Recent Flame Retardant Consumption: Textiles

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Abstract- Flame retardancy in variety of materials is increasingly a required performance feature. The worldwide consumption of flame retardant chemicals is continuously increasing for the last more than a decade and the trend is forecasted to continue till 2022. Textile fiber is one of the five main product types; that requires flame retardant treatment. The type of flame retardants currently available in market experienced significant growth in quantity; however, the novelty and innovation in chemical structure have not seen major change. Chemistries developed in flame retardancy during 1950- 1980, are currently viable. Flame retardancy is obtainable using flame retardant chemicals, however, the main concern emerged in the last few decades is preventing the hazardous emission during combustion process. Release of undesired gases, smoke, radicals, and toxic content is realized and flame retardants with an increased eco- friendly performance are desired.

Key Words: Flame Retardant, Textile Fiber, Material, Consumption, Environment, Toxicology, FR Consumption

1. INTRODUCTION

Flame retardants provide an important source of enhancing the material protection. Safety and protection of human lives and valuable are strong factors in the consumption of flame retardant (FR) and flame retardant textiles.

Today, textile material is one of major product category for the application of flame retardants. Garment, protective wear, children wear, work wear, mobile- tech, furnishing etc., all are the important product types produced using textile material. Flame retardants are required to achieve desired performance in textiles and passing any regulatory specification.

Flame retardant chemicals, available for textiles, have experienced steady growth, and forecast for future market is positive. Growth is clearly reflected in terms of volume of consumption.

Textiles provided one of the five major product types that consumed 88 % of worldwide flame retardant sales in 2015. The other four product types were construction products, insulated wire and cable, electronic products, and motor vehicles (1).

The available variety of flame retardants (FRs) are useable for the various types of materials including cellulose, PET, polyamides, plastics, polyolefin, wood, cables, electrical and electronic products etc. However, the main concern emerged in the last few decades is preventing the hazardous emission during combustion process. Release of toxic gases, smoke, radicals etc. is realized, and flame retardants with an increased eco- friendly performance are desired.

Currently, the important flame retardants used include the composition based on aluminumtrihydrate (ATH), antimony oxides, bromine, chlorine, organophosphorus (for example tetrakis (hydroxylmethyl) phophonium salt, and alkyl- substituted, N-methylolphosphonopropionamide) etc. Bromine based flame retardants provided the utilization in large amount, however, there are significant environmental concerns associated with the hazard of gases released (2).

Today's critical requirements, in the market, necessitate the flame retardant to demonstrate the desired performance with significant acceptability in terms of environmental sustainability, chemical toxicology, and cost (3).

2. FLAME RETARDANT CONSUMPTION

Market study undertaken in 2014, confirmed the significant increase in FR consumption during the previous four years. The growth trend was determined to continue at a global annualized rate of 3.4 % from 2013 till 2018.

Importantly, an increased growth rate in FR consumption is estimated for the next five years. During the years 2017- 2022, CAGR (compound annual growth rate) of 5.4 % will drive the consumption. Material type and end- use application of material are both influenced by population, awareness, public regulations, and safety and protection requirements.

An increasing utilization of flame retardant finishes in terms of the recent market consumption is shown in Figure 1. It shows the continuous growth for future (4).

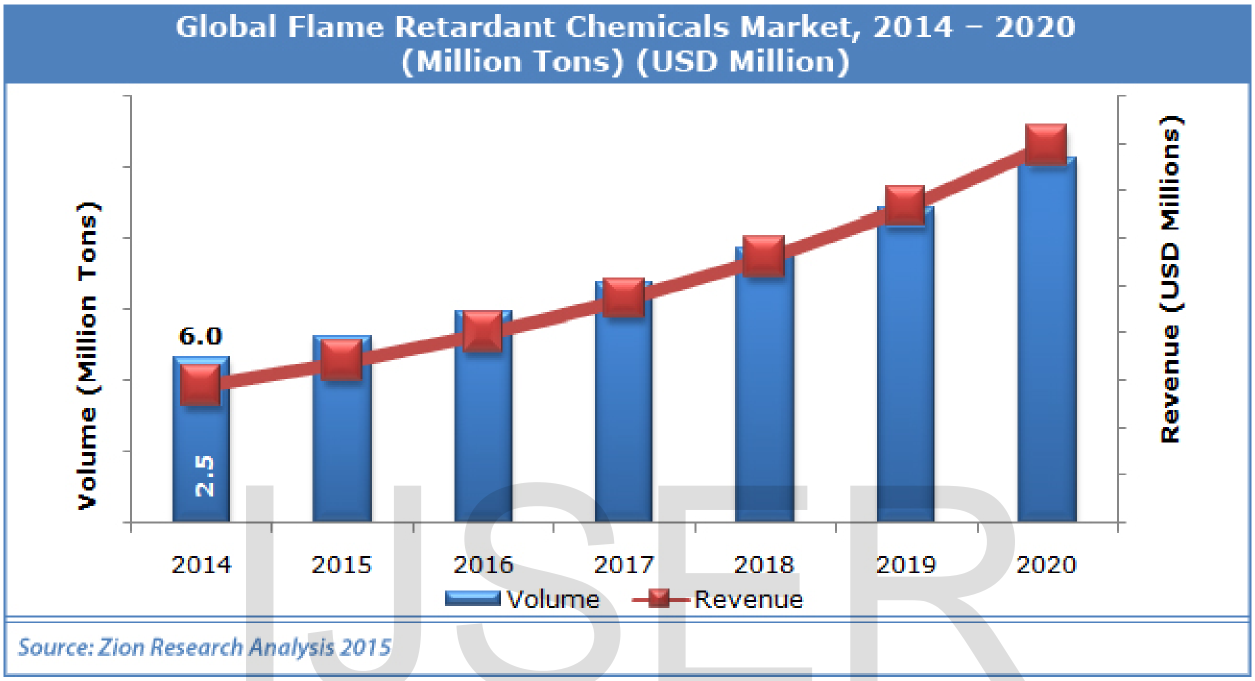

Figure 1. Growth trend in consumption of flame retardant finishes 2014- 2020.

Increasing human population; and construction work around the world directly improve the consumption of flame retardant textile, fiber, and other materials. An increasing awareness and understanding of public organizations in making the protective building and clothing etc., is rapidly contributing in the consumption of flame retardants.

The consumption of flame retardant material is significantly influenced by human population, physical infra- structure, and industrialization. Moreover, societal and public awareness on safety and hazard prevention, fire regulations, work safety etc., may enhance the requirement (Figure 2).

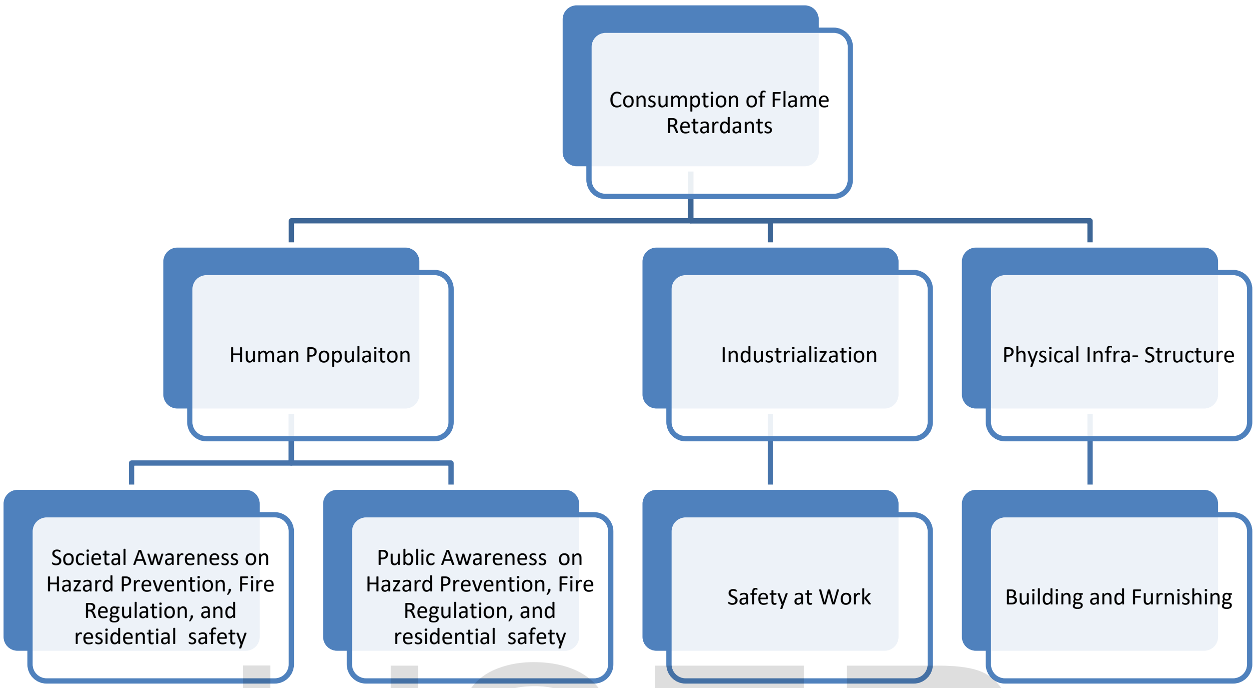

Figure 2. Factors contributing the continuous increase in the consumption of flame retardants.

The growth in the quantity and performance is presently desired. The requirement factors can vary from region to region. Therefore, consumption of FR chemicals by one region can be higher relative to others. For example, in 2015, construction related flame retardants were consumed highest in US market relative to any other material market where FR chemicals were consumed (1).

China, North America and Western Europe are the leading regions that are consistently consuming around 60 % or more of flame retardant volume over the past several years. Most recently the world market survey for flame retardant consumption in 2016 confirmed the these regions as major market (Figure 3) (5).

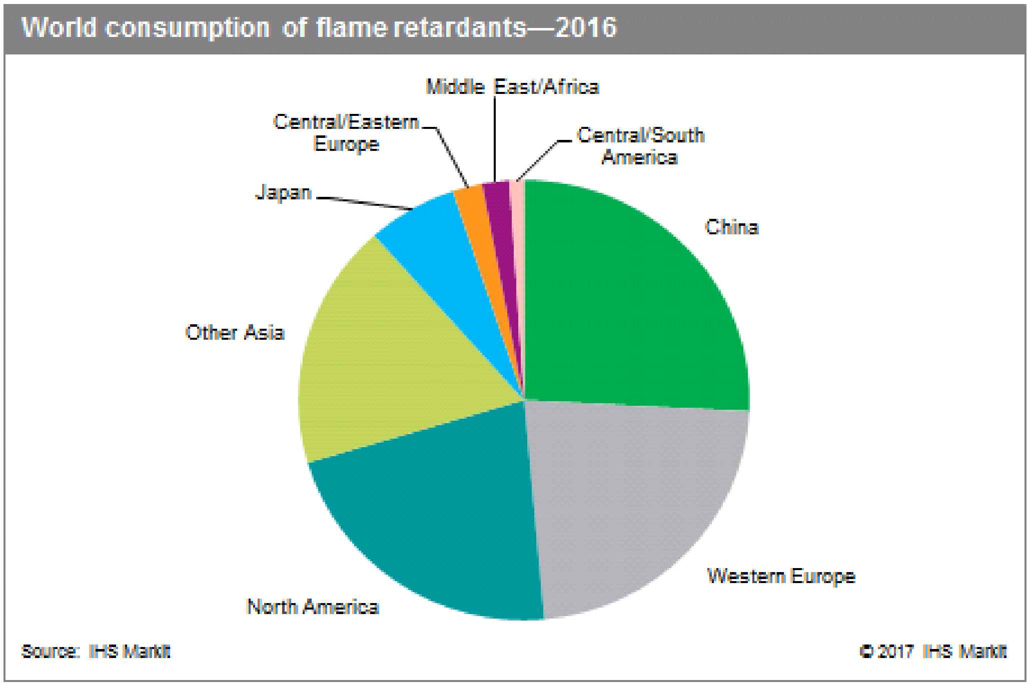

Figure 3. World market survey of flame retardant consumption for 2016 (Source: IHS Markit).

The safety requirements, described by the regulations and standards, influence the consumption market. Importantly, flammability prevention in high- rise building around the world contributed viable and significant utilization of flame retardants. In addition to floor covering, interior furnishing, and office/ room furniture; the cladding used in building siding made of aluminum composite panel are the important reasons for an increased flame retardants used.

Plastics and polymeric materials, from home to office and public buildings, are present in numerous objects. Flame retardant consumption of 85 % was observed in plastics during 2013. Textiles and rubber products account for the remaining consumption of FR. Growth rate of 3.4 % for global annual production was forecasted during the period 2013- 2018 (1).

Importantly, the continuous enhancement in the global consumption of FR is expected at CAGR (compound annual growth rate) of 5.4 % for the period 2017- 2022 (7.51 US billion dollar in 2017, and moves to 9.79 US billion dollars by 2022) (6). This growth rate is significantly higher relative to previous value of 3.4 % observed for the period 2013- 2018.

Possibly, the continuous enhancement in human population, along with public and societal awareness on safety at home and work, are main contributors for growth in consumption.

2.1. FLAME RETARDANT TYPE UTILIZED

Continuous provision of an increasing amount of heat may result in the combustion of most materials surround us including textile fibers, electrical and electronic components, wood plastics etc. All these materials require flame retardancy.

The FR chemicals that currently used in large amount include aluminumtrihydrate, antimony trioxide, brominated FR, chlorinated FR, magnesium hydroxide, melamine- based FR, boron-containing FR, and phosphorous- based FR.

A number of criteria may be exercised in the selection of particular FR. The performance of FR can be assessed in terms of lasting effect (durability), retardancy to heat release and flame propagation, char formation, ignition resistance, burning rate, release of hazardous and toxic soot or radicals during combustion etc. Aluminum trihydroxide was the largest single FR, staying at 35 % share consumption. It is followed by halogenated (brominated and chlorinated) FRs used synergistically with antimony trioxide, and consumed at 37 % share altogether. The FRs utilized were organic and inorganic phosphorous based FR, nitrogen and zinc based. The said consumption was indicated for the years 2013-2018 (7).

Another recent worldwide consumption of flame retardant types provided the similar level of consumption that is shown in Figure 4 (IHS Markit).

Tetrakis(hydroxymethyl) phosphonium salts, reacted with urea and cured with gaseous ammonia, can provide durable flame retardancy to cellulose fibers. The flame retardant finishing of cellulose fibers based on tetrakis(hydroxymethyl)phosphonium salts is in use for more than 50 years. However, FR based on phosphate or phosphonate salts are generally used for semi- durable, and non- durable performance. Intumescence back-coating can be obtained on charrable fabrics using ammonium polyphosphate (8).

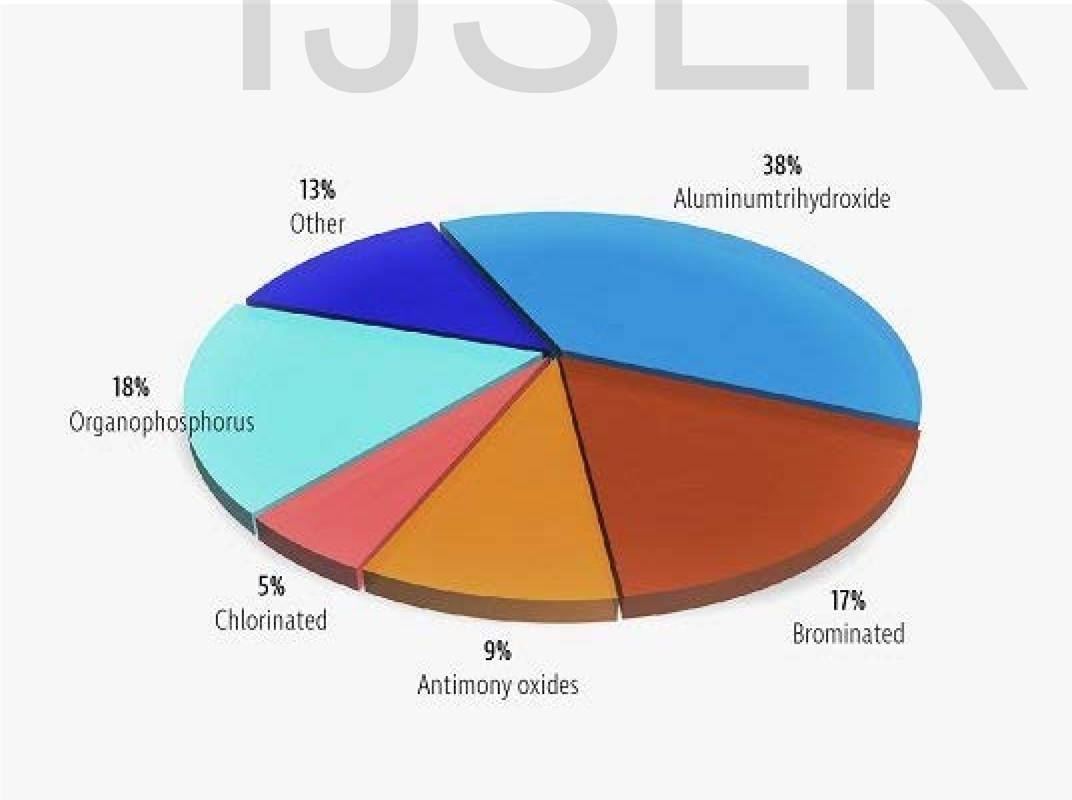

Figure 4. Recent percentage consumption of important flame retardant types (Source: IHS Markit).

3. IMPARTING FLAME RETARDANCY TO TEXTILE FIBER

Flame retardants can be made part of textile fiber surface or structure through various means. Flame retardant applied can chemically react with the molecular structure of fiber, or it may self-polymerized or cross- linked at the fiber surface.

A flame retardant finish can retard the development of combustion or fire during heating, material pyrolysis/ decomposition, ignition or flame propagation.

Flame retardant finishing in industry is performed on fabric to produce a number of textile products. However, fiber and yarn can be finished. Inherent flame retardancy is obtainable through modifying the molecular structure of material. However, flame retardancy in textile finishing industry is more often required on fabric at the terminal finishing process.

An important example is polyester fabric, abundantly used in various textile products. Polyester fabric can be flame retarded through conventional padding application. Alternately, adding flame retardant in melt- spinning may produce built- in flame retardancy in polyester fiber.

Built- in flame retardancy can be obtained in synthetic fibers through melt- spinning. However, such fibers are desired when the end- use of fiber is known prior production. Polyester and nylon fibers, produced through melt- spinning with flame retardant properties, are largely used in conventional and home- textile products.

Polyester fabric can be thermosol finished to obtained flame retardancy using a dialkyl phosphate or hexabromocyclododecane. Polypropylene fiber is flame retardant finished using tribromoneopentyl phosphate through melt-spinning.

Inherent flame retardancy can be demonstrated by fibers having constituent unit in molecular structure that resist pyrolysis and combustion. The molecular structure is resistant and stable to heat. Examples of inherent flame retardant fibers include melamine- based fiber, viscose rayon containing silicic acid, aramides, oxidized polyacrylonitrile, polyphenylene sulfide fibers.

Brominated and chlorinated flame retardants are important finishes that perform in gaseous phase. The treated substrate, on receiving heat, will release HCl or HBr. These react with highly reactive radicals $H^{\cdot}$ and $OH^{\cdot}$ producing stable molecules (H_2 or H_2O) and $Cl^{\cdot}$ or $Br^{\cdot}$ radical. The energy of halogen radicals $Cl^{\cdot}$ or $Br^{\cdot}$ is much lower than $H^{\cdot}$ and $OH^{\cdot}$. Therefore, the possibility of radical oxidation reaction of combustion is reduced.

Flame retardancy offered by brominated and chlorinate finishes can be enhanced synergistically using antimony oxide. (9).

4. DEVELOPMENT IN FLAME RETARDANT CHEMICALS

Most FRs researched and developed during the years 1950- 1980, are mainly present in the current global FRs market (10).

In the last three decades, there was not significant addition in new flame retardant types with novel chemistry. However, the realization of researching the environment- friendly, and non- toxic FRs is indicated and emphasized continuously.

The novelty and innovation have not significantly experienced advancement in expanding the current gamut of traditional flame retardant. Scientifically, the major concern in the advancement of current variety of flame retardant (FR) chemicals is the regulatory pressure to prevent the hazardous effects. Environmental and toxicological effects of FR chemicals are required to be prevented.

The progress made in the development of FR chemicals has clearly recognized the following directions:

1. Providing the flame retardancy and heat resistant effects to finished substrate at desired performance requirements, and
2. Prevention of hazard and toxicity caused by the smoke, gases, or radicals produced during the combustion process.

The environmental and market acceptability of any important flame retardant product can be hindered by hazardous or toxic specie released in the combustion process, or during the useful life of finished substrate.

4.1. CLAY MINERAL UTILIZATION

The search of finding flame retardant with improved performance and reduced toxicological environmental hazard has attracted research and development interest for using clay mineral.

The evaluation of clay minerals, for imparting flame retardancy and thermal stability to fibers and polymers, can be seen. Achievement of reduced peak heat released rate is considered important using functionalizednanoclay into polymers (10).

Clay minerals are naturally available and significant natural clay reserves are known. These are inexpensive, and demonstrate improved environmental sustainability. The toxicity and health- risk concerns were indicated for nanosized particles, and they excluded the bulk materials or polymer products.

The type of clay mineral used in enhancing the required properties of polymers and fibers is montmorillonite (MMT). The chemical structure formula for MMT is $(Ca,Na,H)(Al,Mg,Fe,Zn)_2$

$(Si,Al)_4O_210(OH)_2X_{H2O}$, where X indicates the varying of amount of water molecules in particular type.

In natural clay mineral type Bentonite is an important source of montmorillonite. The natural clay minerals, for example *MultaniMitti*, of Pakistani origin will be arrange for study and analyze to determine the structure type. Our previous study has reported detailed study on the structure and properties of clay minerals and MMT (11). Flame retardant and thermal stability can be obtained in variety of polymers using clay mineral.

Clay mineral can improve the thermal stability of fiber and polymers. It is used in heat resistant and flame retardant applications mainly in polymer, and polymer composite. Generally, the order of thermal-expansion magnitude in these materials can be shown by the following relationship:

polymer> metal > ceramic

This order can be observed in the values of the linear thermal-expansion coefficient, which are in the

range of 20 to 100 ppm/ ^oC, 3 to 20 ppm/ ^oC, and 3 to 5 ppm/ ^oC for polymers, metals, and ceramics, respectively (12).

Interest received in producing clay mineral-polymer composite is significant to achieve improve effects in polymer. Improvement in application properties, including abrasion resistance, UV resistance, strength characteristics, thermal stability, and flame retardancy, were achievable in finished polymer using nanoparticle form of clay mineral (13).

Variety of polymers including Nylon 11, Nylon 6, Polyethylene (LLDPE, HDPE), polypropylene, Maleic anhydride-modified polypropylene, and Fluorinated synthetic mica-polypropylene (nm) composite etc., have shown desired effects using clay mineral ad additive (14).

Discussion on structure, properties, and surface modification of clay mineral and the enhanced properties (mechanical, barrier, thermal, electrical conductivity, biodegradability, etc.) of clay mineral-polymer (nm) composite were reported (15). Thermal and photo aging durability of clay mineralpolymer (nano) composite coupled with the enhancement achieved in polymer durability using layered silicates against the effects of light, microwave energy, heat, and mechanical abrasion were reviewed (16).

Textile fiber requires improved flame retardancy, and thermal stability in important applications including protective wear, children wear, air transport, defense etc.However, its utilization in making the cotton fabric or cellulose fibers require research studies to find out clay mineral composition and application method that produces best results.

Branched polyethylenimine (BPEI) and sodium MMT via layer- by- layer coating on cotton fabric (17), and polymer dimethyl diallyl ammonium chloride-allylglycidyl ether (a quaternary ammonium salt copolymer)/ MMT composite coated on cotton fabric through dip- pad- dry method (18) were investigated. In both of these studies, an enhancement in the flame retardancy and thermal stability of cotton was achieved. Aqueous dispersion application of clay mineral via pad- dry method may be useful for conventional textile processing industries (19).

5. ENVIRONMENTAL HAZARD AND TOXICOLOGICAL CONCERN

Toxicological data, health effects, environmental fate, and material effects were reviewed more than sixty years back for halogenated monomers, halogenated phosphate esters, and formaldehyde derivatives of phosphorous and nitrogen compounds. The seriousness of environmental and toxicological concerns of these compounds was emphasized for further studies (20).

Environmental hazard and toxicological concerns for using a flame retardant finish were realized in the literature, particularly for brominated flame retardants. However, finding scientific data for the release of particular flame retardant content from a treated substrate during service life, or in combustion process, and its consumption by living organism is a slow process. Scientifically, proving a particular chemical as toxic for a chosen living organism is tedious contribution.

Environmental and toxicological concerns for polybrominated diphenylethers (PBDEs), tetrabromobisphenol were researched and found significant in sediment and biota (21). Useful information was observed in the study.

Most of the polybrominated diphenyl ethers (PBDEs), were agreed by industry to phase out in the United States in 2004. New fire-safety chemical is evaluated for its safety, and the findings are made available to government regulatory bodies before that FR product is used (22).

All the chemicals including any flame retardant currently in use is subjected to review by the U.S. Environmental Protection Agency (EPA) and national regulators around the globe. Further evaluation for safety of chemicals for their intended use in commerce is made by The Toxic Substance Control Act (TSCA) and over a dozen other federal laws and regulations, including consumer product safety laws, food safety laws and product liability laws.

The amount of PBDEs isomers can show adverse influence in some wildlife. It may produce undesired effects in young children, senior citizen and fish consumers. However, insufficient scientific details hinder the precise conclusion on the toxicity and environmental hazard of PBDEs.

Additive flame retardants are not chemically bound to textile fiber structure. Therefore, such FRs may release or leach the fiber surface. Additive type FRs include PBDEs, PBBs (polybrominated biphenyls, and HBCD (hexabromo cyclododecane).

Reactant type FRs, for example TBBPA (tetrabromobisphenol A), chemically react with fiber structure. Some content of reactant FRs not polymerized in fiber structure may be released to environment.

6. CONLCUSION

Flame retardancy in variety of materials is increasingly required. The worldwide consumption of flame retardant chemicals is continuously increasing for the last more than a decade and the trend is presently forecasted to continue till 2022. Textile fiber is one of the five main product types; that requires flame retardant treatment. The type of flame retardants currently available in market experienced significant growth in quantity; however, the novelty and innovation in chemical structure have not seen major change. The main concern in the last few decades is preventing the hazardous emission during combustion process.

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