FLAME RETARDANTS, PHOSPHORUS

1. Introduction

One of the principal classes of flame retardants used in plastics and textiles is that comprising phosphorus, phosphorus–nitrogen, and phosphorus–halogen compounds (see also FLAME RETARDANTS FOR TEXTILES). Several reviews of phosphorus flame retardants have been published (1–3) (see also PHOSPHORUS COMPOUNDS).

2. Mechanisms of Action

A recent review of this topic is available (4). Phosphorus flame retardants have a multiplicity of modes of action, both condensed and vapor phase.

2.1. Condensed-Phase Mechanisms. The mode of action of phosphorus-based flame retardants is probably best understood in cellulosic systems. Cellulose (qv) decomposes by a noncatalyzed route to tarry depolymerization products, notably levoglucosan, which then decompose to volatile combustible fragments such as alcohols, aldehydes (qv), ketones (qv), and hydrocarbons (qv) (7–9). However, when catalyzed by acids, the decomposition of cellulose proceeds primarily as an endothermic dehydration of the carbohydrate to water vapor and char. Phosphoric acid is particularly efficaceous in this catalytic role because of its low volatility (see PHOSPHORIC ACID AND PHOSPHATES). Also, when strongly heated, phosphoric acid yields polyphosphoric acid, which is even more effective in catalyzing the cellulose dehydration reaction. The flame-retardant action is believed to proceed by way of initial phosphorylation of the cellulose. Certain nitrogen compounds such as melamines, guanidines, and ureas appear to catalyze the cellulose phosphorylation step and are found to enhance or synergize the flame-retardant action of phosphorus on cellulose (8–11). The nonvolatile phosphorus acids are also able to coat the char, rendering the char less permeable and protecting it from further oxidation by adsorption on or phosphorylation of reactive sites (12). The retention of phosphorus in the char may be aided by nitrogen synergists, possibly by formation of nonvolatile polyphosphoramidic or polyphosphorimidic acids (13).

In poly(ethylene terephthalate) (14–16) and poly(methyl methacrylate) (17–19), the mechanism of action of phosphorus flame retardants is at least partly attributable to a decrease in the amount of combustible volatiles and a corresponding increase in nonvolatile residue (char). In poly(methyl methacrylate), the phosphorus flame retardant additive or comonomer appears to cause an initial cross-linking through anhydride linkages (19,20), reducing the amount of volatile fuel and increasing residue.

The amount and physical character of the char from rigid urethane foams is found to be affected by the retardant (21–24) (see FOAMS; URETHANE POLYMERS). The presence of a phosphorus-containing flame retardant causes a rigid urethane foam to form a more coherent char, possibly serving as a physical barrier to the combustion process. There is evidence that a substantial fraction of the phosphorus may be retained in the char. This barrier action may at least partly explain the inhibition of glowing combustion of char by phosphorus compounds. Flexible urethane foams do not yield much char on burning, but often form a decomposition product layer that may contribute to extinguishment (25).

In polymers such as polystyrene that do not readily undergo charring, phosphorus-based flame retardants tend to be less effective, and such polymers are often flame retarded by antimony–halogen combinations (see STYRENE). However, even in such noncharring polymers, phosphorus additives exhibit some activity, which suggests at least one other mode of action. Phosphorus compounds may produce a barrier layer of polyphosphoric acid on the burning polymer (26,27). Phosphorus-based flame retardants are more effective in styrenic polymers blended with a char-forming polymer such as polyphenylene oxide or polycarbonate. In these mixtures, the relatively nonvolatile phosphates such as tetraphenyl resorcinol diphosphate appear to catalyze rearrangement reactions of the oxygen-containing polymeric component that lead to char formation (28–30).

Phosphorus-containing additives can act in some cases by catalyzing thermal breakdown of the polymer melt, reducing viscosity, and favoring the flow or drip of molten polymer from the combustion zone; this can be enhanced by prodegradants such as peroxides (31). On the other hand, red phosphorus [7723-14-0] has been shown to retard the nonoxidative pyrolysis of polyethylene (a radical scission). For that reason, the scavenging of radicals in the condensed phase has been proposed as one of several modes of action of red phosphorus (32).

Several commercial polyester fabrics are flame retarded using low levels of phosphorus additives that cause them to melt and drip more readily than fabrics without the flame retardant. This mechanism can be defeated by the presence of nonthermoplastic component such as infusible fibers, pigments, or by silicone oils that can form pyrolysis products capable of impeding melt flow (33,34).

2.2. Vapor-Phase Mechanisms. Phosphorus flame retardants can also exert vapor-phase flame-retardant action. Trimethyl phosphate [512-56-1], $C_3H_9O_4P$, retards the velocity of a methane–oxygen flame with about the same molar efficiency as antimony trichloride (35–37).

Both physical and chemical vapor-phase mechanisms have been proposed for the flame-retardant action of certain phosphorus compounds. Physical (endothermic) modes of action have been shown to be of dominant importance in the flame-retardant action of a wide range of non-phosphorus-containing volatile compounds (38,39).

Triphenylphosphine oxide [791-28-6], $C_{18}H_{15}OP$, and triphenyl phosphate [115-86-6], $C_{18}H_{15}O_4P$, as model phosphorus flame retardants were shown by mass spectroscopy to break down in a flame to give small molecular species such as PO, HPO_2, and P_2 (40,41). The rate-controlling hydrogen atom concentration in the flame was shown spectroscopically to be reduced when these phosphorus species were present, indicating the existence of a vapor-phase mechanism.

Physical or chemical vapor-phase mechanisms may be reasonably hypothesized in cases where a phosphorus flame retardant is found to be effective in a noncharring polymer, and especially where the flame retardant or phosphorus-containing breakdown products are capable of being vaporized at the temperature of the pyrolyzing surface. In the engineering thermoplastic Noryl (General Electric), which consists of a blend of a charrable poly(phenylene oxide) and a poorly charrable polystyrene, experimental evidence indicates that effective flame retardants such as triphenyl phosphate act in the vapor phase to suppress the flammability of the polystyrene pyrolysis products (42).

The question as to whether a flame retardant operates mainly by a condensed-phase mechanism or mainly by a vapor-phase mechanism is especially complicated in the case of the haloalkyl phosphorus esters. A number of these compounds can volatilize undecomposed or undergo some thermal degradation to release volatile halogenated hydrocarbons (43). The intact compounds or these halogenated hydrocarbons are plausible flame inhibitors. At the same time, the phosphorus content may remain at least in part as relatively nonvolatile phosphorus acids that are plausible condensed-phase flame retardants (44). There is no direct evidence for the occasionally postulated formation of phosphorus halides, occasionally postulated by analogy to the antimony–halogen systems. Some evidence has been presented that the endothermic vaporization, heat capacity, and dilution of vaporized fuel by the intact chloroalkyl phosphates may be a main part of their action (45).

2.3. Interaction with Other Flame Retardants.

Some claims have been made for a phosphorus–halogen synergism, ie, activity greater than that predicted by some additivity model. Unlike the firmly established antimony–halogen synergism, however, phosphorus–halogen interactions are often merely additive and in some cases slightly less than additive (10,11). Some reports of phosphorus–halogen synergism can be shown to be artifactual results of nonlinear response–concentration relationships. Nevertheless, combinations of phosphorus and halogens are often quite useful, and there are data supporting synergism with specific combinations and compounds (46,47). The strongest synergism has been found with certain compounds having bromine and phosphorus in the same molecule, such as tris(2,4-dibromophenyl) phosphate (48).

Antagonism between antimony oxide and phosphorus flame retardants has been reported in several polymer systems, and has been explained on the basis of phosphorus interfering with the formation or volatilization of antimony halides, perhaps by forming antimony phosphate (49,50). This phenomenon is also not universal, and depends on the relative amounts of antimony and phosphorus. Some useful commercial poly(vinyl chloride) (PVC) formulations have been described for antimony oxide and triaryl phosphates (49,50). Combinations of antimony oxide, halogen compounds, and phosphates have also been found useful in commercial flexible urethane foams (51).

Although no general synergist for phosphorus has been found, some useful synergisms have been found in specific systems between phosphorus flame retardants and other additives (11). Zeolites and other acidic additives appear to help in intumescent ammonium polyphosphate formulations (52). Synergistic interactions of relatively nonvolatile and relatively volatile phosphorus flame retardants have been detected (53).

3. Commercial Phosphorus-Based Flame Retardants

A large number of phosphorus compounds have been described as having flame-retardant utility (54). The compounds demonstrating commercial utility are much more limited in number.

3.1. Inorganic Phosphorus Compounds.

Red Phosphorus. This allotropic form of phosphorus is relatively nontoxic and, unlike white phosphorus, is not spontaneously flammable. Red phosphorus is, however, easily ignited. It is a polymeric form of phosphorus having thermal stability up to ~450°C. In finely divided form, it has been found to be a powerful flame-retardant additive (32,55–57). In Europe, it has found commercial use in molded nylon 66 electrical parts in a coated and stabilized form. In Japan, it is used in some wire and cable products. Handling hazards of the powder and color have deterred broad usage. The availability of masterbatches may overcome the handling problems. The tendency to react with moisture to produce traces of phosphine is lessened by stabilizers such as aluminum hydroxide.

Ammonium Phosphates. These salts were first recommended for flame retardancy of theater curtains by Gay-Lussac in 1821. Monoammonium phosphate [7722-76-1], $NH_4H_2PO_4$, and diammonium phosphate [7783-28-0], $(NH_4)_2HPO_4$, or mixtures of the two, which are more water soluble and nearly neutral, are used in large amounts for nondurable flame retarding of paper (qv), textiles (qv), disposable nonwoven cellulosic fabrics, and wood (qv) products (5–7) (see FLAME RETARDANTS FOR TEXTILES). The advantage is high efficiency and low cost. Ammonium phosphate finishes are resistant to dry-cleaning solvents but not to laundering or even to leaching by water. One general advantage of ammonium phosphates and phosphorus compounds as flame retardants, especially in comparison to borax, which is also used for nondurable cellulosic flame retardancy, is effectiveness in preventing afterglow.

Formulations of ammonium phosphates and ammonium bromide are sold for use on cellulosic–synthetic fiber blends. Other ammonium phosphate formulations contain wetting and softening agents. A large volume, ~9000 t/yr in 1991, of ammonium phosphate was used in the United States (58) in forest fire control, usually by aerial application, often in combination with ammonium sulfate (see also AMMONIUM COMPOUNDS).

Some other water-soluble ammonium salts of phosphorus acids are used in nondurable textile flame retardancy to minimize the effect on "hand" (texture). An example is Rhodia's Antiblaze RD-1, which is a neutral ammonium salt of $N(CH_2PO_3H_2)_3$. This salt is useful on automotive and aircraft upholstery.

Insoluble Ammonium Polyphosphate. When ammonium phosphates are heated by themselves under ammonia pressure or preferably in the presence of urea, relatively water-insoluble ammonium polyphosphate [68333-79-9] is produced (59,60). There are several crystal forms, depending on heating conditions. The commercial products, available from a number of manufacturers, differ in molecular weight, morphology, particle size, solubility, and surface coating. Insoluble ammonium polyphosphate consists of long chains of repeating $OP(O)(ONH_4)$ units. Grades are available that are coated with melamine–formaldehyde or other thermoset resins to impede hydrolysis.

These finely divided solids are principal ingredients of intumescent paint (qv) and mastics (61). In such formulations, ammonium polyphosphate is considered to function as a catalyst. Thus when the intumescent coating is exposed to a high temperature, the ammonium polyphosphate yields a phosphorus acid that then interacts with an organic component such as a pentaerythritol to form a carbonaceous char. The chemistry has been described in detail (62). A blowing (gas-generating) agent, such as melamine or chlorowax, is also present to impart a foamed character to the char, thus forming a fire-resistant insulating barrier to protect the substrate. In addition, the intumescent formulations typically contain resinous binders, pigments, and other fillers. Mastics are related but generally more viscous formulations, intended to be applied in thick layers to girders, trusses, and decking; these generally contain mineral fibers to increase coherence. Besides the well-established coating applications, many studies have been done and some commercialization has resulted with intumescent formulations for thermoplastics (63–69), in particular for polyolefins, ethylene–vinyl acetate, and urethane elastomers. The char-forming resin can be, eg, an ethyleneurea–formaldehyde condensation polymer, a hydroxyethyl isocyanurate , or a piperazine–triazine resin. In noncharrable polymers such as polypropylene, blending of charrable polymers such as thermoplastic polyurethanes can make ammonium polyphosphate perform as a flame retardant (70).

Phosphoric Acid-Based Systems for Cellulosics. Semidurable flame-retardant treatments for cotton (qv) or wood (qv) can be attained by phosphorylation of cellulose, preferably in the presence of a nitrogenous compound. Commercial leach-resistant flame-retardant treatments for wood have been developed based on a reaction product of phosphoric acid with urea–formaldehyde and dicyandiamide resins (71,72).

3.2. Additive Organic Phosphorus Flame Retardants. *Melamine and Other Amine Phosphates.* Four melamine phosphate are commercial products (73,74); these are melamine orthophosphate [20208-95-1], $C_3H_6N_6 \cdot H_3O_4P$, [41583-09-9]; dimelamine orthophosphate, $2C_3H_6N_6 \cdot H_3O_4P$, [56974-60-8]; melamine pyrophosphate [15541-60-3], 2 $C_3H_6N_6 \cdot H_4O_7P_2$; and a newly introduced melamine polyphosphate. The pyrophosphate is reported to be only soluble to the extent of 0.09 g/100 mL water, whereas melamine orthophosphate is soluble to 0.35 g/mL. Melamine orthophosphate is converted to the pyrophosphate with loss of water on heating. All four are available as finely divided solids. All are used commercially in flame-retardant coatings (qv) and from patents also appear to have utility in a variety of thermoplastics and thermosets. A detailed study of the thermal decomposition of the melamine phosphates has been published (75). Recently, melamine polyphosphate was introduced by DSM; it has an even higher thermal stability and a lower water solubility than the pyrophosphate. A low-cost method for flame retarding unsaturated polyester resins uses melamine phosphate made *in situ* by adding superphosphoric acid to a dispersion of melamine in the liquid resin (76).

A self-intumescent phosphoric acid salt has been introduced by Albright & Wilson as Amgard NK (formerly Amgard EDAP), the ethylenediamine salt of phosphoric acid (1:1), mainly as an additive for polyolefins (77,78). It is a finely divided solid, mp 250°C, having a phosphorus content of 63 wt% as H_3PO_4.

Unlike ammonium polyphosphate, it does not require a char-forming synergist. Its performance is improved by admixture with melamine in Amgard NP.

Trialkyl Phosphates. Triethyl phosphate [78-40-0], $C_6H_{15}O_4P$, is a colorless liquid boiling at 209–218°C containing 17 wt% phosphorus. It is made from diethyl ether and phosphorus pentoxide via a metaphosphate (79,80). Triethyl phosphate is used as an additive for polyester laminates, rigid polyurethane foams, and in cellulosics. It is added precure to unsaturated polyester resins and also to the polyol precursor of rigid polyurethane foams, where it functions as a viscosity depressant and remains in the foam as a flame retardant. Its viscosity depressant effect in polyester resins permits high loadings of alumina trihydrate, a fire-retardant smoke-suppressant filler (81).

Higher trialkyl phosphates are relatively flame retardant liquids; tributyl phosphate is used in fire-resistant aircraft hydraulic fluids and trioctyl phosphate is used as a low-flammability low-temperature vinyl plasticizer.

3.3. Oligomeric Ethyl Ethylene Phosphate. The reaction of triethyl phosphate, P_2O_5 and ethylene oxide produces an oligomeric additive containing 19% phosphorus (Akzo Nobel's FYROL PNX). It has been introduced as a high efficiency flame retardant for flexible or rigid polyurethane and polyisocyanurate foams. Because of its oligomeric character, it has low vapor emission (thus freedom from window fogging) in applications such as automobile seating (82).

Dimethyl Methylphosphonate. Dimethyl methylphosphonate [756-79-6] (DMMP), $C_3H_9O_3P$, a water-soluble liquid, bp 185°C, is made by the Arbuzov rearrangement of trimethyl phosphite. DMMP contains 25% phosphorus, which is near the maximum possible for a phosphorus ester, and therefore on a weight basis is highly efficient as a flame retardant. It is a viscosity depressant and flame retardant in alumina trihydrate (ATH) filled unsaturated polyester resins (76,83) such as these used for bathtubs, shower stalls, and in halogenated resins such as used in ductwork. Applications have been found in rigid polyurethane foams and as an intermediate for making other flame retardants such as Fyrol 76, Fyrol 51, and Antiblaze NT.

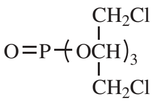
Diethyl Ethylphosphonate. A liquid compound introduced for applications similar to those of DMMP is diethyl ethylphosphonate [78-38-6], $C_6H_{15}O_3P$. This material is claimed to be less susceptible to undesirable interactions with haloaliphatic components, such as blowing agents, or with amine catalysts.

3.4. Halogenated Alkyl Phosphates and Phosphonates. In this important class of additives, the halogen contributes somewhat to flame retardancy although this contribution is offset by the lower phosphorus content. The halogens reduce vapor pressure and water solubility, thus aiding retention of these additives. Efficient manufacturing processes lead to favorable economics.

2-Chloroethanol Phosphate (3:1). Tris(2-chloroethyl) phosphate [115-96-8], $C_6H_{12}Cl_3O_4P$ [2-chloroethanol phosphate (3:1)], is a low viscosity liquid product that has found widespread usage because of low cost, low odor, high percent phosphorus, and compatibility with most polymers containing polar groups. Akzo Nobel's Fyrol CEF contains 10.8% phosphorus and 36.7% chlorine, and is made from a 3:1 mole ratio of ethylene oxide (qv) and phosphorus oxychloride (84). This phosphate is used in rigid polyurethane and polyisocyanurate foams, carpet backing, flame-laminated and rebonded flexible foam, flame-retardant coatings, most classes of thermosets, adhesives (qv), cast acrylic sheet, and wood–resin composites such as particle board. It is used with melamine in flexible urethane foam cushions and institutional mattresses.

1-Chloro-2-Propanol Phosphate (3:1). Tris(1-chloro-2-propyl) phosphate [13674-84-5], $C_9H_{18}Cl_3O_4P$, is a liquid containing 33% chlorine and 9.5% phosphorus. It is produced by reaction of propylene oxide (qv) and phosphorus oxychloride, and most of the alkyl groups are the secondary (isopropyl) isomer. Because of the branchy structure, this phosphate is much lower in reactivity to water and bases than the 2-chloroethyl homologue (85). It is sold as Akzo Nobel's Fyrol PCF or Albright & Wilson's Antiblaze 80 and is a preferred additive for rigid urethane foams where favorable price and good storage stability in the isocyanate or the polyol–catalyst mixture are required. It is used in isocyanurate foam to reduce friability and brittleness, and is also used in flexible urethane foams in combination with melamine.

1,3-Dichloro-2-Propanol Phosphate (3:1). Tris(1,3-dichloro-2-propyl) phosphate [13674-87-8], $C_9H_{15}Cl_6O_4P$, sold by Akzo Nobel as Fyrol FR-2 and by Albright & Wilson as Antiblaze 195, contains 49% chlorine and 7.2% phosphorus. It is made from epichlorohydrin and phosphorus oxychloride. The principal structure has 1,3-dichloro-2-propyl groups.



$$O{=}P\left(O\underset{CH_2Cl}{\overset{CH_2Cl}{C}}H\right)_3$$

There is also a small quantity of the compound having a single 2,3-dichloropropyl group and two 1,3-dichloro-2-propyl groups. There are many erroneous literature references where the product is named as if it were the tris(2,3-dichloropropyl) isomer, which has been made by addition of chlorine to triallyl phosphate, an impractical route. Compared to the foregoing chloroalkyl phosphates, this product has a greatly reduced volatility, much lower water solubility, and high stability toward the amine catalysts used in foam manufacture. It is a leading additive for flexible urethane foams (86), but is also used in rigid foams, and can be added to the isocyanate or the polyol–catalyst mixture. This phosphate shows little tendency to scorch, ie, to cause discoloration and degradation, even in high exotherm flexible foam formulations. Flexible foam formulations containing this and other haloalkyl phosphates can be further stabilized against scorch by appropriate antioxidants and acid acceptors (87,88). Combinations with melamine are used in cushioning formulations (89). This halogenated phosphate is also useful as a flame retardant in styrene–butadiene and acrylic latices for textile backcoating and binding of nonwovens.

Bis(2-Chloroethyl) 2-Chloroethylphosphonate. The commercial product, Albright & Wilson's (now Rhodia's) Antiblaze 78, is a mixture having various related higher boiling diphosphonates. This product is made by the Arbuzov rearrangement of tris(2-chloroethyl) phosphite [140-08-9], $C_6H_{12}Cl_{13}O_3P$, itself made by the reaction of ethylene oxide and phosphorus trichloride. Although bis(2-chloroethyl)-2-chloroethyl phosphonate [6294-34-4], $C_6H_{12}Cl_3O_3P$, is not as stable as the corresponding phosphate, it is useful as a flame-retardant additive in rigid urethane foams (90), rebonded foams, adhesives, and coatings. It is also an intermediate that upon dehydrochlorination by the action of bases produces bis(2-chloroethyl) vinylphosphonate, a copolymerizable monomer (91).

Diphosphates. Three 2-chloroethyl diphosphates have been sold commercially. These have low volatility and good-to-fair thermal stability, and are thus useful in those open cell (flexible) foams that have requirements for improved resistance to dry and humid aging.

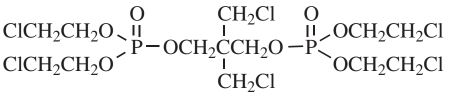
The simplest was Olin's Thermolin 101, tetrakis(2-chloroethyl) ethylenediphosphate [33125-86-9], $C_{10}H_{20}Cl_4O_8P_2$ (92), used extensively in flexible foams (93,94). This compound has been discontinued, reportedly because of by-product problems.

The commercially available tetrakis(2-chloroethyl) ethyleneoxyethylenediphosphate [53461-82-8], $C_{12}H_{24}Cl_4O_9P_2$, has the following structure:

$$(ClCH_2CH_2O)_2P(=O)-OCH_2CH_2OCH_2CH_2O-P(=O)(OCH_2CH_2Cl)_2$$

This liquid contains 27% chlorine and 12% phosphorus. It is made from ethylene oxide, diethylene glycol, and phosphorus oxychloride (95) and is available in Japan from Daihachi.

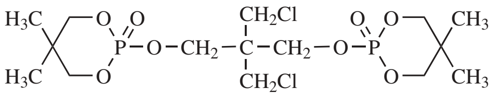
A third member of this family was introduced originally as Monsanto's Phosgard 2XC20 [38051-10-4], $C_{13}H_{24}Cl_6O_8P_2$, but is now available as Albright & Wilson's (now Rhodia's) Antiblaze 100. The synthesis (96) involves reaction of pentaerythritol and phosphorus trichloride to produce a spirobis(chlorophosphite), then chlorination with ring opening, followed by treatment of the resultant bis(phosphorodichloridate) with ethylene oxide. The compound has the following structure:



$$(ClCH_2CH_2O)_2P(=O)-OCH_2C(CH_2Cl)_2CH_2O-P(=O)(OCH_2CH_2Cl)_2$$

Because of the bulky neo structure in the middle of the molecule, this compound has enhanced hydrolytic stability in addition to low volatility. It is useful in many types of flexible foam, as well as in adhesives and epoxy- or phenolic-based laminates.

VP Sandoflam 5085 (Clariant) is a dichloroneopentyl diphosphate with neopentylene phosphate rings (97). It is a solid melting at 186–190°C and processable to 240–250°C, stable enough for use in injection molded polymethyl methacrylate.

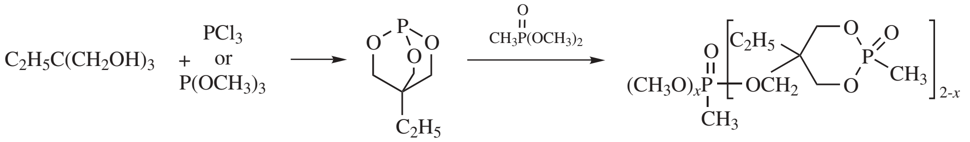


Oligomeric esters with chloroethyl groups attached to both phosphate and phosphonate linkages are available or have been available from Monsanto, Daihachi, and Clariant. These have been used in polyurethanes, cast acrylics, and various thermosets.

Oligomeric 2-Chloroethyl Phosphate. Akzo's Fyrol 99 [109640-81-5], is produced either by self-condensation of tris(2-chloroethyl) phosphate (98) or by insertion of phosphorus pentoxide into this phosphate (99) followed by ethoxylation. It is low in volatility and useful in resin-impregnated air filters, in flexible urethane foam, rebonded foam, and structural foam.

Tris(tribromoneopentyl) Phosphate. This high melting solid is a promising flame retardant additive for polyolefins, such as polypropylene (100). Its structural formula is $[(BrCH_2)_3CCH_2O]_3P{=}O$. This compound has been in the flame retardancy patent literature for several decades (101, 102) but it has only recently been made commercially available by FMC (103) and Dead Sea Bromine. Because of steric hindrance in this molecule, it is hydrolytically and thermally stable, and has a favorable toxicological profile in contrast to the now-discontinued tris(2,3-dibromopropyl) phosphate. Tris(tribromoneopentyl) phosphate is one of the few retardants that appears to be useful in polypropylene fibers.

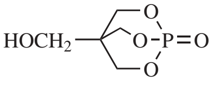
Oligomeric Cyclic Phosphonates. Rhodia's (formerly Albright & Wilson's) Antiblaze N or NT (formerly 19) and 1045 (probably also Clariant's Exolit 910) are mixtures of the material shown where $x = 1$ has the CAS Registry Number [41203-81-0], $C_9H_{20}O_6P_2$, and $x = 0$, [42595-49-9], $C_{15}H_{31}O_9P_3$. The chemistry of manufacture appears to be the following (104):



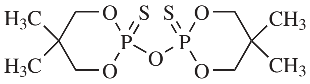
Antiblaze 1045 contains a larger amount of the triphosphonate [42595-45-9]. Both materials are water-soluble thermally stable low volatility liquids having about 20% phosphorus content and no halogen.

The bicyclic phosphite intermediate is highly neurotoxic, but, after the ring-opening step, the product is low in toxicity. Antiblaze N and 1045 are used as flame-retardant finishes for polyester fabric (105). After the phosphonate is applied from an aqueous solution, the fabric is heated to swell and soften the fibers, allowing the phosphonate to be absorbed and strongly held. These high-percent phosphorus-content products are also useful flame retardants in polyester resins, polyurethanes, polycarbonates, nylon-6, and textile backcoating.

Pentaerythritol Phosphates. A bicyclic pentaerythritol phosphate, CN-1197, has more recently been introduced by Great Lakes Chemical for use in thermosets, preferably in combination with melamine or ammonium polyphosphate (106). It is a high melting solid having the following structure [5301-78-0] (87):



Cyclic Neopentyl Thiophosphoric Anhydride. This solid additive, Sandoflam 5060, has been commercialized in Europe by Sandoz for use in viscose rayon (107,108). It has the following structure [4090-50-1]:



Despite the anhydride structure, it is remarkably stable, surviving addition to the highly alkaline viscose, the acidic coagulating bath, and also resisting multiple laundering of the rayon fabric. The unusual stability may be attributed to the sulfur atoms, which enhance hydrophobicity, and to the sterically hindering neopentyl groups that retard hydrolysis.

Phosphinates. Alkaline earth or aluminum salts of phosphinic acids, $RR'PO_2H$, where R and R′ are small organic radicals, have been introduced on a development basis by Hoechst (Clariant). These phosphorus-rich additives appear effective as flame retardants at unusually low loadings in thermoplastics such as acrylonitrile–butadiene–styrene (ABS), polybutylene terephthalate (PBT), or polyamide (109,110).

Aryl Phosphates. Aryl phosphates were introduced into commercial use early in the twentieth century for flammable plastics such as cellulose nitrate and later for cellulose acetate. Cellulosics are a significant area of use but are exceeded now by plasticized vinyls (111). Principal applications are in wire and cable insulation, connectors, automotive interiors, vinyl moisture barriers, plastic greenhouses (Japan), furniture upholstery, conveyer belts (especially in mining), and vinyl foams.

Triaryl phosphates are also used on a large scale as flame-retardant hydraulic fluids (112), lubricants, and lubricant additives (see LUBRICATIONS AND LUBRICANTS). Smaller amounts are used as nonflammable dispersing media for peroxide catalysts.

In vinyls, the aryl phosphates are frequently used in combinations with phthalate plasticizers. The proportion of the more expensive phosphate is usually chosen so as to permit the product to reliably pass the flammability specifications. In plasticized vinyls used in automotive interiors, these phosphates are used to pass the Federal Motor Vehicle Safety Standard 302.

Triaryl phosphates are produced from the corresponding phenols (usually mixtures) by reaction with phosphorus oxychloride, usually in the presence of a catalyst (113,114). They are subsequently distilled and usually washed with aqueous bases to the desired level of purity. Tricresyl phosphate and trixylenyl phosphate were originally made from petroleum-derived or coal-tar-derived cresylic acids, ie, cresols and xylenols. Discovery of the toxicity of the ortho-cresyl phosphates led manufacturers to select cresols having very little *o*-cresol.

In the 1960–1980 period, the use of more economical synthetic isopropyl- and *tert*-butylphenols as alternatives to cresols was developed (115,116). Commercial triaryl phosphates such as FMCs Kronitex 100 and Akzo Nobel's Phosflex 31P and 41B are based on partially isopropylated or *tert*-butylated phenol. The relative volatilities and oxidative stabilities of these phosphates have been compared; the *tert*-butylphenyl phosphates are the most oxidatively stable of the alkylphenyl phosphates (117).

Blends of triaryl phosphates and pentabromodiphenyl oxide are leading flame-retardant additives for flexible urethane foams. A principal advantage is their freedom from scorch.

Triphenyl phosphate [115-86-6], $C_{18}H_{15}O_4P$, is a colorless solid, mp 48–49°C, usually produced in the form of flakes or shipped in heated vessels as a liquid. An early application was as a flame retardant for cellulose acetate safety film. It is also used in cellulose nitrate, various coatings, triacetate film and sheet, and rigid urethane foam. It has been used as a flame-retardant additive for engineering thermoplastics such as polyphenylene oxide–high impact polystyrene and ABS–polycarbonate blends.

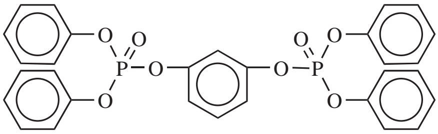
The commercial tricresyl phosphate product is essentially a *meta, para*-isomer mixture. Typical products of this class are Akzo's Lindol [1330-78-5], $C_{21}H_{21}O_4P$, or FMCs Kronitex TCP [68952-35-2], nearly colorless liquids, bp $\sim$260–275°C at 1.3 kPa (10 mmHg). Tricresyl phosphate is used in flexible PVC, cellulose nitrate, ethylcellulose coatings, and various rubbers. Typical applications are vinyl tarpaulins, mine conveyer belts, air ducts, cable insulation, and vinyl films. Trixylenyl phosphate is a related product of lower volatility and less extractability, having advantages for wire and cable insulation. These phosphates are usually used in blends with phthalates.

The plasticizer performance of isopropylphenyl diphenyl phosphate [28108-99-8], [68937-41-7], [68782-95-6], $C_{21}H_{21}O_4P$, is close to that of tricresyl phosphate. It is made from the product of isopropylation of phenol by propylene. The phosphate is a mixture of mainly *ortho*- and *para*-isomers and contains a distribution of different levels of alkylation (118,119).

tert-Butylphenyl diphenyl phosphate [56803-37-3], [68937-40-6] is a slightly less efficient plasticizer for PVC by itself but it is quite effective in blends with, eg, phthalates. It has been used as a flame retardant in engineering thermoplastics and as a fire-retardant hydraulic fluid. It is very resistant to oxidation.

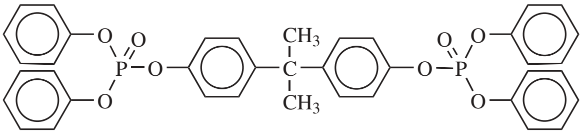
Alkyl diphenyl phosphates are products originally developed to provide improved low temperature flexibility, a fault of triaryl phosphate plasticizers in PVC (120). These phosphates generally provide slightly less flame-retardant efficacy but are generally superior to the triaryl phosphates in regard to smoke when the vinyl formulation is burned. Two commercial products of this family are 2-ethylhexyl diphenyl phosphate [1241-94-7], $C_{20}H_{27}O_4P$, and isodecyl diphenyl phosphate [29761-21-5], $C_{22}H_{31}O_4P$. The 2-ethylhexyl compound has FDA approval for certain food packaging (qv) applications. A longer chain homologue was introduced by Monsanto (now Solutia); it has improved low temperature properties with reduced volatility (121). Butyl diphenyl phosphate and dibutyl phenyl phosphate are used in fire-resistant aircraft hydraulic fluids, along with tributyl phosphate.

Tetraphenyl resorcinol diphosphate [57583-54-7], $C_{30}H_{24}O_8P_2$, is the main component of a relatively new oligomeric phosphate flame retardant, Akzo Nobel's Fyrolflex RDP, designed for use in engineering thermoplastics such as polyphenylene oxide blends (122), thermoplastic polyesters, polyamides, vinyls, and polycarbonates. It is a colorless to light yellow liquid, viscosity 400–800 mPa $\cdot$ s(= cP) at 25°C, and a pour point of −12°C. It is less volatile than the triaryl phosphates and has a higher (11%) percentage of phosphorus than triphenyl phosphate. Although it is an oligomeric mixture, its predominant component has the following structural formula:



and higher oligomers

A newer development in this area is tetraphenyl bisphenol-A diphosphate (123–125), available from Akzo Nobel and Albemarle. Its predominant component has the following structure:



and higher oligomers

This diphosphate is apt to be somewhat lower in cost than the resorcinol diphosphate since the bisphenol-A is more widely produced than resorcinol. Although the bisphenol-A diphosphate is somewhat lower in phosphorus content, in some polymers it is about comparable in flame-retardant effectiveness; this could be because of a better match of thermal behavior to that of the polymer. It is generally favorable for flame retardancy to have a good match of the thermogravimetric curve of the retardant to that of the polymer.

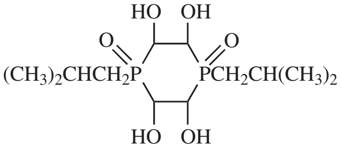
Tetraphenyl bisphenol-A diphosphate has a lower vapor pressure than the resorcinol analogue and tends to migrate less during processing. It is distinctly better than the resorcinol analogue in hydrolysis resistance. On the other hand, the resorcinol diphosphate shows an advantage in flow properties during processing. In some plastics, it may be found that the higher %P in the tetraphenyl resorcinol diphosphate may permit a lower level of addition to reach a given flame-retardancy rating.

Somewhat more costly alkyl-substituted phenyl arylene diphosphates are available in the Far East, in particular from Daihachi. These may be expected to have enhanced thermal and hydrolytic stability, but are more costly. In particular, Daihachi's PX-200, tetrakis(2,6-dimethylphenyl) resorcinol diphosphate may be expected to have enhanced stability to humidity and heat because of the steric hindrance built into the molecule. It finds use, eg, in printed wiring boards.

Combinations of a volatile monophosphate and a less volatile diphosphate have been shown to have possible synergism in a styrenic system (53) and such combinations are shown in various recent patents.

Phosphine Oxides. Triphenylphosphine oxide [791-28-6], $C_{18}H_{15}OP$, is disclosed in many patents as a flame retardant, and may find some limited usage as such, in the role of a vapor-phase flame inhibitor.

A diphosphine oxide of the following structure [124788-09-6] has been offered for several years by American Cyanamid (now by Cytec).



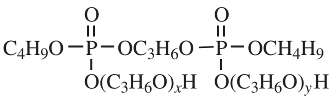
This compound, designated Cyagard RF1204, has been recommended for use in polypropylene. Despite its high hydroxyl content, it is proposed not as a polyol but as a stable, high melting additive for polypropylene (126) or coatings. It has some self-intumescent character that contributes to its flame retardant efficacy.

3.5. Reactive Organic Phosphorus Compounds. *Organophosphorus Monomers.* Many vinyl monomers containing phosphorus have been described in the literature (127), but few have gone beyond the laboratory. Bis(2-chloroethyl) vinylphosphonate [115-98-0], $C_6H_{11}Cl_2O_3P$, has been commercially available (Akzo Nobel's Fyrol Bis-Beta). Vinylphosphonic acid and its dimethyl ester are available from Germany but seem not to have found flame retardant application, probably because of cost.

Several applications have been found for bis(2-chloroethyl) vinylphosphonate as a comonomer imparting flame retardancy for textiles and specialty wood and paper applications. Its copolymerization characteristics have been studied (128). It has also been an intermediate for the preparation of an oligomeric vinylphosphonate textile finish, Fyrol 76 [41222-33-7] (110), which was commercial in the 1970s.

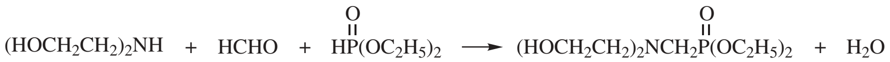
Phosphorus-Containing Diols and Polyols. The commercial development of several phosphorus-containing diols occurred in response to the need to flame retard rigid urethane foam insulation used in transportation and construction. There are a large number of references to phosphorus polyols (129) but only a few of these have been used commercially.

Rhodia's (formerly Albright & Wilson's) Vircol 82 is a diol mixture obtained by the reaction of propylene oxide and dibutyl acid pyrophosphate (130). The neutral liquid has an OH number of 205 mg KOH/g and contains 11.3% phosphorus corresponding to the formula shown where $x + y = 3.4$. The product is a mixture of isomers.



$$C_4H_9O-\underset{\underset{\displaystyle O(C_3H_6O)_xH}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}}-OC_3H_6O-\underset{\underset{\displaystyle O(C_3H_6O)_yH}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}}-OCH_4H_9$$

Significant commercial usage has been made of a phosphonate diol containing nitrogen. The nitrogen may exert a synergistic effect on the flame-retardant effect of the phosphorus. This diol, diethyl *N,N*-bis(2-hydroxyethyl)aminomethylphosphonate [2781-11-5] (Akzo Nobel's Fyrol 6), is synthesized by the following reaction (131):



$$\mathrm{(HOCH_2CH_2)_2NH} + \mathrm{HCHO} + \mathrm{H}\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{(OC_2H_5)_2} \longrightarrow \mathrm{(HOCH_2CH_2)_2NCH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{(OC_2H_5)_2} + \mathrm{H_2O}$$

The product contains 12.6% phosphorus and has an OH number in the 450 mg KOH/g range. Fyrol 6 is used to impart a permanent Class II E-84 flame spread rating to rigid foam for insulating walls and roofs. Particular advantages are low viscosity, stability in polyol–catalyst mixtures, contribution to catalysis, and outstanding humid aging resistance. Fyrol 6 is used in both spray foam, froth, pour-in-place, and slab stock.

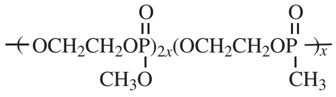
Nonreactive additive flame retardants dominate the flexible urethane foam field. Auto seating applications exist, particularly in Europe, for a reactive polyol or nonvolatile additive for flexible foams to avoid windshield fogging, which can be caused by vapors from the more volatile additive flame retardants.

Reactive Phosphate Diol Oligomer. A recently introduced reactive flame retardant for flexible foam is Clariant's OP 550, an 18% P diol that is made by reaction of P_2O_5 with triethyl phosphate and ethoxylation of the metaphosphate intermediate (99,132).

$$\mathrm{HOCH_2CH_2OP({=}O)(OC_2H_5)[OCH_2CH_2OP({=}O)(OC_2H_5)]}_n\mathrm{OCH_2CH_2OH}$$

This product reacts into the foam structure and provides flame retardancy, eg, in automobile seat cushions, without the disadvantage of windshield fogging caused by additives. A related oligomer with chloroethyl groups had been developed earlier (99,133).

Oligomeric Phosphate–Phosphonate. A commercially used reactive oligomeric alcohol, Akzo Nobel's Fyrol 51 [70715-06-9], has a structure approximately represented by the following (127):



$$-\!\!\left(\mathrm{OCH_2CH_2O}\underset{\mathrm{CH_3O}}{\underset{|}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}}}\right)_{2x}\left(\mathrm{OCH_2CH_2O}\underset{\mathrm{CH_3}}{\underset{|}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}}}\right)_{x}\!\!-$$

Fyrol 51 is a water-soluble liquid containing ~21% phosphorus. It is made by a multistep process from dimethyl methylphosphonate, phosphorus pentoxide, and ethylene oxide. The end groups are principally primary hydroxyl and the compound can thus be incorporated chemically into aminoplasts, phenolic resins, and polyurethanes. Fyrol 51, or 58 if diluted with a small amount of isopropyl alcohol, is used along with amino resins to produce a flame-retardant resin finish on paper used for automotive air filters, or for backcoating of upholstery fabric to pass the British or California flammability standards.

This phosphorus-rich oligomer can also be incorporated into polyurethanes. Combinations with Fyrol 6 permit the OH number to be adjusted to typical values used in flexible foam, urethane coating, or reaction injection molding (RIM) applications (134,135).

3.6. Reactive Organophosphorus Compounds in Textile Finishing. Although synthetic fibers can be flame retarded using additives or comonomers, the flame retarding of cotton (qv) requires the application of a textile finish. Markets for such finishes have been in military goods, industrial protective clothing, curtains, hospital goods, and children's sleepwear. Recent reviews of flame retardant textile finishing are available (136,137).

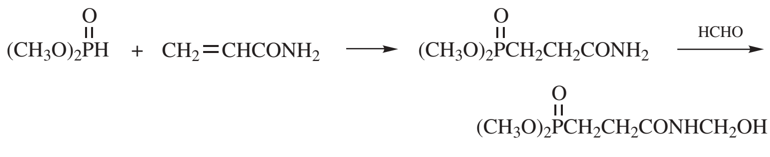
Tetrakis(hydroxymethyl)phosphonium Salts. The reaction of formaldehyde (qv) and phosphine in aqueous hydrochloric or sulfuric acid yields tetrakis-(hydroxymethyl)phosphonium chloride [124-62-1], Albright & Wilson's (now Rhodie's) Retardol C, or the sulfate [55566-30-8] (Retardol S), $(C_4H_{12}O_4P)_2SO_4$ [55566-30-8].

$$PH_3 + 4\,HCHO + HCl \longrightarrow (HOCH_2)_4P^+Cl^-$$

These are water-soluble crystalline compounds sold as concentrated aqueous solutions.

The methylol groups are highly reactive (138–142) and capable of being cured on the fabric by reaction with ammonia or amino compounds to form durable cross-linked finishes, probably having phosphine oxide structures after postoxidizing. Finishes based on these reagents are durable to numerous launderings. An improved process, the Proban treatment, was developed by Albright & Wilson and is now marketed by Rhodia. By prereacting the phosphonium salt and urea (143), neutralizing with inorganic base, applying to cotton, curing with ammonia in a special chamber, and postoxidizing with hydrogen peroxide or perborate, an excellent durable finish with good hand and fabric strength properties can be obtained.

3.7. Phosphonate Finish. A competitive cotton finish, Ciba's Pyrovatex CP, was introduced in the 1970s especially for children's cotton sleepwear, workwear, and other uses. Its Chemical Abstracts name is phosphonic acid, (3-{[hydroxymethyl]amino}-3-oxopropyl)-, dimethyl ester. It is based on the following chemistry:



$$(CH_3O)_2\overset{O}{\overset{\|}{P}}H + CH_2{=}CHCONH_2 \longrightarrow (CH_3O)_2\overset{O}{\overset{\|}{P}}CH_2CH_2CONH_2 \xrightarrow{HCHO} (CH_3O)_2\overset{O}{\overset{\|}{P}}CH_2CH_2CONHCH_2OH$$

Pyrovatex CP coreacts on cellulose with an amino resin in the presence of a latent acid catalyst to produce finishes durable to laundering (144,145). To avoid problems caused by non-reactive or unstable components (146), a higher assay version, Pyrovatex CP New, was later introduced. Amgard TFR-1 (Rhodia) is substantially the same compound. The sleepwear use in the United States appears minimal but there are workwear and other applications particularly in Canada, Europe, and the Far East.

3.8. Phosphorus-Containing Polymers. A large number of addition and condensation polymers having phosphorus built in have been described, but few have been commercialized (147,148). No general statement seems warranted regarding the efficacy of built-in vs. additive phosphorus (149). However, in textile fibers, there is greater assurance of permanency.

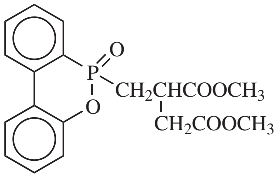
Polyester Fibers Containing Phosphorus. Numerous patents describe poly(ethylene terephthalate) (PET) flame retarded with phosphorus-containing difunctional reactants. At least two of these appear to be commercial.

Hoechst-Celanese's (now Ticona's FR Trevira CS in Europe or KoSa's Avora CS in America) appears to be based on the following chemistry (150,151):

This phosphinic anhydride [15171-48-9], $C_4H_7O_3P$, is then reacted with glycol and other precursors of poly(ethylene terephthalate), to produce a flame-retardant polyester [82690-14-0], having phosphinate units of the structure $-OP(O)(CH_3)CH_2CH_2COO-$. This fabric is useful for children's sleepwear, work clothing, and home furnishings. A phosphorus content as low as 0.6% is reported to be sufficient for draperies and upholstery tests if melt-drip is not retarded by print pigments, silicone contaminants, or the presence of nonthermoplastic fibers (33,34).

Alternative technology for modifying a poly(alkylene terephthalate) by incorporation of a phosphinate structure has been developed by Enichem. Phosphinate units of the structure $—P(C_6H_5)(O)CH_2O—$ are introduced into a polyester such as PET or PBT by transesterification with an oligomer comprised of the aforementioned units (152).

Toyobo's HEIM II (former GH) is apparently based on the following intermediate [63562-31-2] (153):



This dicarboxylic ester is then copolycondensed with the other reactants in PET manufacture to produce a flame-retardant polyester [63745-01-7]. The advantage of this rather unusual phosphinate structure is its high thermal and hydrolytic stability. The fabric is used mainly for furnishings in public buildings in Japan.

4. Epoxy Resins

Epoxy resins used in intumescent paints and mastics are often flame retarded by combinations of additives including the chloroalkyl phosphates discussed above.

Electrical and electronic circuit boards (wiring boards) as well as encapsulated electronic components utilizing epoxy resins often must be flame retardant to meet a standard such as the UL 94 V-0 rating. The usual means for meeting this standard is to incorporate tetrabromobisphenol-A by chain extension into the epoxy resin; indeed, this is the largest single use of a brominated flame retardant. Concerns over waste disposal regulations, particularly those proposed in Europe, creating problems for halogen systems have stimulated effort into finding replacements, particularly based on phosphorus-containing flame retardant components.

Phosphate ester additives may depress the thermomechanical properties and water-resistance excessively. The sterically hindered Daihachi tetrakis(2,6-dimethylphenyl) resorcinol diphosphate (Daihachi's PX-200) has been used as an additive. However, the use of reactive phosphorus compounds has been the object of much recent effort.

Diglycidyl phenylphosphonate (154) has been found useful for electronic epoxy products but cost has retarded its commercial development.

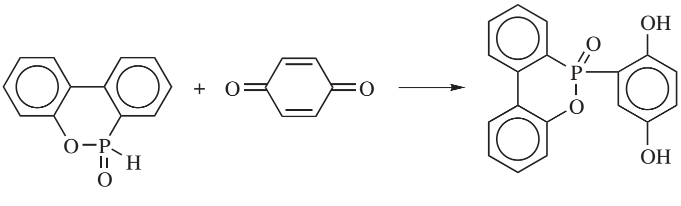
The chain extension of epoxy resins can be conducted with dihydric phenolic resins containing phosphate linkages. Bis(3-hydroxyphenyl) phenyl phosphate can be used as a chain extender for epoxy resins, and can afford a UL 94 V-0 level of flame retardancy with phosphorus content as low as 1.5% after cure (155); however, the glass transition temperature (T_g) is lowered by the flexible phosphate group.

The problem of achieving a high T_g in a circuitboard laminate (to avoid distortion during soldering) may be alleviated by the use of a pendant rigid phosphorus-containing ring structure, namely, the 9,10-dihydro-9-oxa-10-phosphaphenanthrene group, synthesized from o-phenylphenol and phosphorous trichloride.

This ring system has been used in epoxy resins as well as in thermoplastic polyesters (see POLYESTERS, THERMOPLASTIC). It has been the subject of many patents and publications, and is commercially produced in Europe and the Far East. Its original use was in Toyobo's flame retardant polyester fiber, in the form of the itaconic ester adduct shown above.

The hydrogen phosphinate itself can be reacted directly into epoxy resins to produce presumably a β-hydroxyphosphonate structure (156,157). However, this consumes epoxy functionality and creates chain ends which may affect mechanical properties.

A more selective means for incorporation of this ring system is to react the hydrogen phosphinate with benzoquinone by reductive addition to produce the phosphinyl-substituted hydroquinone (158).



This compound can be used as a chain extension reagent with an epoxy resin to obtain flame retardancy with an improvement of T_g. A still-further elaboration of this cyclic structure is the reaction of the hydroquinone with epichlorohydrin and base to make a diglycidyl ether (159) that can be used as part of the epoxy resin.

The same ring system can also be introduced into a novolac hardener by phosphinylation of one or more of the hydroxyl groups of the novolac, leaving the remaining groups to serve for the cross-linking (160).

A cyclic neopentyl hydrogen phosphonate can be added to the epoxy group to impart flame retardancy although the creation of an end group tends to lower T_g (161).

Phosphine oxide diols and triols were shown at FMC to be excellent reactive flame retardants or synergists with good thermal and hydrolytic stability in epoxy resins (162). Bis(3-hydroxypropyl)isobutylphosphine oxide is available as a development product (Cyagard RF-1243) from Cytec. Cost has retarded commercialization.

5. Health, Safety, and Environmental Factors

5.1. Toxicology. Two factors should be considered when discussing the toxicity of flame-retardant materials: the toxicity of the compounds themselves and the effect of the flame retardants on combustion product toxicity.

Product Toxicology. A review of the structure–toxicity and structure–biodegradation relationships of organophosphorus compounds shows clearly that toxicity and biodegradation properties differs greatly from compound to compound, and therefore no general statement is valid (163). The phosphorus-based flame retardants as a class exhibit moderate-to-low toxicity.

A critical review of the toxicity of the haloalkyl phosphates and the potential metabolic products is available (164). As a guide to the Consumer Product Safety Commission in their promulgation of standards, a select committee of toxicologists published a lengthy review and assessment of the toxicity of flame retardants that might be used in upholstered furniture textiles (165). The committee concluded that textile finishes based on ammonium polyphosphate, Pyrovatex, and tetrakis (hydroxymethyl) phosphonium chloride would have minimal risk, whereas, by extremely conservative criteria, more exposure data was needed for the chloroalkyl and aryl phosphates.

An extensive review was conducted and published in the United Kingdom on behalf of the government covering all modes of toxicity of a series of common flame retardants, including tris(chloropropyl) phosphate (166). They indicated that in general the benefits outweighed the risks, and that specifically, tris(chloropropyl) phosphate had minimal toxic risk for its intended use.

A particular mode of neurotoxicity was discovered for tricresyl phosphate that correlated with the presence of the *o*-cresyl isomer (or certain other specific alkylphenyl isomers) in the triaryl phosphates. Many details of the chemistry and biochemistry of the toxic process have been elucidated (167–174). The use of low ortho-content cresols has become the accepted practice in industrial production of tricresyl phosphate. Standard *in vivo* tests, usually conducted with chickens sensitive to this mode of toxicity, have been developed for premarket testing of new or modified triaryl phosphates. Indeed, this series demonstrates the criticality of structure vs. toxicity, and shows that rational avoidance of toxicity-causing structures is made possible by understanding there mode of action.

For example, the *tert*-butylphenyl diphenyl phosphate was correctly predicted to have little or no neurotoxicity since it lacks the benzylic hydrogen needed for biooxidation to a toxic species.

As of 1992, the EPA called for extensive new toxicity and environmental data on this group of products (175). The *Federal Register* document calling for this data has an extensive bibliography on aryl phosphate toxicology as well as a discussion of human exposure.

Mutagenic and later carcinogenic properties were found for tris(2,3-dibromopropyl) phosphate (176–178), a flame retardant briefly used on polyester fabric in the 1970s. This product was withdrawn from the market when the problem was discovered. The chemically somewhat-related tris(dichloroisopropyl) phosphate (used in foams) has been intensively studied and found not to display significant mutagenic activity (176,177).

Tris(2-chloroethyl) phosphate appears to be a weak tumor inducer in a susceptible rodent strain while the chloropropyl homologue is not (178).

The newer tetraphenyl resorcinol diphosphate has been the subject of very thorough toxicological studies and has been found to have a very low degree of inhalation toxicity (179), rapid metabolism and clearance when fed to test animals (180), low or no reproductive toxicity (181), no significant teratogenic effect (182), and no demonstrable immunotoxicity (183), so it appears quite safe for its intended flame retardant use in styrenic polymer blends.

Effects on Combustion Toxicology. There appears to be no documented case of any type of fire retardant contributing to human fire casualties. Carbon monoxide appears to be the dominant lethal gas. A survey of data from small-scale combustion or pyrolysis experiments allows no valid generalization regarding decrease or increase in the yields of toxic gases (CO, HCN) when phosphorus flame retardants were present (184–187). Laboratory experiments using rodents, or the use of gas analysis, tend to be confused by the dominant variable of fuel/air ratio as well as important effects of burning configuration, heat input, equipment design, and toxicity criteria used, ie, death vs incapacitation, time to death, lethal concentration, etc (188,189) . Moreover, data from small-scale tests have doubtful relevance to real fire hazards.

One noteworthy neurotoxic response was demonstrated in laboratory pyrolysis studies using various types of phosphorus flame retardants in rigid urethane foam, but the response was traced to a highly specific interaction of trimethylolpropane polyols, producing a toxic bicyclic trimethylolpropane phosphate [1005-93-2] (184). Formulations with the same phosphorus flame retardants but other polyols avoided this neurotoxic effect completely.

5.2. Effects on Visible Smoke. Smoke is a main impediment to egress from a burning building. Although some examples are known where specific phosphorus flame retardants increased smoke in small-scale tests, other instances are reported where the presence of the retardant reduced smoke. The effect appears to be a complex function of burning conditions and of other ingredients in the formulation (185,190,191). In a careful Japanese study, ammonium phosphate raised or lowered the smoke from wood depending on pyrolysis temperature (192).

5.3. Environmental Considerations. The phosphate flame retardants, plasticizers, and functional fluids have come under intense environmental scrutiny. Results published to date on acute toxicity to aquatic algae, invertebrates, and fish indicate substantial differences between the various aryl phosphates (193–196). The Environmental Protection Agency (EPA) has summarized this data as well as the apparent need for additional testing (175).

Tests in pure water, river water, and activated sludge showed that commercial triaryl phosphates and alkyl diphenyl phosphates undergo reasonably facile conversion to inorganic phosphate by hydrolysis and biodegradation (197–199). The phosphonates can undergo biodegradation of the carbon-to-phosphorus bond by certain microorganisms (200,201).

6. Economic Aspects

Usage of phosphorus-based flame retardants for 2000 in the United States has been estimated to be 102 million lb or $173 million (202) with an annual growth rate of 7%. The largest volume use may be in plasticized vinyl. Other large use areas for phosphorus flame retardants are flexible and rigid urethane foams, polyester resins, epoxy and phenolic resins, adhesives, cotton and polyester textiles, polycarbonate–ABS blends, and poly(phenylene oxide) high impact polystyrene (PPO–HIPS) blends. Development efforts are very active on finding phosphorus flame retardants to replace halogen and halogen–antimony systems, especially in Europe and the Far East. To some extent, this has already happened where phosphate-flame-retarded polyphenylene ether–HIPS, or polycarbonate–ABS blends have replaced bromine–antimony–retarded HIPS or ABS. A more difficult challenge is to replace tetrabromobisphenol-A, the largest single brominated flame retardant, in electrical and electronic circuit boards. To date, only limited penetration of phosphorus flame retardants into this market has occurred.

The main driving force seems to be debatable environmental concerns about the halogens and heavy metals, although the halogens have other less-controversial shortcomings such as enhancement of smoke and problems of light stability and corrosivity. Stringent waste-disposal and recycling regulations, pending in Europe and Japan, and “eco-labeling” may be further factors in favor of phosphorus flame retardants and against halogens. Phosphorus flame retardants have not escaped environmentalist concerns, however. Obviously, in combustion, phosphorus compounds may produce phosphoric acids, which are moderate irritants (203) although in many formulations, a substantial part of the phosphorus remains in the char.

Trends in the research and development of phosphorus flame retardants have been in the direction of less volatile, less toxic, more stable compounds, and where feasible, in the direction of built-in phosphorus structures. At the same time, there are regulatory delays in the introduction of new compounds, so the existent phosphorus flame retardants are finding increased exploitation in the form of mixtures with synergists and adjuvants.

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