that does contain halogenated materials are capable of achieving the required fire performance, in terms of flame spread and smoke release. The result of that is that, if halogenated materials were not allowed in plenum cables, a complete type of product would have to be discontinued. I understand that electrical and optical fiber cables are (fortunately) not covered by the proposed regulation.

I attach three documents that I authored demonstrating the improvements in fire safety as a result of the use of flame retardants. They are a short 2016 report on the benefits of flame retardants[5], and two studies on the effects of flame retardants on heat release, published in Fire and Materials (a scientific journal)[6][7]. The studies on the effects of flame retardants on heat release are particularly important because it has been shown that heat release rate is the most critical parameter associated with fire safety[8]. Consequently, eliminating the use of flame retardants will lead to a significant lowering of fire safety.

Studies by the Swedish scientist Dr. Margaret Simonson on life cycle analyses (LCA) on TV sets[9], cables[10], and upholstered furniture[11] showed that flame retardants do not pose environmental damage by virtue of effectively improving fire performance and releasing much fewer polynuclear aromatic

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[3] "Recent developments in flame-retardant mechanisms", M.M. Hirschler, in "Developments in Polymer Stabilisation, Vol. 5", Ed. G. Scott, pp. 107-52, Applied Science Publ., London, 1982.

[4] https://www.epa.gov/saferchoice/flame-retardants-used-flexible-polyurethane-foam

[5] "Benefits of Flame Retardants", by Marcelo Hirschler (unpublished report, January 2016).

[6] "Flame Retardants and Heat Release: Review of Traditional Studies on Products and on Groups of Polymers", M.M. Hirschler, Fire and Materials (Article published online, Fire and Materials, 03/11/2014, DOI: 10.1002/fam.2243), 2014 [39, 207-231, 2015].

[7] "Flame Retardants and Heat Release: Review of Data on Individual Polymers", M.M. Hirschler, Fire and Materials (Article published online, Fire and Materials, 03/11/2014, DOI: 10.1002/fam.2242), 2014 [39, 232-258, 2015].

[8] " Heat Release Rate: The Single Most Important Variable in Fire Hazard", V. Babrauskas and R.D. Peacock, Fire Safety J. 18, 255-272 (1992).

[9] "Fire-LCA Model: TV Case Study", SP Report 2000:13, Simonson, M., Blomqvist, P., Boldizar, A., Möller, K., Rosell, L., Tullin, C., Stripple, H. and Sundqvist, J.O., , Swedish National Testing and Research Institute, Fire Technology (2000).

[10] "Fire-LCA Model: Cables Case Study" SP Report 2001:22, Simonson, M., Andersson, P., Rosell L., Emanuelsson, V. and Stripple H., Swedish National Testing and Research Institute, Fire Technology (2001).

[11] "Fire Safety of Upholstered Furniture - LCA Analysis" SP Report 2003:22, Andersson, P., Simonson, M. and Stripple H., Swedish National Testing and Research Institute, Fire Technology (2003).

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hydrocarbons (PAH). Data from these studies demonstrated that PAH emissions from the improved fire performance materials (such as TVs or upholstered furniture) were only some 3% of those from the products with low fire performance. Thus, the studies showed that a reduction in the number of fires because of the use of products containing materials with improved fire performance was associated with significant benefit to the environment as well as saving lives from fires. In fact, the studies also identified the fact that the reduction in problematic emissions of combustion products when using flame retardants also led to a significant decrease in the overall toxicity of the products emitted.

Another study of particular interest was conducted at the National Bureau of Standards (now called the National Institute of Standards and technology, NIST) published in 1988, where they compared the effect on a variety of fire safety parameters of fire retarded and non-fire retarded products[12]. The products involved were the following: a TV cabinet, a business machine housing, an upholstered chair, an electric cable, and an electric circuit board. Studies involved small-scale tests and room-scale tests. The conclusions were overwhelming: the fire retarded products were much safer. From the other studies mentioned above it was to be expected that the heat released by the fire retarded products was much lower than that released by the non-fire retarded ones. Of special interest, however, were the facts that the time available for escape was so much longer when the products were fire retarded (in fact 15 times longer times available for escape for the fire retarded products) as was the toxicity of the atmosphere containing the combustion products (3 times lower toxicity for the fire retarded products).

It is useful also to compare the amount of flame retardant that needs to be added to a plastic to achieve an acceptable level of fire performance. For example, inorganic halogen-free flame retardants such as alumina trihydrate needs to be used at additive levels as high as 70% for a variety of different polymeric materials while brominated flame retardants can generate similar fire performance at additive (or reactive) levels that are on the order of 10% only.

Summary

- The proposed ban on using any halogenated fire retardants without specifying the actual material involved is technically incorrect since it does not distinguish (a) between materials that should not be used and those that are safe for use, (b) between monomeric and polymeric flame retardants and (c) between additive and reactive flame retardants.
- The proposed ban on using halogenated flame retardants has the potential for making it not possible to achieve certain levels of fire performance that may not be obtainable with other flame retardants.
- The proposed ban on using halogenated flame retardants may lead to a lowering of fire safety without any associated advantage in terms of other environmental or toxicity issues.

Marcelo M. Hirschler – January 30, 2023

[12] "Fire Hazard Comparison of Fire-Retarded and Non-Fire-Retarded Products (NBS Special Publication SP 749)", Babrauskas, V., Harris, R. H., Jr., Gann, R. G., Levin, B. C., Lee, B. T., Peacock, R. D., Paabo, M., Twilley, W., Yoklavich, M. F., and Clark, H. M., National Bureau of Standards, Gaithersburg, MD (1988).