

Reactive and Polymeric Flame Retardants in Polyurethane Foams

Sergei Levchik, PhD, Research and Development Director,
ICL-IP America, 769 Old Saw Mill River Road, Tarrytown, NY 10520

Ignition and combustion PU foams

Polyurethane foams encompass a wide range of foamed materials with very different properties starting from low density open cell flexible and rigid foams all the way to high density isocyanurate closed cell foams. From the point of view of response to heat, PU foams exhibit low thermal inertia. This means that the heat applied to the foam doesn't dissipate deeply but stays in the surface layer. The surface reaches high temperature quickly and therefore PU foams are easy to ignite. Paradoxically, although PU foams are easy to ignite it is also easy to extinguish the fire when the flame is still small. This relates to the same inherent property of the PU foam of low thermal inertia. Since the heat cannot penetrate into the depth of the foam, the heated layer where the foam decomposes and produces combustible gases is shallow. Burning foam shows significant turbulence and fluctuation of the flame (Figure) which is an indication of the instability of combustion. Such small flames can be extinguished by small changes in the fuel supply or by decreasing the heat by means of incomplete combustion. Flame retardants added to the PU foams are specifically designed to extinguish small accidental fires. Flame retardants provide a variety of fire extinguishing mechanisms which will be discussed later on.



Flame retarded foam (left) and untreated foam (right) in vertical ignition resistance test.

“No ignition – no fire” is the best strategy to mitigate the fire hazard of PU foams. However if the ignition source is too large it can overcome the first line of defense - ignition resistance. In this case flame retardants can provide the second line of defense which decreases the heat release rate (the key property governing the intensity of a fire [1,2]) and the rate of fire growth and limits fire spread. This strategy is required to be used for rigid PU (and polyisocyanurate) foam insulation materials. Foam plastic insulation materials used in construction are required by US codes (International Building Code [3] and International Residential Code [4]) to meet a very severe fire test (NFPA 286, room-corner test [5]) or be covered by a thermal barrier and also meet a somewhat less severe fire test (ASTM E84, Steiner tunnel [6], Class B) in order to be permitted for use in habitable locations (such as rooms in houses). When foam plastic insulation is used as part of exterior wall systems (in facades) or of roofing systems, they are also required to comply with severe fire tests and be protected. Even more severe requirements exist for foam plastic insulation used in concealed areas such as plenums. The proper flame retardant treatment of the foam will decrease the probability of fires spreading quickly throughout buildings.

Traditional Flame retardants in PU foams.

Recently Weil and Levchik published two reviews [7,8] and a book chapter [9] on flame retardancy of polyurethane foams. Traditionally aliphatic chlorophosphates, aliphatic phosphates and aliphatic phosphonates were used or are currently being used as flame retardants for PU foams (Table 1). General observation from the long history of use of these flame retardants is that the efficiency is somehow related to the phosphorus or phosphorus plus chlorine content. However, it seems that the volatility of phosphate esters also plays an important role, probably as important as the content of phosphorus and chlorine in the molecule. Although many of the early flame retardants were selected on a trial and error basis there is a clear indication that gas phase action is needed for PU foams. The mechanism and chemistries of scavenging of active free radicals in the flame by halogen and phosphorus species have been well documented [10,11].

Table 1. List of traditional flame retardants used (some discontinued) in PU foams.

Chemical name	Abbreviation	Structure	Mw	P %, wt.	Cl %, wt.	Vapor pressure,* kPa at °C		
						93	121	149
Tris-(2-chloroethyl phosphate)	TCEP	$\begin{array}{c} \text{O} \\ \parallel \\ \text{P} - \left[\text{O} - \text{CH}_2 - \text{CH}_2\text{Cl} \right]_3 \end{array}$	285	10.9	37	0.3	0.8	1.8
Tris-(2-chloroisopropyl phosphate)	TCPP	$\begin{array}{c} \text{O} \\ \parallel \\ \text{P} - \left[\text{O} - \begin{array}{c} \text{CH}_3 \\ \\ \text{CH} \\ \\ \text{CH}_2\text{Cl} \end{array} \right]_3 \end{array}$	328	9.5	32	0.15	0.4	1.1
Tris-(2-dichloroisopropyl phosphate)	TDCP	$\begin{array}{c} \text{O} \\ \parallel \\ \text{P} - \left[\text{O} - \begin{array}{c} \text{CH}_2\text{Cl} \\ \\ \text{CH} \\ \\ \text{CH}_2\text{Cl} \end{array} \right]_3 \end{array}$	431	7.2	49	0.09	0.2	0.5

Triethyl phosphate	TEP	$\begin{array}{c} \text{O} \\ \\ \text{P} - \{ \text{OC}_2\text{H}_5 \}_3 \end{array}$	182	17		2.1	5.9	15
Dimethyl methylphosphonate	DMMP	$\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{CO} - \text{P} - \text{OCH}_3 \\ \\ \text{CH}_3 \end{array}$	124	25		3.3	11	32

*Isoteniscope, ASTM D2879

Researchers at Polytechnic University [12,13] studied in detail the mechanism of flame retardant action of TDCP in flexible PU foams. Interestingly, they found that the flexible foam extinguishes quickly if it is ignited from the bottom up because of massive volatilization of TDCP into the flame. Very little flame scorched molten material was observed on the surface of the extinguished foam. This points to the limited supply of combustible gases and explains instability of combustion of the foam. It takes a longer time to extinguish the foam when it is ignited from the top, because of the pool of molten decomposing foam (mostly polyol) that is formed and stabilizes the flame. The flame still extinguishes when the critical concentration of the flame retardant is built up in the condensed phase and in the gas *via* evaporation and decomposition.

Different from the flexible foams, rigid foams have a closed cell structure which prevents flash volatilization of the flame retardant, but still the flame retardant easily goes into the gas phase when cells open due to pyrolysis. The ignition of the rigid foams is an interesting phenomenon because the flame flashes over the surface and then quickly retreats. If the heat flux to the surface is not sufficient the flame can extinguish. The foam may reignite again if the heating is continued. Since the rigid foam is more densely cross-linked compared to the flexible foam, it doesn't melt away but undergoes charring. In such a scenario the best strategy to flame retard foam is to try to leverage both the gas phase and condensed phase modes of action. This is achieved by combining phosphate ester flame retardants and reactive bromine based flame retardants. In the technical literature there is a common perception that brominated FRs provide gas phase action (true), but their important condensed phase action is often overlooked [14,15,16]. Commercial brominated flame retardants for rigid foams are typically diols or monohydric alcohols. They become part of the PU network and cannot volatilize as a molecule, but instead, bromine radicals are produced in the condensed phase. The bromine radicals need to find hydrogen in order to form stable HBr. Therefore, bromine attacks PU aliphatic chains and this leads to more crosslinks, unsaturation and aromatization which are all precursors of the char [17].

Isocyanurate foams are made with a significant 2.0-3.5 times excess of isocyanate over polyol. Excess of isocyanate forms an isocyanurate cross-linked network. Since the isocyanurate groups are rich in nitrogen and they are thermally more stable than the urethane groups, the isocyanurate foam is intrinsically more flame retardant than rigid spray PU foams and typically do not require the help of brominated flame retardants.

Although high volatility alkyl phosphates or chloroalkyl phosphates were correct choices for good flame retardant efficiency, after a few decades in use they started showing other problems. Flame retardants initially dissolved in the polymer (foam walls) will eventually migrate to the surface and slowly start volatilizing. This is especially true for open cell flexible

and rigid foams. This may not lead to significant deterioration of the flame retardant performance but volatile flame retardants can be detected in houses and eventually in the environment. Furthermore, some of the flame retardants not associated with hazards to the humans or environment at the time of introduction to the market showed problems later on after additional studies. For example, the most efficient flame retardants used in rigid PU foams, DMMP and TCEP (Table 1), were found to exhibit some degree of mutagenicity and were removed from the market. Because of high volatility, DMMP and TCEP were never used in flexible foams. TDCP (Table 1), with significantly lower volatility, was traditionally used in flexible PU foams to pass the California (TB-117) open flame standard for upholstered furniture and also in automotive foams to pass MVSS 302. Although the vapor pressure of TDCP is very low, it can still migrate from the foam by thermal or photo initiated decomposition mechanisms [18]. TDCP was also listed in Proposition 65 as a suspected carcinogen in California and requires special labeling. Since 2013 California doesn't require furniture to comply with the open flame test and therefore TDCP is not used in furniture anymore. It was probably a good decision to remove TDCP from its use in furniture, but lowering the California regulation on the fire safety of upholstered furniture was a move in the wrong direction, especially in view of the new flame retardant alternatives being made available and developed in the market, as discussed in the next section.

Polymeric and Reactive Flame Retardants.

Because of issues related to exposure to high volatility flame retardants in foams it seems the logical solution would be the use of non-volatile and relatively heavy molecules such as polymeric flame retardants. The potential of such polymeric molecules to migrate from foam is very low. In addition, due to their large size, they are not likely to penetrate the cell membranes of living organisms' cells and thus, are not expected to be bioavailable or possess intrinsic toxicity. An even more attractive idea is to use flame retardants with alcohol or isocyanate functionalities that will participate in the foaming process and become part of the PU network. These flame retardants no longer exist as chemical species once reacted into the polymer backbone making it impossible to leach, bloom or escape from the polymer into the environment.

These reactive flame retardants are not new ideas and were discussed in the technical literature already in the 70s [19,20]. Then, why was this not practiced? One of the main problems is losing the gas phase flame retardant mode of action which is very important for PU foams. Polymeric molecules are heavy and obviously will not volatilize as easily as the flame retardants listed in Table 1. Reactive flame retardants built into the PU polymer chains will not volatilize before the chains break and may not deliver flame retardant species to the flame fast enough to achieve critical concentration.

There are also other problems associated with the process of producing the foam. Polymeric or oligomeric FRs are high viscosity products and this adds challenges when pumping and mixing them. Keeping low viscosity is especially important for rigid spray foams applied on site and often outdoors at low temperature. Reactive FRs pose a problem with the production of the foam as well. Typical reactive FRs would be short chain polyols. It might be not problematic to use short chain polyols in rigid foams or in PIR foams, but it is a significant challenge in the flexible foams where short chain polyols tend to close cells and cause shrinkage.

Nevertheless, there are a few successful examples of commercially available reactive and polymeric FRs. One of the earliest reactive FRs for rigid PU foams is diethyl N,N bis(2-hydroxyethyl) aminomethylphosphonate (Figure 3). It is made by reacting diethylphosphite, diethanol amine and paraformaldehyde. ICL sells it as Fyrol® 6, but there are also other producers. It is a short chain diol with a pendant phosphonate group. P-CH₂-N is a relatively weak link and it breaks during combustion releasing diethyl phosphite which can easily volatilize to the gas phase. Thus diethyl N,N bis(2-hydroxyethyl) aminomethylphosphonate enables permanency of the flame retardant in the foam during service time, but provides essential gas phase mode of action in the case of fire. Because it is a short chain diol, diethyl N,N bis(2-hydroxyethyl) aminomethylphosphonate cannot be used in flexible foams.

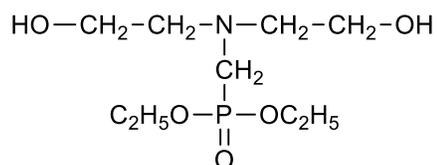
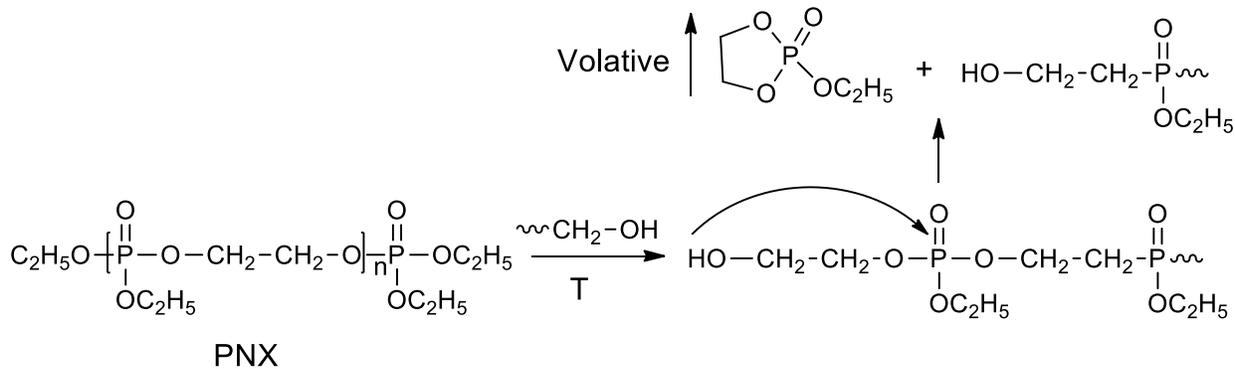


Figure 3

Another old phosphorus containing diol available in the market for rigid foams is Amgard® 82 (formerly known as Vircol® 82). It is the reaction product of dibutyl acid pyrophosphate and propylene oxide. More recently Clariant started marketing two phosphorus-based diols Exolit® OP 550 and OP 560 for flexible PU foams.

A number of brominated diols (PHT-4 Diol®, Chemtura, Saytex® RB-79, Albemarle and Ixol®, Solvay) as well as a monoalcohol (FR-513, ICL) are available for use in rigid PU foams. Since brominated reactive FRs are very viscous liquids or solids they are typically dissolved in TCPP. The bromine radicals can split from the brominated FR indifferently whether the FR is situated in the main chain or as the pendant group and therefore design of reactive brominated FRs is less challenging.

One successful example of a polymeric FR, poly(ethyl ethylene phosphate) (Figure 4), is being sold by ICL under the trade names of Fyrol® PNX and Fyrol® PNX-LE. It is especially favored by the automotive industry where low emissions (VOC) and fogging are critical. Although the average molecular weight of PNX is about 900 Dalton, it is not bioaccumulative and it shows very high efficiency in flexible PU foams. It has a high phosphorus content of 19% which is partially responsible for the high efficiency. It is also believed that PNX can depolymerize upon heating perhaps initiated by the attack of polyol OH groups which results in producing cyclic 1,2-ethylene ethyl phosphate (Figure 4). This volatile cyclic phosphate provides gas phase action. Thus, PNX can be considered as a “smart” flame retardant that sits dormant during normal use, but where flame triggers its action. PNX still has a high viscosity, however due to very high efficiency it is used in the foam at low loading levels and therefore high viscosity can be tolerated. Based on data available so far, this polymer is not expected to be toxic.



New Developments

As discussed above, the first generation of flame retardants for PU foams was developed with maximum flame retardant efficiency in mind. This was achieved with additive or non-reactive flame retardants. Other unintended consequences of using relatively mobile chemicals in the high surface application (foam) were not taken into consideration at the time. To be fair, at the time there were no sensitive analytical methods available to monitor chemicals in the environment at very low concentrations. During the last years, it has become clear that new sustainable flame retardants for foams should be either reactive, or polymeric, or solid inorganics (not desirable for the PU industry, traditionally using only liquids). An interesting example for a similar PU application is also available, i.e. polystyrene foam insulation. In this case, a new polymeric bromine based FR was developed by Dow Chemical [21] and embraced by the industry and the regulatory bodies in USA and Europe.

Under its commitment to the development and use of sustainable chemistries and products ICL recently introduced to the market two new products: E06-16, presented at the CPI conference in 2014 [22] and E15-143T, presented at the CPI conference in 2016 [23]. E06-16 is a reactive monofunctional, an all phosphorus-based flame retardant specifically designed for PIR foams as a single FR and it is also used in combination with reactive brominated FRs in PUR spray foam. Preliminary VOC and solvent extraction experiments confirmed the complete incorporation of E06-16 in the PU network. The efficiency of E06-16 is similar to TCPP and it can replace TCPP on a one-to-one basis in most rigid PU foam applications. Being halogen free E06-16 also shows lower smoke generation. Based on data available so far, the product is not expected to be toxic to human health or the environment.

E15-143T is also monofunctional and an all phosphorus-based flame retardant, but it is designed for flexible PU foams. E15-143T is highly efficient and requires 1.5-2.5 times lower loading compared to TDCP. Because of such low loading essential physical properties of the foam are fully preserved. As measured in common automotive industry emission tests DIN 75201 and VDA -277, E15-143T based foam shows FOG and VOC numbers similar to non-flame retardant foam and significantly lower than TDCP. Toxicity studies performed on this product came out favorably.

It seems counterintuitive that we are focusing on monofunctional flame retardants which are in essence chain-terminators in the foaming process and may affect physical properties of the foam. However, due to the high efficiency and low concentration, it doesn't happen. In contrast, monofunctional FRs give obvious advantages because they are always present as

pendant groups attached to the PU network and therefore, provide life service permanence, but at the same time labile enough to split from the polymer in the case of fire and provide very desirable gas phase action. Another benefit of monofunctional FR is the relative forgiveness in the foaming process. Being monofunctional alcohols they don't tighten foam as much as difunctional and multifunctional FRs and can be formulated with the minimal adjustments. And finally, a few remarks about cost and long term benefits of polymeric and reactive flame retardants. There is a common notion that any new and more sophisticated flame retardant product introduced to the market is likely to be more expensive than the old one being replaced. However, we always need look at cost-performance in use. As it was just discussed above, proper design of polymeric and reactive flame retardants can significantly cut use dosage and as a result cost in use becomes similar or sometimes even more favorable than traditional flame retardants. Combining safer toxicology and environmental profile of reactive and polymeric FRs with lower use levels brings their safety margins even higher. Although there are no studies available on the potential loss of flame retardant performance of traditional flame retardants over long service life, it is clear that reactive and polymeric flame retardants by design should not have this problem.

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