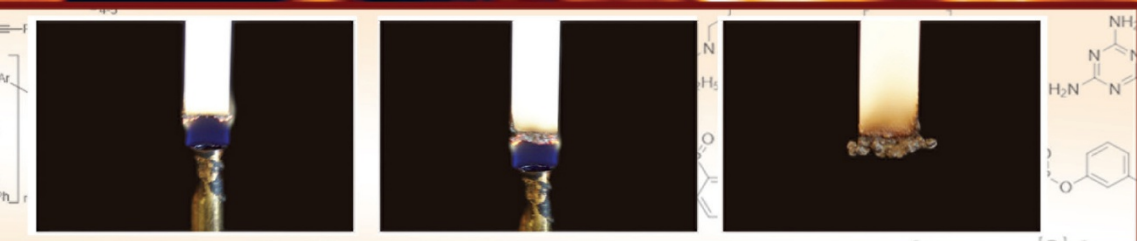


NON-HALOGENATED FLAME RETARDANT HANDBOOK

— SECOND EDITION —



EDITED BY
ALEXANDER B. MORGAN

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Non-Halogenated Flame
Retardant Handbook
2nd Edition

Scrivener Publishing

100 Cummings Center, Suite 541J
Beverly, MA 01915-6106

Publishers at Scrivener

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2nd Edition

Edited by

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This edition first published 2022 by John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA and Scrivener Publishing LLC, 100 Cummings Center, Suite 541J, Beverly, MA 01915, USA
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1st edition (2014), 2nd edition (2022)

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Library of Congress Cataloging-in-Publication Data

ISBN 978-1-119-75056-7

Cover image: Wikimedia

Cover design by Russell Richardson

Set in size of 11pt and Minion Pro by Manila Typesetting Company, Makati, Philippines

Printed in the USA

10 9 8 7 6 5 4 3 2 1

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Preface to the 2nd Edition of the Non-Halogenated Flame Retardant Handbook

Since the writing of the first edition in 2014, and the writing/publishing of this book in the 2020-21 timeframe, there have been some notable changes to the non-halogenated flame retardant field. Mostly, there have been an increase in regulations of flame retardant (FR) chemicals, further de-selection of chlorinated/brominated flame retardants, and some diversification of the flame retardants that exist in the “non-halogenated” category. Therefore, a need for a 2nd edition existed. This is actually quite rapid for the FR field and for generation of a 2nd edition of a book only 6 years after the publishing of the first, vs. the typical 10-15 years for FR book updates. FR technology tends to move at a slow pace due to flame retardant material science being a reactive field in response to regulations. Regulations take a notable amount of time to develop, be debated, and put into law, and so developments in FR chemistry in response to those regulations takes equally long. It can take even longer to take those developments out of the lab and scientific literature and then commercialize them.

The need of a book dedicated to non-halogenated flame retardant chemistry remains as strong as it did with the 1st edition, and this book includes chapters on FRs including Phosphorus-based (Chapter 2), Mineral-based (Chapter 3), Intumescent-based (Chapter 4), Nitrogen-based (Chapter 5), Silicon-based (Chapter 6), Boron-based (Chapter 7), and all the other non-halogenated FR systems which are not based upon the above elements (Chapter 10). All of these chapters existed in the 1st edition of the book, but each of these chapters has been updated for this book, and in some cases, significantly so. Chapter 10 is significantly revised, and includes bio-based FR chemicals, as well as some newer concepts. There are three new chapters in this book, including a chapter on regulations (Chapter 1), a chapter on conformal non-halogenated flame retardant coatings (Chapter 8), and a chapter on multi-component flame

retardant systems (Chapter 9). Overall, the revised content in the chapters from the 1st edition, and the new chapters to this edition create an excellent contribution to flame retardant materials science. Or I hope you'll come to that conclusion after you read the book.

As stated in the first edition, the fire threat for materials has not changed just because the regulatory environment around FR chemicals has. There is still a pressing need for flame retardant solutions for materials throughout modern society. One could argue that in some cases, with an increase in electrification of vehicles and buildings, that there may be more need, rather than less, for fire protection, and so non-halogenated solutions are part of that solution space. So with that, I believe you'll find that this book is a single source of practical non-halogenated FR technology and information that will guide whatever research, development, testing, and evaluation (RDT&E) is needed for new fire safe solutions. I further believe that even with the many recent changes in regulations occurring as we speak, and in the years to come, that the book will still be very useful for many years beyond the 2021 publishing of this book.

As with all prefaces, I would like to thank those who helped make this book possible, especially the authors of the individual chapters who have taken time out of their busy lives to write the chapters. I also want to thank Scrivener Publishing again for their willingness to publish the 2nd edition. Special thanks goes out to Dr. Anteneh Worku of FR Adviser LLC and Dr. Adrian Beard of Clariant GmbH for helping review chapters in this book. I certainly must thank my (now retired) colleague, Prof. (emeritus) Charles Wilkie of Marquette University, for getting me started into flame retardant book publishing many years ago. This is now the sixth book I've edited, and my first one on my own. Chuck taught me how to navigate this area, and for this I'm quite grateful. Finally, I want to thank my wife, Julie Ann G. Morgan, for her continual support during my career, and for teaching me enough grammar that I can finally write on my own, although she may still take issue that I actually learned those lessons.

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Dayton, Ohio, USA

October, 2021

Regulations and Other Developments/ Trends/Initiatives Driving Non-Halogenated Flame Retardant Use

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Abstract

Fire safety of materials is regulated via laws like building codes or product safety laws, which in turn refer to standards of performance and testing needs to meet various fire risk scenarios. As such, fire safety of materials, and the individual components and chemicals involved in these materials are highly regulated. Indeed, as a field of materials science, it is performance needs together with regulatory requirements or voluntary schemes like ecolabels and market trends which drive chemical selection for fire safety needs – in addition to economical constraints. This chapter will discuss the regulatory requirements which affect the choice flame retardant chemicals. Specific regulations of the chemicals themselves, and new regulatory issues that are driving selection and de-selection of specific flame retardant chemicals for fire safety needs will be presented as well.

Keywords: Regulations, codes, standards, fire risk scenarios, fire safety, environment, chemical regulation, politics, ecolabels

1.1 Regulatory History of Halogenated vs. Non-Halogenated Flame Retardants

Before beginning any book on non-halogenated flame retardants, it is important to understand the history of why there is such a book focused

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Alexander B. Morgan (ed.) Non-Halogenated Flame Retardant Handbook 2nd edition, (1–22)
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on non-halogenated flame retardants. Prior to the late 20th century, flame retardants were not necessarily singled out by any particular chemistry. Indeed, prior to the 1930s, halogen was not used at all as a flame retardant chemical, and even after its discovery and use, it was just another class of chemicals used to impart fire safety to other materials.

To begin with, a flame retardant chemical is a chemical that shows the ability to retard flame growth and spread in a particular material in a particular fire risk scenario. This flame retarding function can be achieved with very diverse chemistries based on the elements bromine, chlorine, phosphorus, nitrogen, and aluminum to name the most prominent. Many of these elements, other than halogen, are discussed throughout this book. On top of these elements, both organic and inorganic substances are being used. The only common feature is that the flame retardant interferes with some of the chemical reactions which are necessary for sustained burning of a material and generally raises the energy that is necessary to ignite a material – flame retardants do not make materials non-combustible.

Not all flame retardants are universally able to flame retard all polymers in all fire risk scenarios. A particular chemical may be very effective in one polymer, but not in another. This is really no different than most chemicals in use throughout the world today: each has its specific chemistry it is capable of, and its own chemical structure-property relationships that yield certain end effects when a chemical reaction occurs. There can be simplicity in grouping chemicals by general structural class and similarity due to how they chemically react. For example, halogenated flame retardants tend to have very similar flame retardant mechanisms of vapor phase combustion inhibition, regardless of chemical structure. There are exceptions where aliphatic and aromatic halogenated compounds can have different reactivity in fire events, as well as additional fuel/chemical interactions that one class will show and the other will not, but some general mechanisms of flame retardancy can be assigned to a group of similar chemicals. As will be discussed, some general classes of flame retardant chemicals include halogenated, phosphorus-based, mineral fillers, nitrogen-based, silicon-based, boron-based, and a wide range of other niche chemicals ranging from transition metal materials to metalloids to carbon-based structures. So while it is possible to group chemicals by flame retardant activity and mechanism, it becomes more complicated to group those same chemicals for reactivity in non-flame retardant scenarios. For example, one mineral filler used as a flame retardant, magnesium hydroxide, works as a flame retardant chemical for wire and cable applications. It also is the active ingredient in “Milk of Magnesia”, which is an oral antacid for heartburn and digestive issues. Other mineral fillers with flame retardant effect may not have this same

dual effect and further, may not be safe for ingestion at all. Environmental chemical effects, as well as chemical persistence, bioaccumulation, and toxicity (PBT) profiles are very chemical structure dependent when interacting with humans and the natural environment. All mineral fillers may be persistent (and it is debatable that persistence for minerals is really a problem or not), but they will have very different bioaccumulation and toxicity profiles dependent upon their chemical structure. Likewise, all chemicals and chemical flame retardants will have different PBT profiles, even if they are in the same general chemical class. With this in mind, we can discuss some regulatory history of halogenated vs. non-halogenated flame retardant chemicals.

Halogenated flame retardants began use in earnest in the 1930s and onwards, as they were found to be potent flame retardant additives for flammable materials, as well as strong extinguishing agents such that liquid halogenated solvents were used in fire extinguishers. Indeed, there are reports of fire extinguishing “hand grenades” that were glass globes filled with carbon tetrachloride (now known to be a potent carcinogen) that firemen would lob into fires to help put them out, and, this same halogenated chemical was used in hand-held fire extinguishers [1]. As hazards of these liquid chemicals were found, these liquid halogenated flame retardants were pulled from service and other active extinguishing agents were instead put into fire extinguishers. Halon gas extinguishers were used for severe fire situations, but even these have been pulled from service due to ozone depletion issues. Their relative chemical stability made them non-toxic and therefore a preferred choice, however, for the same reason the chemicals were able to reach the stratosphere where they finally reacted with ozone. Halogenated flame retardant additives put into plastics began to be under regulatory scrutiny in the late 1990s to early 2000s as part of a move to prevent dioxin formation when end-of-life plastics (and other household waste) would be sent to incinerators. Incineration of waste is commonly carried out in Europe due to the lack of landfill space there, and for waste-to-energy efforts that are present in some European countries, especially in Scandinavia. Waste is difficult to presort, and so large amounts of polyvinyl chloride (PVC), as well as other halogenated compounds, ended up in the waste and large amounts of dioxin were formed as part of the emissions from these incineration facilities. As this was discovered, regulations were put in place to mitigate and cease dioxin formation via two methods. The first was with improved emissions capture and cleanup systems (baghouses, scrubbing systems, afterburners), and the second was to remove halogen from the waste stream. The second approach was where regulations against halogenated flame retardants began in earnest, with two

well-known directives, the Reduction of Hazardous Substances (RoHS) [2, 3] and Waste Electrical and Electronic Equipment (WEEE) [4, 5]. These initiatives sought to reduce and eliminate the use of halogenated additives in consumer products, namely electronics, which would in turn reduce the amount of halogenated additives going to incinerators, or, accidentally released to the environment. The directives also aim at eliminating legacy brominated flame retardants from recycle streams, so that they do not end up in new E&E equipment via recycling.

Another reason for banning or limiting use of halogenated flame retardant additives in flammable materials (such as polymers) is the corrosive gases that form from these flame retardants as they activate in a fire. The vapor phase flame inhibition mechanism of halogenated flame retardants is well known to produce acid gases (HF, HCl, HBr) [6–9] which can present some secondary health effects (irritation of eyes and lungs) which can exacerbate the toxicity situation caused by the primary toxicant in fires, carbon monoxide [10–14]. Additionally, the acid gases can cause significant economic damage to materials that are sensitive to corrosive gases. Modern electronics are particularly sensitive to corrosive gas damage, and so there have been new regulations banning halogenated flame retardants from computer server facilities computer chip fabrication sites for this very reason. There are also some acidic gas regulations for aerospace, maritime, and mass transportation which also limit or effectively ban halogenated flame retardants from use.

Other European Union (EU) regulations have come into effect banning specific brominated flame retardant molecules found to have negative persistence, bioaccumulation, and toxicity (PBT) profiles, especially as new information comes to light indicating that a particular chemical structure is hazardous. This is how things evolve from a chemical use perspective, and is how it should occur. With new information about hazards, hazardous materials should be removed from use and commerce. However, as new information comes along, sometimes the regulatory picture becomes clouded. Going back to the main issue with dioxin formation, it is now well known that with halogen being naturally present everywhere in our environment, any time you have a fire or combustion event where halogen is present, you will form dioxins. Halogenated dioxins can be found in forest fires [15] as well as from electrical/electronic fires [16]. Unless you have capture systems and afterburners, dioxins will be emitted. The amount of dioxins formed depends on the materials involved in the fire event, as well as combustion conditions. It's impossible to remove halogen from the environment, and indeed, fires themselves, especially accidental ones involving modern materials, produce all sorts of toxins and

pollutants including sub-lethal gasses, lethal gases, and carcinogens such as polyaromatic hydrocarbons (PAHs) [17–22]. These toxins can be found in fires where flame retardants are present, as well as those without flame retardants, although the total volume of pollutants produced is less if the fire growth is lowered by the presence of effective flame retardants [23–29]. Therefore, the original regulatory reason behind halogenated flame retardant regulation and use (to prevent dioxin formation) is still correct, but with new information, the benefits and drawbacks of said regulations are now not as clear as they once were.

Stepping aside from the emission issue of hazards from halogenated flame retardant in fire events, there is the non-fire “emission” of the halogenated flame retardant when it gets into the environment. Going back to the above mentioned PBT issue, any chemical will be of concern in the environment if it should be emitted, spilled or introduced outside of controlled situations and the chemical is persistent (lasts for a long time), bioaccumulates (enters and concentrates in living organisms), and is toxic. Halogenated flame retardants of old are by design persistent due to their chemical structure, and the fact that one wants the flame retardant to last for years inside the product. One does not want to buy something with a 20 year lifetime only to have the fire protection wear out in the first year. This persistence has found halogenated flame retardants in many different places in the environment [30–39], and it is rightfully troubling. Many of the older halogenated flame retardants are small lipophilic molecules, meaning they can also be bioaccumulative (in the fatty tissue of many organisms), and some have also been found to be toxic. These negative PBT issues are why polybrominated diphenyl ethers (PBDEs), which are small molecule halogenated flame retardants, have been banned from use in the EU and US, as well as many other countries [3, 5, 33–38]. By extension, several countries and US states have started to extend the bans on PBDEs to all halogenated flame retardants, regardless of chemical structure. It is important here to note that small molecule flame retardants are of concern when they migrate out of the plastic, but polymeric brominated flame retardants are of high molecular weight and while they are persistent, current data indicates they are not bioaccumulative or toxic. Likewise, reactive flame retardants which covalently bond into a polymer structure cannot get into the environment and cannot become bioaccumulative or toxic, even if they may be persistent. So wholesale bans on entire classes of chemicals may not be merited, but regardless of the lack of scientific merit, these wholesale bans are being implemented. Further, the volume of data against small molecule halogenated flame retardants having negative PBT profiles is such that even

when halogenated flame retardants are polymeric or reactive, market conditions shy away from their use. Still, technology moves forward, as do opinions and personal/market tastes, and so there is still a need for fire safety protection/flame retardant chemistry, and therefore the market moves to non-halogenated flame retardants. Hence the reason for this book to guide materials scientists toward how to use non-halogenated flame retardant chemicals to provide fire safety, and to guide them on the newest information available.

1.2 Regulations of Fire Safety and Flame Retardant Chemicals

With some basic history about halogenated and non-halogenated flame retardants in place, we can now discuss more detailed regulation of flame retardants. In general, regulations are mostly reactive to information and events, rather than proactive to potential or perceived hazards. There are exceptions, but this reactive mode of regulation is applied in the majority of regulatory cases.

Modern fire safety regulations are often found within various legal codes, especially building codes, aviation regulations, and federal registers that describe particular requirements and test methods to ensure fire safety in a structure, vehicle, component, sub-component, or material. These regulations do not require any particular flame retardant chemistry to be used, but instead prescribe a particular level of performance. In fact, regulations really do not mandate flame retardants to be used at all. Flame retardants get used because it is one of many ways to provide fire protection, and may be selected depending upon all the other “non-fire” requirements for a functional item, including cost, thermal/mechanical/electrical performance, manufacturing requirements, intellectual property, and so on. It is important to emphasize this point as there is some perception that fire safety regulations mandate or push the use of flame retardants. This is not correct. The only time a particular chemical will be mandated for use is when it is prescribed in a manufacturer requirement document after certifications for use have been achieved. For example, a composite part inside the cabin of an aircraft that meets flame spread and heat release requirements and has been deemed “airworthy” may have manufacturer requirements to hold to a particular polymer formulation to ensure the part meets the requirements and does not have to be recertified for use. This requirement may then specify specific flame retardant chemicals, and loading levels, to meet the performance. But again, if one reads the original

fire safety requirements, the original laws will not mandate any particular approach or chemical to be used.

Fire safety regulations will seek to mimic a particular fire risk scenario where there has been a notable hazard identified, and some probabilities of that hazard occurring with notable loss of life or property. Within the regulation is a test method that seeks to mimic the fire risk scenario, and validate, in a reproducible way, that the item does meet the fire safety goals of the regulation. This typically means pass/fail test methods, but sometimes it can be a quantitative test that assigns levels of fire safety to the item tested depending upon that measured quantity. For example, different fire safety classes may be assigned to some building materials depending upon their ability to resist various heat sources, as well as levels of flame spread and smoke release. Therefore, for anyone to be able to sell a product into an application that has a fire safety requirement, one must test their materials via the regulatory test method. If the material should not pass the test, then flame retardant or fire protection methodology may be required. This is where flame retardants often get introduced into products, when the product tested does not meet the fire safety test. Flame retardants will not be added to a material if the material already passes a fire test, as it just adds cost and complexity to a material. Flame retardants will be added to the material if it enables that material to pass the particular regulatory test *and* it meets all the other product requirements. Sometimes, flame retardants are not needed if simple engineering controls can be used to provide fire protection for the item. Examples of engineering controls can be isolating the flammable material from ignition sources or using sprinkler systems. However, when flame retardant additives are used, they are tailored for each fire risk scenario and for each material – they are not universal and cannot be swapped from material to material without careful consideration. Therefore, one must study each specific material in each specific fire risk scenario to know what flame retardant chemical to use. This chapter will not see to cover the wide range of fire risk scenarios and test methods, as there are other excellent resources for this [9, 14, 40–42, 57]. Instead, keeping in mind that specific flame retardants get used for specific materials in specific fire risk scenarios, we can discuss flame retardant chemical regulations.

Returning to the historical perspective of flame retardancy for a moment, many of the older flame retardants now banned were used for decades because they worked very well in a particular material to provide fire protection against a particular fire risk scenario. Just as new information can come to light on the PBT profile of a chemical which will affect its use, fire risk scenarios can change over time. However, in other cases, the fire risk scenario may remain the same, but particular chemicals or classes

of chemicals may be regulated differently. As discussed previously, halogenated flame retardants have been heavily regulated in recent years due to concerns about their dioxin formation, as well as specific PBT issues. So in more recent times, there are regulatory changes to which chemicals may be used, while not changing the regulatory fire test, and in other cases, the regulatory change is made to the fire test *and* to the chemicals allowed to be used. As will be discussed below, there have been approaches taken to dis-incentivize the use of flame retardant chemicals through other product regulation, while maintaining the need for particular fire safety, or, to change the fire safety regulations themselves. When the latter is chosen, the current approach has been to lessen the fire safety requirements. While there can be changes in fire risk scenario that can support this approach, as will be discussed below, sometimes the change in fire risk scenario is driven by perceptions and political considerations, and not actual fire safety requirements. Fundamentally, the assessment of fire risks for certain products like upholstered furniture should be done separately from the chemical safety assessment of flame retardants which might be used. Reducing fire safety requirements to get rid of “unwanted” FRs is the wrong approach, as one should rather restrict the use of any problematic chemicals directly and promote the use of safer alternatives (see detailed discussion below).

1.3 Current Regulations

As previously discussed, regulations are often reactive based upon past historical events in a particular location where local or national fire events drive new requirements to prevent a particular fire event from happening again. Likewise, local cultural uses of building products, building styles, and operating of technology may drive particular fire safety requirements, especially if there are local population density issues, or environmental effects (earthquakes, wildfires) that may drive fire safety requirements in one direction or another. Therefore, regulations are best discussed at the national and regional level.

1.3.1 International – United Nations

Legacy halogenated flame retardants have meanwhile been restricted under the United Nations Persistent Organic Pollutants (POP) convention: HBCD, PBDEs including DecaBDE, and short-chain chlorinated paraffins (SCCP) [43].

1.3.2 United States (Federal vs. State)

In the United States (US), federal government regulations overrule state regulations. However, if there is no specific federal regulation on a particular topic or chemical, then state regulations apply. This can mean that a product sold in the US could have to meet 50 different state regulations if they are different. Currently, most chemicals are regulated by the Toxic Substances Control Act (TSCA, 1976) which was “updated” by the Frank R. Lautenberg Chemical Safety Act for the 21st Century in 2016. Under TSCA, only very few chemicals were banned and it generally took many years. Regarding flame retardant chemicals, there have been voluntary phase outs of brominated diphenyl ethers in the US due to rulemaking and agreements with the US Environmental Protection Agency (EPA), and some scrutiny of hexabromocyclododecane (HBCD), [44–49]. The US EPA set up a workplan on flame retardants already in 2012 but with slow progress. In March 2019 they concluded TCEP, TBBPA and TPP as “high priority substance” candidates for risk assessments.

In addition to these regulatory workstreams, from 2005 to 2015, the US EPA did run a series of extensive Design for Environment (DfE) projects which evaluated alternatives to the legacy brominated flame retardants pentabromo- and decabromo diphenylether, hexabromocyclo dodecane and tetrabromo bisphenol-A [50]. The conclusion was that often halogen free alternatives exist with a better environmental and health profile. Furthermore, in 2017 the US Consumer Product Safety Commission (CPSC) voted to initiate rulemaking based on a petition to protect consumers from “toxic” flame retardant chemicals commonly referred to as organohalogens (OFRs), under the Federal Hazardous Substances Act [51]. The initiative refers to children’s products, furniture, mattresses, and electronic device casings. CPSC further advised setting up a Chronic Hazard Advisory Panel to further study the effects of OFRs as a class of chemicals on consumers’ health. The petition lists 24 organohalogens including decabromodiphenyl ether and several chlorinated phosphate esters, believed to be toxic, that tend to migrate out of products, and can bioaccumulate.

At the state level however, there has been a lot of regulatory movement to ban flame retardant chemicals by broad chemical class, rather than by specific molecule. Most of the bans are focused around keeping flame retardant chemicals out of mattresses and furniture, but some bans on manufacture and use of flame retardant chemicals are broader in scope than just furniture and mattresses. The wide range of state regulations is far too much to cover in this chapter, and a reasonable summary of each rule with links to each state law is available online [52]. That being said,

the emphasis of most state laws is to ban flame retardants by class (halogen, phosphorus, nitrogen, etc.) in specific consumer products (mostly furniture and mattresses) rather than by specific chemistry. If TSCA change does occur which lists particular flame retardants as safe/not safe to use, that TSCA change would overrule all of the individual state laws. Otherwise, it is highly recommended that material scientists work with their respective regulatory experts if they are planning on using any flame retardant chemical for products in the US, whether halogenated or not. As of the writing of this chapter, the situation is still very uncertain how these state laws will move forward, or if they will get challenged and found to be unworkable by generating broad bans of chemical classes vs. specific negative PBT profile chemicals.

1.3.3 Canada

Chemical regulation in Canada is governed by the Canadian Environmental Protection Act (CEPA) [53] as well as new substances/existing substance under its Chemical Management Plan. Flame retardant chemicals which are regulated under this law include brominated diphenyl ethers (BDPEs), hexabromocyclododecane (HBCD), and tetrabromobisphenol A. As per the law, new chemicals are investigated and added to the regulatory list as PBT data becomes available. Similar to laws in the US, known brominated flame retardants with known negative PBT profiles are banned from use and import into Canada. In 2019 Environment Canada stated that decabromo diphenylethane (DBDPE) may contribute to the formation of persistent, bioaccumulative, and inherently toxic transformation products, such as lower brominated BDPEs, in the environment. A ban on the manufacture, sale or import of the brominated FR DBDPE has been proposed (pending as of 2021-03). This is remarkable in so far as DBDPE has often been cited as an example of regrettable substitution, where a regulated substance (decabromodiphenylether, DBDE) is replaced by industry with a molecule that is just slightly modified, so evading the regulatory restriction whilst still having similar environmental properties.

1.3.4 European Union

The European Union (EU) has been at the forefront of chemical regulation for chemicals used in commerce. Relevant to flame retardant use, the Restriction of Hazardous Substances in Electrical and Electronic Equipment (RoHS) [4, 5] and Waste Electrical and Electronic Equipment (WEEE) [6, 7] laws have forced out the legacy brominated flame retardants

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