

# Insights into Phosphorus-Containing Flame Retardants and Their Textile Applications



Mohd Yusuf

**Abstract** In recent years, flame retardants (FRs) focused on eco-friendliness, eco-viable and durable, are in great social demand and one of the most growing area of research interest on account of increased awareness towards environmental concerns. In this regard, strategies are considered onto FRs for textiles as well as other substrates with their applicability and selectivity. Phosphorus-based FRs provide a foundation for the directed design of nontoxic FRs mainly because of its versatility, for example, it can act in both the condensed and gas phase, as an additive or as a reactive component, in various oxidization states, and in synergy with numerous adjuvant elements. Various P-moieties make valuable contribution and combinations including elemental, inorganic salts and organophosphorus compounds. This chapter highlights general insight into phosphorus-based flame retardants for polymeric systems with future R&D opportunities.

**Keywords** Flame retardants · Textile finishing · Phosphorus compounds · OPFRs

## 1 Introduction

Flame-retardation ability to the polymeric substrates such as textiles (woven or non-woven), plastics, rubber and others, is vastly needed because they have been applied to a myriad of applications for general and engineering purposes. Specific chemical bonding was shown in several polymeric materials (*i.e.* cotton, linen, hemp; silk and wool; nylon; polypropylene; polyester etc.) acquired specificity towards implanting flame-retardancy. Textile materials have been applied worldwide in both civilian as well as military fields due to their inherent and excellent properties such as air-permeability, softness, comfortableness, hydrophilicity etc. In a general opinion, fire can be described as the combustion cycle which is illustrated by a fire triangle for which three components are necessary to be fire to occur; one is heated, secondly a combustible fuel and thirdly a combustive process. The most important factor in the combustive process is the air (oxygen). According to the fact that fire or flame is

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M. Shahid and R. Adivarekar (eds.), *Advances in Functional Finishing of Textiles*, Textile Science and Clothing Technology, [https://doi.org/10.1007/978-981-15-3669-4\\_10](https://doi.org/10.1007/978-981-15-3669-4_10)

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often initiated from the burning of the textile materials which subsequently results in burns and even loss of human life, causing serious damage to furniture, carpets, upholstery, buildings, properties, etc. [1, 2]. Thus, flame retardant (FR) finishing of textile substrates is extremely necessary for many applications for the prevention of fire and for protection of human life. Most of the polymeric materials such as cellulose, wool, nylon, polyesters, polyurathanes possess higher flammability [3], and therefore, required high performance flame retardant finishes to overcome flammable aspects.

FRs provide fire resistance ability to the textiles through the heat absorbing, the covering effect, inhibition of chain reaction and gas dilution phase [4]. In general, there are many chemical treatments that are commonly employed to impart flame retardant finish for textile/polymeric materials. Main six categories of FRs are highly discussed and accepted, for example; halogenated, formaldehyde-based, P-based, N-based, Si-based and other mixed formulations [5]. However, the purpose of FR finishes is to reduce the amount of heat that is supplied to the polymer system to be below the level for flame stability [6]. Halogenated, phosphorus and formaldehydes based compounds such as Proban, THPC-TMM (Tetrakis(hydroxymethyl)phosphonium chloride-Trimethylolmelamine) and Pyrovatex CP, have been widely employed as the commonest FRs to impart durable fire-resistant ability to the cotton substrates [3–7].

In early 1990s serious environmental concerns have been noticed concerning halogenated FRs, especially brominated flame retardants (BFRs). It is found that under severe thermal stress or when they were burnt in accidental fires or uncontrolled combustion, BFRs could form halogen-based dioxins and furan derivatives [8, 9]. Furthermore, it is noteworthy that the environmental and health concerns limited not only of BFRs, but also of other types of flame retardants and have been studied extensively at a global scale. Several scientific meetings and conversations were organized in the late 90 s onto flame retardants: uses, risk assessments and safety globally until the transition to Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), a European Union Regulation Authority came existence in 2006. In 2008, REACH, [10] (REACH, 1907/2006/EC) entered “No data no market” slogan which requires the basic health and environmental data to be submitted for all chemicals before commercialization for their safety evaluation [10]. Halogenated FRs generate poisonous substances on fire and combustion [2] whereas formaldehyde-based FRs release formaldehyde which found carcinogenic [3]. They are found to have adverse health effects in animals and humans, including endocrine and thyroid disruption, immunotoxicity, reproductive toxicity, cancer, and adverse effects on fetal and child development and neurologic function [9–13].

As a result, health and environmental hazards associated with these FRs driven R&D for identifying and utilizing safer alternatives. Because of the social concerns onto eco-preservation using eco-friendly FRs, the new FRs needs to be halogen-free and formaldehyde-free. Phosphorus, nitrogen, and silicon-containing compounds are generally considered as environment-friendly FRs, because they do not generate harmful substances to human-ecosystem on burning with fire and their synergistic effects [6, 14]. P-based FRs are found very effective inert towards fire (most effective

in high oxidation states) mainly because of its characteristics such as (i) low water solubility, (ii) low volatility, (iii) low dose requirement, (iv) less degradation to possibly hazardous substances, and (v) no toxic emissions [2, 6]. Mechanistically, phosphorous based flame retardants, during a fire form poly and meta-phosphoric acids which form an oxygen-barrier layer [15] and commonly used due to the environmental scrutiny halogenated and formaldehyde-free FRs.

The flame retardant mechanism described for phosphorus containing flame retardants includes both a condensed and a vapor phase mechanism depending on the type of phosphorus compound and the polymer. Specific applications for red phosphorus, organophosphates, chlorophosphates and bromophosphates are described. The use of triarylphosphates in PVC, modified polyphenylene oxide, and polycarbonate/ABS is described. The chlorophosphates are used in polyurethanes and the bromophosphates in engineering thermoplastics. Flammability and mechanical properties are given for specific polymers [16].

Phosphorous based flame resistant materials have long been used since the 1940s–1950s. P-based FRs exhibit excellent fire inertness ability and found effective both in the vapour and condensed phases. They vary in oxidation states (0 to +5) and can be classified into elemental, inorganic, and organic or organo-phosphorus [17] categories.

## ***1.1 Elemental Phosphorus as FR***

Phosphorus ( $P^0$ ) has several allotropic forms [18] out of which white phosphorus (WP) and red phosphorus (RP) are most common. WP is a white, soft, waxy solid consists of tetrahedral  $P_4$  molecules, in which each atom is bound to the other three atoms by a single bond. It ignites spontaneously and is very toxic and reactive in nature, and therefore cannot be used as FR [17].

Samples of WP always contain red phosphorus in a very little amount and accordingly appear yellow. On heating, WP can be converted into RP in the absence of air. It is harder, denser, more stable, less toxic, less reactive than WP and polymeric in structure with  $P_4$  units [19]. Although, it ignites easily but possesses thermal stability up to 450 °C (approx.) and thus, the ability to be used as sufficient FR agent [18]. RP is observed as an efficient FR especially for oxygen-containing polymers that work in the vapor and condensed phases [19, 20]. Among the high performance flame retardants (HFFR) additives, RP is a type of powerful FR and has been significantly used for polymeric moieties other than textiles such as polyethylene [21], poly(ethylene terephthalate) [22], nylon [23, 24] etc.

Moreover, the combination of RP with other HFFR additives, metal hydroxide or intumescent FR can improve the overall fire retardancy of highly flammable substrates like polyolefins (PO) blends have been investigated and reported as effective [25]. However, the main disadvantages of RP are because of poor thermostability, the evolution of highly toxic phosphine ( $PH_3$ ) during the reaction with moisture and the lack of compatibility with synthetic resins [26]. A novel technology was

developed to prepare microencapsulated RP with suitable filling/supported agent to minimize the associated problems. Wu et al. [27] investigated microencapsulated RP as FR agent for synthetic polymers. In this study, they conclude that the microencapsulation of red phosphorus efficiently improved its water absorption, thermostability, ignition point, and decrease the amount of phosphine evolution with 5% amount [27]. A similar study was carried out by Liu and Wang [26]. In this study, a composite system of RP encapsulated by N-based FR was used for polyamide 6 (PA6) due to higher N-P synergistic effects. The action and mechanisms of the NFR-microencapsulated RPFR on PA6 were investigated in terms of limiting oxygen index (LOI) by using vertical burning experiment (UL94), thermogravimetric analysis (TGA), and scanning electron microscope (SEM) observations. It was concluded that the NFR-microencapsulated RPFR combination possessed desired flame retardancy because of effective char-formation of the condensed phase and it also showed satisfactory mechanical properties as the result of the good compatibility between flame retardant and PA6 resin.

## ***1.2 Inorganic Phosphorus-Based FRs***

Inorganic phosphorus-based FRs were developed and commonly used in the nineteenth century, mainly phosphates and polyphosphates. However, the great scientist Gay Lussac in 1821 used ammonium phosphate solution to impart flame retardancy of theater curtains [19, 20]. Ammonium phosphates (APs) possess fairly fire retarding ability and prevent afterglow. Monoammonium phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) and diammonium phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ ) or mixtures of these two phosphates have good water solubility and found very effective for many substrates as FR, for example, textiles, cellulosic fibers, wooden and paper products [19, 28]. With respect to susceptibility to bloom out of the material, matrix is a down-manner of APs. The low susceptibility of APs introduces ammonium polyphosphates (APPs) which have higher susceptibility. APPs are moderately soluble in water with several crystalline forms that differ in molecular weight ratio and particle size. APPs have been heated with a small amount of urea to enhance the solubility [19]. APPs are used as the principal ingredients in intumescent FR coatings because of their decomposition temperature (greater than 256 °C). The decomposition of APPs produces phosphorus acid that will interact with the carbon source to produce a carbonaceous char [19, 20]. APPs are cheaper, low toxic, quite thermally stable than their organic counterparts, and good thermal stability, and can be used for other non-textile materials such as plastics, rubber, paper, epoxy resins and wood [29].

### 1.3 Organic or Organophosphorus-Based FRs

Organophosphorus-based FRs gain increased attention preventing the risks of fire in recent times because of their significant efficacy and environmentally safer nature over halogenated and formaldehyde containing FRs [30]. Organophosphorus FRs have been used from last few decades and widely used for several various polymeric consumer products like plastics, textiles, polyurathanes (PU), polyamides (PA), polyethyleneterephthalate (PET), epoxy-materials etc. [31, 32]. Organophosphorus compounds containing P–C bonds are developed extensively as FR additives due to their excellent thermal and hydrolytic stability as well as ease of generation. In a mechanistic pathway it was observed that during the fire, phosphorus compounds break down to phosphorus acid which blocks polymer's oxygen functionality, and therefore lead to the char-formation in the high ratio [33].

Wendels et al. [34] has published an exhausted and comprehensive review on organophosphorus compounds for the recent developments in organophosphorus flame retardants (OPFRs) having P–C bonding with their synthesis pathways and applications [34].

Nowadays, various products, large in numbers are commercially available based on organophosphorous compound. On the basis of carbon unit/moiety OPFRs can be broadly categorized into five main classes (Table 1) [17, 32–36]:

- (i) *organophosphates*,
- (ii) *organophosphonates*,
- (iii) *organophosphinites*,
- (iv) *organophosphine oxide*, and
- (v) *organophosphites*.

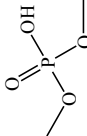
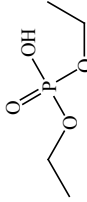
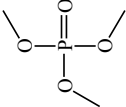
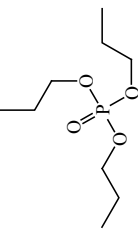
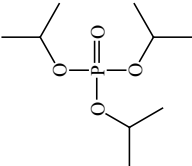
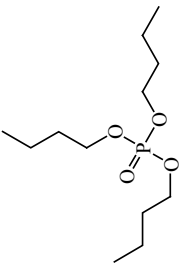
#### 1.3.1 Organophosphate FRs

Organophosphate FRs with a wide range in their polarity, solubility and persistence have been produced and used as significant FRs in substitutes to the stringent regulation in the use of brominated FRs. These FRs are widely used as flame retardants in various consumer products such as textiles, electronics, industrial materials and furniture to prevent the high risk of fire [1, 32]. A large number of OPFRs have been fabricated with varied P–C assemblies. Some commonest OPFRs are shown in Table 1.

**Aliphatic:** P–C<sub>aliphatic</sub> bond containing organophosphorus compounds have been utilized as good FRs to polymeric materials such as Dimethyl phosphate (DMP), Diethyl phosphate (DEP), Trimethyl phosphate (TMP), Tripropyl phosphate (TPP), Tri-isopropyl phosphate (TIPP), Tri-*n*-butyl phosphate (TNBP) Tris(2-butoxyethyl) phosphate (TBOEP) etc.

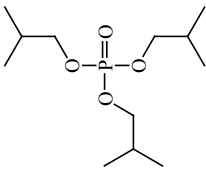
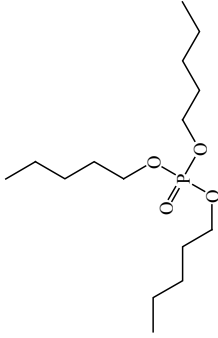
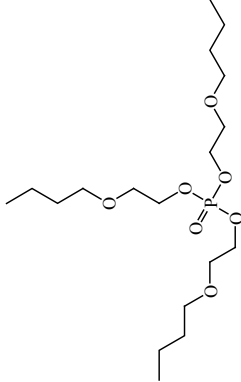
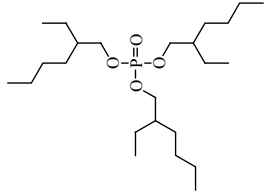
**Cl-aliphatic:** Chlorine-based P–C<sub>aliphatic</sub> bond containing organophosphorus compounds have superior flame retardancy. Examples of this subclass include

**Table 1** Various OPFRs classes

OPFRs classes	Chemical structures	
Organophosphates <i>Aliphatic</i>	 <p data-bbox="326 993 353 1241">Dimethyl phosphate (DMP)</p>	 <p data-bbox="333 412 361 642">Diethyl phosphate (DEP)</p>
	 <p data-bbox="522 993 549 1241">Trimethyl phosphate (TMP)</p>	 <p data-bbox="533 400 560 642">Tripropyl phosphate (TPP)</p>
	 <p data-bbox="792 963 819 1241">Tri-isopropyl phosphate (TIPP)</p>	 <p data-bbox="800 365 827 642">Tri-<i>n</i>-butyl phosphate (TNBP)</p>

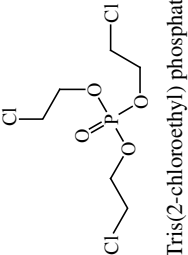
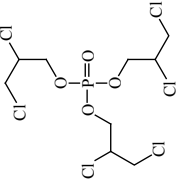
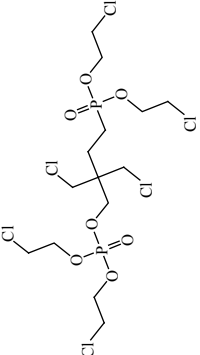
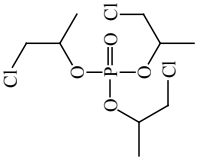
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**Table 1** (continued)

OPFRs classes	Chemical structures	
	 <p data-bbox="446 979 476 1243">Triisobutyl phosphate (TIBP)</p>	 <p data-bbox="452 388 482 643">Tripentyl phosphate (TPeP)</p>
	 <p data-bbox="758 882 787 1243">Tris(2-butoxyethyl) phosphate (TBOEP)</p>	 <p data-bbox="770 308 799 643">Tris(2-ethylhexyl) phosphate (TEHP)</p>

(continued)

Table 1 (continued)

OPFRs classes	Chemical structures	
<i>Cl-aliphatic</i>	 <p data-bbox="389 901 416 1241">Tris(2-chloroethyl) phosphate (TCEP)</p>	 <p data-bbox="416 324 443 642">Tris(2,3-dichloropropyl) phosphate</p>
4-((bis(2-chloroethoxy)phosphoryl)-2,2-bis(chloromethyl)butyl bis(2-chloroethyl) phosphate (BCPBCBBCP)	 <p data-bbox="678 665 735 1241">4-((bis(2-chloroethoxy)phosphoryl)-2,2-bis(chloromethyl)butyl bis(2-chloroethyl) phosphate (BCPBCBBCP)</p>	 <p data-bbox="678 259 705 642">Tris(1-chloro-2-propyl) phosphate (TCPP)</p>

(continued)



**Table 1** (continued)

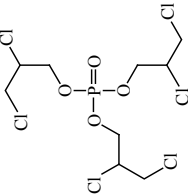
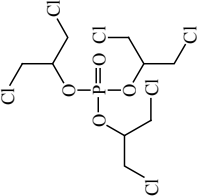
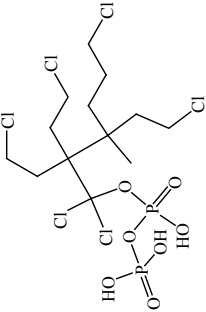
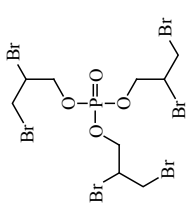
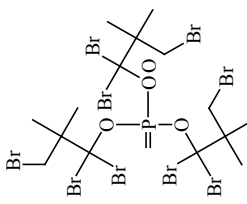
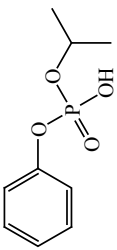
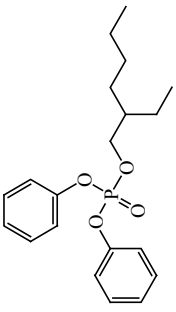
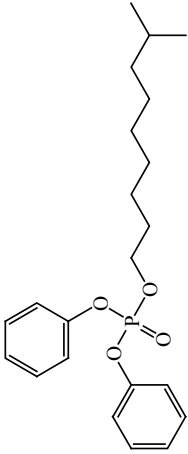
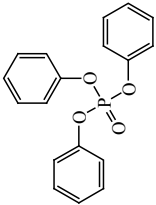
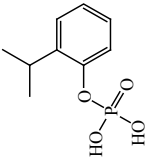
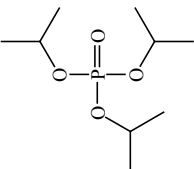
OPFRs classes	Chemical structures	
	 <p data-bbox="441 837 464 1243">Tris(2,3-Dichloropropyl) phosphate (TDCPP)</p>	 <p data-bbox="464 202 488 643">Tris(1,3-dichloro-2-propyl) phosphate (TDCPP)</p>
	 <p data-bbox="729 661 752 1243">Tetrakis(2-Chloroethyl) dichloro-isopentyl diphosphate (TCDIDPP)</p>	(continued)

Table 1 (continued)

OPFRs classes	Chemical structures	
<i>Br-aliphatic</i>	 <p data-bbox="417 837 452 1252">Tris(2,3-dibromopropyl) phosphate (TDBPP)</p>	 <p data-bbox="493 326 546 643">Tris(tribromoneopentyl) phosphate (TTBPP)</p>
<i>Aromatic-aliphatic</i>	 <p data-bbox="699 820 729 1252">Phenylpropan-2-ylhydrogen phosphate (PPHP)</p>	 <p data-bbox="776 255 805 643">2-Ethylhexyldiphenyl phosphate (EHDPP)</p>

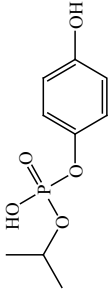
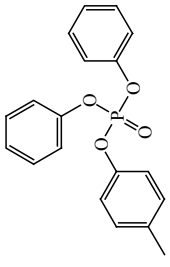
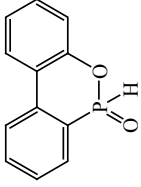
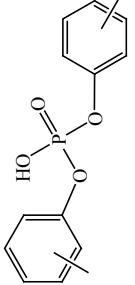
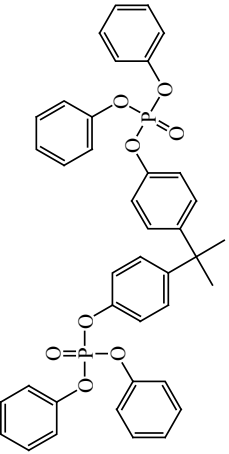
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**Table 1** (continued)

OPFRs classes	Chemical structures
<i>Aromatic</i>	 <p>Isodecylidiphenyl phosphate (IDPP)</p>
	 <p>Triphenyl phosphate (TPP)</p>
	 <p>Isopropylphenyl phosphate (IPPP)</p>
	 <p>Triisopropyl phosphate (TIPP)</p>

(continued)

Table 1 (continued)

OPFRs classes	Chemical structures
	 <p data-bbox="341 238 370 643">Phenol,4-(1-methylethyl) phosphate (PMEP)</p>
<p data-bbox="423 934 452 1252">Cresyl diphenylphosphate (CDPP)</p> 	 <p data-bbox="629 238 682 643">6H-Dibenz[c,e][1,2]oxaphosphorin,6-oxide (DOPO)</p>
<p data-bbox="617 899 646 1252">Alkylated diphenylphosphate (ADPP)</p> 	 <p data-bbox="940 784 970 1252">Bisphenol-A bis-(diphenylphosphate) (BPA-BDPP)</p>

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**Table 1** (continued)

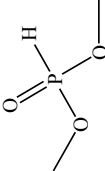
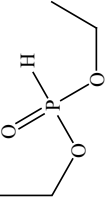
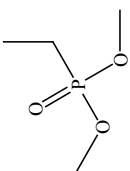
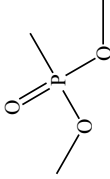
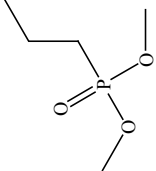
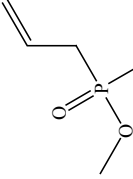
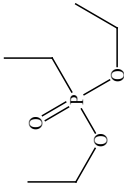
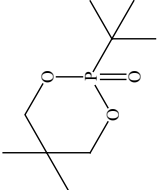
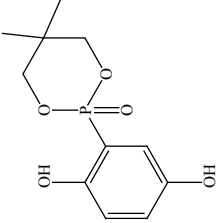
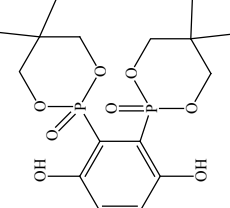
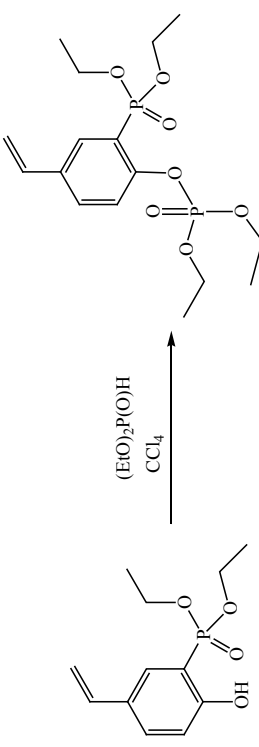
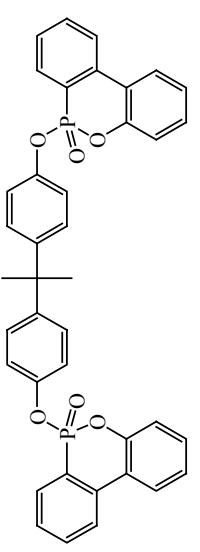
OPFRs classes	Chemical structures	
Organophosphonates <i>Aliphatic</i>	 <p data-bbox="353 866 377 1241">Dimethyl hydrogen phosphonate (DMHP)</p>	 <p data-bbox="353 284 377 642">Diethyl hydrogen phosphonate (DEHP)</p>
	 <p data-bbox="542 913 565 1241">Dimethylethyl phosphonate (DMEP)</p>	 <p data-bbox="526 284 550 642">Dimethylmethyl phosphonate (DMMP)</p>
	 <p data-bbox="753 901 777 1241">Dimethylpropyl phosphonate (DMPP)</p>	 <p data-bbox="753 313 777 642">Dimethylallyl phosphonate (DMAP)</p>
	(continued)	

Table 1 (continued)

OPFRs classes	Chemical structures	
	 <p data-bbox="369 936 392 1245">Diethylethyl phosphonate (DEEP)</p>	 <p data-bbox="392 296 416 636">Cyclic <i>tert</i>-butyl phosphonate (CTBP)</p>
<i>Aromatic</i>	 <p data-bbox="677 989 700 1245">Ar-Phosphonate derivative 1</p>	 <p data-bbox="683 384 706 636">Ar-Phosphonate derivative 2</p>

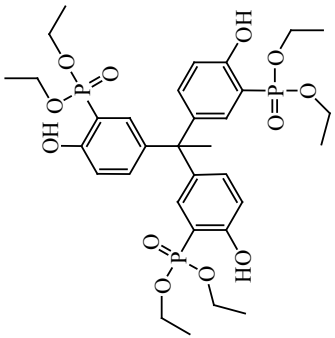
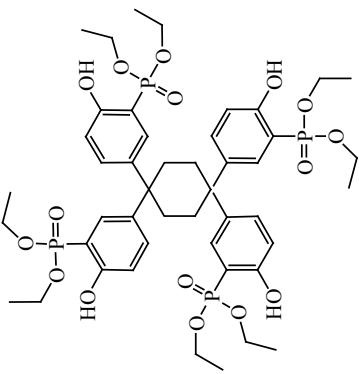
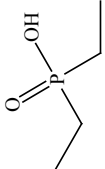
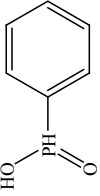
(continued)

**Table 1** (continued)

OPFRs classes	Chemical structures
	 <p style="text-align: center;">(EtO)<sub>2</sub>P(O)H CCl<sub>4</sub></p> <p style="text-align: center;">Ar-Phosphonate derivative 3      Ar-Phosphonate derivative 4</p>
	 <p style="text-align: center;">Ar-Phosphonate derivative 3      Ar-Phosphonate derivative 5 (Bisphosphonate)</p>

(continued)

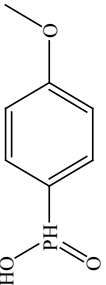
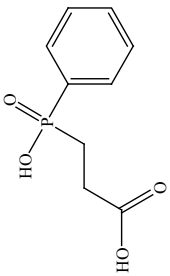
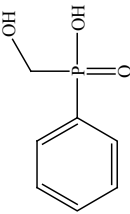
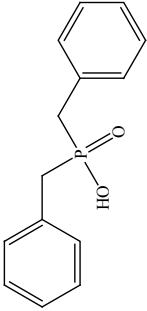
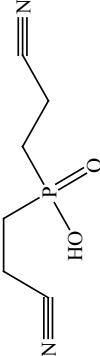
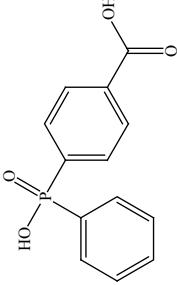
Table 1 (continued)

OPFRs classes	Chemical structures	
	 <p data-bbox="570 882 605 1243">Ar-Phosphonate derivative 6 (Phenolic)</p>	 <p data-bbox="588 282 617 643">Ar-Phosphonate derivative 7 (Phenolic)</p>
Organophosphinites	 <p data-bbox="746 952 776 1243">Diethylphosphinic acid (DEPA)</p>	 <p data-bbox="746 370 776 643">Phenylphosphinic acid (PPA)</p>

(continued)

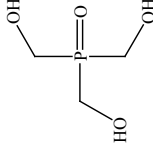
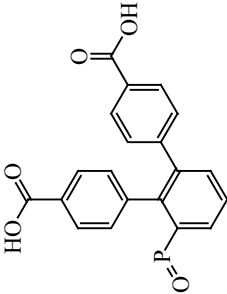
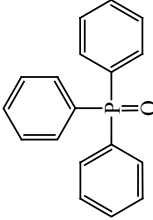
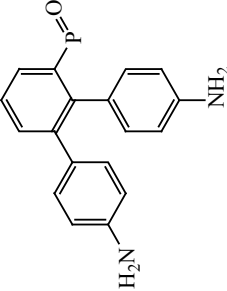
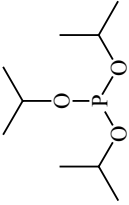
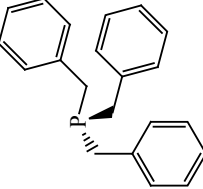


**Table 1** (continued)

OPFRs classes	Chemical structures	
	 <p data-bbox="341 846 370 1243"><i>p</i>-Methoxyphenylphosphinic acid (PMPPA)</p>	 <p data-bbox="399 220 429 643">Carboxyethyl-phenylphosphinic acid (CEPPA)</p>
	 <p data-bbox="593 802 623 1243">Hydroxymethylphenylphosphinic acid (HMPPA)</p>	 <p data-bbox="599 335 629 643">Dibenzylphosphinic acid (DBPA)</p>
	 <p data-bbox="758 846 787 1243">Bis(2-cyanoethyl)phosphinic acid (BCEPA)</p>	 <p data-bbox="834 194 864 643">4-Carboxyphenylphenylphosphinic acid (CPPPA)</p>

(continued)

Table 1 (continued)

OPFRs classes	Chemical structures	
Organophosphine oxide	 <p data-bbox="397 813 421 1245">Tris(hydroxymethyl) phosphineoxide (THMPO)</p>  <p data-bbox="683 730 706 1245">Bis(4-carboxyphenyl) phenylphosphine oxide (BCPPPO)</p>	 <p data-bbox="397 336 421 642">Triphenylphosphineoxide (TPPO)</p>  <p data-bbox="683 248 706 642">Bis(4-aminophenyl) phenylphosphine oxide (BAPPO)</p>
Organophosphites	 <p data-bbox="903 971 926 1245">Triisopropyl Phosphite (TIPP)</p>	 <p data-bbox="977 384 1000 642">Tri-phenyl Phosphite (TPPi)</p>

Tris(2,3-dibromopropyl) phosphate (TDBPP) and Tris(tribromoneopentyl) phosphate (TTBPP).

**Br-aliphatic:** Bromine-based P-C<sub>aliphatic</sub> bond containing FRs are found effective FRs, for example, Phenylpropan-2-ylhydrogen phosphate (PPHP), 2-Ethylhexyldiphenyl phosphate (EHDPP), Isodecyldiphenyl phosphate (IDPP) etc.

**Aromatic:** In the previous few decades aromatic phosphates possess strong flame-retardant properties [34]. Common examples are Triphenyl phosphate (TPP), Tricresyl phosphate (TCP), Triisopropyl phosphate (TIPP), Cresyl diphenylphosphate (CDPP), 6H-Dibenz[c,e] [1, 2] oxaphosphorin,6-oxide (DOPO), Bisphenol-A bis-(diphenylphosphate) (BPA-BDPP) etc.

### 1.3.2 Organophosphonate FRs

Organophosphonates were extensively developed and used as FRs. Many commercially accepted compounds based on organophosphonate specification have been generated and successfully employed as FRs and composed of two types:

**Aliphatic:** FRs with P-C<sub>aliphatic</sub> bond having phosphonate group are shown in Table 1 and commonly include Dimethyl hydrogen phosphonate (DMHP), Diethyl hydrogen phosphonate (DEHP), Dimethylethyl phosphonate (DMEP), Dimethylmethyl phosphonate (DMMP), Dimethylpropyl phosphonate (DMPP), Dimethylallyl phosphonate (DMAP) as well as a Cyclic tert-butyl phosphonate (TBP).

**Aromatic:** FRs with P-C<sub>aromatic</sub> bond having phosphonate group FRs were derived from the transformation of aliphatic moiety with aromatic units. A monosubstituted phosphorus compound (Ar-Phosphonate derivative 1, m.p. 184–187 °C) and a disubstituted phosphorus compound (Ar-Phosphonate derivative 2, m.p. 258–260 °C) were obtained as a mixture using modified separation and purification steps [37]. The phosphonate product diethyl-(2-hydroxy-5-vinylphenyl) phosphonate (Ar-Phosphonate derivative 4) was fabricated from diethyl-(4-vinylphenyl)phosphate (Ar-Phosphonate derivative 3) using ethoxy-P-acid [38]. Su et al. [39] patented the P-enabled esterification of phenol or polyhydroxybenzenes to develop several OPFRs. one example is compounds Ar-Phosphonate derivative 5 obtained from bisphenol A [39].

Another two phenolic white crystals/compounds (Ar-Phosphonate derivative 6, m.p. 169–171 °C and 7, m.p. 216–217 °C) were prepared through [1, 3]-sigmatropic rearrangement and were found to have high-performance against polymers [40].

### 1.3.3 Organophosphinites FRs

Recently, synthesis and applications of different phosphinic acid derivatives have been reported excel flame resistant abilities [41]. Examples of organophosphinites FRs are Diethylphosphinic acid (DEPA), Phenylphosphinic acid (PPA),

*p*-Methoxyphenylphosphinic acid (PMPPA), Carboxyethyl-phenylphosphinic acid (CEPPA), Bis(2-cyanoethyl)phosphinic acid (BCEPA) etc.

### 1.3.4 Organophosphine Oxide FRs

Organophosphine oxide derivatives found to have limited FRs capabilities. Examples are Tris(hydroxymethyl) phosphineoxide (THMPO), Triphenylphosphineoxide (TPPO) and Bis(4-carboxyphenyl) phenylphosphine oxide (BCPPPO). In addition, Bis(4-aminophenyl) phenylphosphine oxide (BAPPO) was developed as a moderate water-soluble compound that found effectiveness towards Polyurathane-based materials with environmental susceptibility [42].

### 1.3.5 Organophosphites FRs

Like organophosphine oxide derivatives, organophosphites were also least responsive FRs because of their cholinergic neurotoxicity [43, 44]. Examples are Triisopropyl Phosphite (TIPP) and Tri-phenyl Phosphite (TPP).

## 2 Textile Applications of P-Based Flame Retardants

Organophosphorus compounds with P–C moieties have shown a wide range of design and development of exciting organophosphorus FRs due their high thermal and hydrolytic stability (P–C bond), ease of synthesis and suitability of processing even at high temperature. Extensive works have been published regarding the creation of P–C bond and their potential applications [1–6, 11–13, 22, 31–35]. These P–C containing organophosphorus compounds have shown several applications along with fire resistancy, for example, reagents, catalysts, pesticides, insecticides, herbicides, surfactants, lubricants and even more [1–4, 45].

Textiles and clothing are prepared from various fiber forming substrates either natural origin polymers such as cellulose and protein, or a wide variety of semi-synthetic and synthetic polymers such as cellulose acetate, polyesters, polyamides, polyolefins, polyacrylonitriles, polyaramids, polylactides, polyetherketones etc. All of these polymers are allocate a frequent limitation, combustible under normal environmental conditions and sometimes pose serious fire hazards in case of fire accidents.

In the present scenario, fire-caused deaths are a growing global problem. The Fire Administration Authority of US, has reported recently on the basis of 24 industrialized nations as the average rate of fire-related deaths and concluded that 10.7 per million populations every year have been observed [46, 47]. Additionally, The National Fire Protection Association claims that home structure involved fires are the main cause of fire-related death [47].

Textile materials provide an excellent source of fuel during the burning process, are found to be a rich source of inflammable or ideal fire carriers like hydrocarbons. The potential hazards and risks associated with textiles are described in depth by various researchers [1, 2, 7, 11]. In this prospect, textiles with lower flammability are still experiencing some changes like the improvement in effectiveness and the replacement of toxic chemical products with counterparts that have a low environmental impact and, more sustainable [4, 5]. Health and environmental concerns associated with halogenated as well as formaldehyde-based FRs driven R&D for identifying and utilizing safer alternatives. Because of the social concerns onto eco-preservation using eco-friendly FRs, the new FRs needs to be halogen-free and formaldehyde-free. Phosphorus, nitrogen, and silicon-containing compounds are generally considered as environment-friendly FRs, due to their safer-nature for human-ecosystem and synergistic effects [6, 14]. The effectiveness of P-based FRs towards fire mainly because of its characteristics, for example, low water solubility, low volatility, less dose requirement, less degradation to possibly hazardous substances, and no toxic emissions [2, 6, 31]. P-based FRs, play a key role possibly in combination with silicon- or nitrogen-containing structures, to the design of new and efficient FRs for textile substrates. Mechanistically, phosphorous based FRs, during a fire form poly and meta-phosphoric acids which form an oxygen-barrier layer [15].

Phosphorus based FRs have been found very reactive to inhibit fire and are used as thermosets for many substrates such as unsaturated epoxy resins, polyesters or polyurethanes. These type of substrates contain activated functional groups (i.e. halogens, alcohols, epoxy, amines etc.), which allow incorporation into the polymer matrix during the process [42, 43]. In case of cotton fibre, organic assembled phosphorus compounds (i.e. Pyrovatex CP and Pyrovatex CP New) can either with the cotton fabric to form cross-linked adducts/linked structures with the fibers [48]. In a study, a formaldehyde-free, inorganic-organic hybrid FR was developed and markedly found inferior FR performance compared with conventional formaldehyde-containing organic phosphorus FR. Lessan et al. [49] investigated the flame retardant behavior of sodium hypophosphite (SHP)—nano-TiO<sub>2</sub> hybrid on woven cotton fabric through pad-dry-cure process. As a result, decreasing the flammability with increasing the char formation of the treated fabrics was observed [49].

Despite the use of toxic and not environmentally-friendly chemicals, high-molecular-weight proteins even DNA derived from animal or microbial sources have been investigated as “green” FRs for cotton fabrics [42, 49]. Current trends are made towards high-molecular-weight FRs based on P-moiety combined with polymeric/complex textile substrates impart multifunctional structures will aid in reducing flammability without a loss of their valuable properties. A novel organic phosphorus-based flame retardant has reported the enhancement of flame retardancy of cotton fabrics through the high-molecular-weight grafting of cellulose-phosphonic acid by Gao et al. [50] as an alternative to halogen-formaldehyde-based FRs [50]. In this study, an ammonium salt of hexamethylenediamine-N,N,N',N'-tetra(methylphosphonic acid) (AHDTPA), was fabricated using the reaction of urea with hexamethylenediamine-N,N,N',N'-tetra(methylphosphonic acid) (HDTMPA). Further, new P–O–C covalent bonds were formed by this ammoniated salt reacted

with the O-6 hydroxyls of glucose residues of cellulose. The resulted hybrid FR containing both P and N-moieties exhibited excellent flame retardant performance for cotton fabrics (70 g/L hybrid FR with limiting oxygen index (LOI) value of 36.0%) which remained relatively stable after 50 laundering cycles (70 g/L hybrid FR with LOI value 28.0%).

Some particular proteins such as phosphorus and sulphur-rich proteins (i.e. caseins and hydrophobins) derived from animal or microbial sources have been under investigations as a novel as well as green flame retardants for cotton fabrics. Alongi et al. [51] investigated caseins and hydrophobins as a novel and green flame retardants for cotton fabrics [51]. As a consequence, P-based-polymer matrix was achieved with improved flame retardancy, indicated by the increased total burning time as well as by the decreased total burning rate. In this study, the change in the flammability features of the fabric, favouring the dehydration of cellulose to form char as opposed to the depolymerization with further production of combustible volatile species were observed. The familiar results have been observed by the same research group when whey proteins were employed that homogeneously deposited on cotton fabric to impart FR properties, using the layer-by-layer technique [52].

In addition, bio-derived phytic acid exhibits the great potential to improve the flame retardancy of textile materials, but with low washing durability. To overcome the poor durability, Cheng et al. [53] investigated a reactive, efficient P-containing flame retardant using phytic acid, pentaerythritol and 1,2,3,4-butanetetracarboxylic acid [53]. The wool fabric treated with HPPHBTCA 0.14 mol/L HPPHBTCA had self-extinguishing performance even after 20 washing cycles during the vertical burning test, presenting good FR ability and resistance to washing with slight negligible effect on the whiteness, tensile strength and handle of wool fabric.

Therefore, phosphorus-containing compounds offer a novel route to prepare so-called green, eco-friendly and durable flame retardants for textiles or textile-based materials that inhibit or resist the spread of fire.

### 3 Conclusion and Future Outlook

Flame retardants have been added to the polymer systems to prevent the risk of fire and overall the use of FRs has substantially decreased the number of fires and fire fatalities in our social wardrobe. With increased awareness towards environmental concerns about FRs selectivity, phosphorus-based FRs provide a foundation for the directed design of nontoxic FRs mainly because of its versatility, for example, it can act in both the condensed and gas phase, as an additive or as a reactive component, in various oxidization states, and in synergy with numerous adjuvant elements.

Various P-moieties make a valuable contribution and various combinations including elemental, inorganic salts and organophosphorus compounds. Nowadays, various products, large in numbers are commercially available based on organophosphorus compound. Although the use of a new generation of chemicals known as

Organophosphorus Flame Retardants (OPFRs) is a worthy goal for controlling household fires, on one hand, the other hand, it is also important to control or prevent their toxic effects. Based on carbon unit/moiety OPFRs can be broadly categorized into five main classes; *organophosphates*, *organophosphonates*, *organophosphinites*, *organophosphine oxide*, and *organophosphites*. A vast variety of P–C bond containing efficient FRs are being developed; however, further R&D works are needed in terms of their economical, renewability and green synthetic pathways, environmental impacts, long term durability, acute and chronic toxicity etc. without a loss of valuable properties at laboratory as well as their possible larger exploration.

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