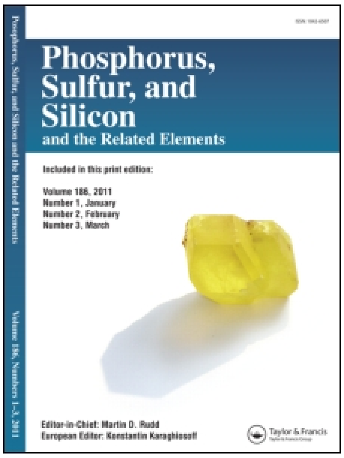

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A Survey of Recent Progress in Phosphorus-Based Flame Retardants and Some Mode of Action Studies

Edward D. Weil; Sergei V. Levchik; Maney Ravey; Weiming Zhu

To cite this Article Weil, Edward D. , Levchik, Sergei V. , Ravey, Maney and Zhu, Weiming(1999) 'A Survey of Recent Progress in Phosphorus-Based Flame Retardants and Some Mode of Action Studies', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 17 — 20

To link to this Article: DOI: 10.1080/10426509908546171
URL: http://dx.doi.org/10.1080/10426509908546171

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 17-20
Reprints available directly from the publisher
Photocopying permitted by license only

A Survey of Recent Progress in Phosphorus-Based Flame Retardants and Some Mode of Action Studies

EDWARD D. WEIL[a], SERGEI V. LEVCHIK[b], MANEY RAVEY[a] and WEIMING ZHU[a]

[a]*Polymer Research Institute, Polytechnic University, 6 Metrotech Center, Brooklyn, NY 11201 and* [b]*Institute for Physical Chemical Problems, Belarussian State University, 220080 Minsk, Belarus*

Phosphorus-based flame retardants have diverse modes of action, Aryl phosphates can have vapor phase action in styrenic polymers but also can contribute to producing a barrier layer. Tris(dichloroisopropyl) phosphate in a flexible polyurethane foam can serve as both a vapor-phase (probably physical) flame inhibitor in bottom ignition but contributes to formation of a barrier in top-down burning. Halogen/phosphorus and nitrogen/phosphorus synergism are not general but examples are known. Red phosphorus and ammonium polyphosphate interact with nylon 6 under burning conditions to produce phosphate esters and eventually chars. The cyclic neopentyl ester of nitrilotris(methylphosphonic acid) as a flame retardant in ethylene vinyl acetate copolymer can serve as a char-former and catalyst. Attempts to find synergists for phosphorus provide clues to improved combinations.

Keywords: flame retardants; phosphates; phosphonates; mode of action; flame; barrier

INTRODUCTION

This paper comprises an overview together with some brief reports on mode of action studies, with special attention to studies done by the coauthors.

Around 1810, Gay-Lussac reported flame retarding curtains with ammonium phosphate, which is still used on cellulosics where wash-durability is not needed. New discoveries have been made in recent years with ammonium phosphate. Marchand has shown that it can be converted thermally to phosphorus oxynitride, which may have utility as a flame retardant especially for nylons.[1] An organic variant of ammonium phosphate, ethylenediamine phosphate (from A&W) has been found to have self-intumescent properties useful in flame retarding polyolefins.[2]

organic variant of ammonium phosphate, ethylenediamine phosphate (from A&W) has been found to have self-intumescent properties useful in flame retarding polyolefins.[2]

Aryl Phosphates

One of the earliest organophosphates to be commercialized was tricresyl phosphate, used as a plasticizer and flame retardant originally in cellulose nitrate, then in cellulose acetate and vinyls. Some of these phosphates were later displaced by isopropylphenyl and tert-butylphenyl diphenyl phosphates. In recent years, the need arose for lower volatility phosphates for engineering thermoplastics, and tetraaryl arylene bisphosphates are now made for these applications.[3-5]

Newer developments in this area of diphosphates (actually oligomeric phosphates predominating in diphosphate) include tetraphenyl bisphenol-A diphosphate[4] and hydroxyphenyl arylene diphosphates.[5]

Mode of Action of Aryl Phosphate Flame Retardants

In engineering thermoplastics, vaporization of the aryl phosphates is a significant part of their action, with some possible interference with flame chemistry but with physical effects as well.[6] Condensed phase chemistry is also important where the aryl phosphate can interact with the pyrolyzing polymer and create a non-volatile barrier. There is evidence that the phosphates can interact with rearranged polyphenylene oxides and polycarbonates to form crosslinks as precursors to char barriers.[7-9]

Regression analyses show that combinations of volatile and less volatile phosphates contribute to flame retardancy with possible synergism, suggesting both vapor phase (physical and chemical) and condensed phase action.[10]

Phosphorus-Halogen Combinations

Tris (1,3-dichloro-2-propyl) phosphate (TDCPP), a leading flame retardant in flexible urethane foam, does not appear to act as a retardant when introduced directly into the flame of the burning foam. In bottom-up burning, it distills from the foam and gives vapor phase (probably physical) action. In top-down burning, residual TDCPP contributes to barrier formation.[11] This study provided no evidence regarding P/Cl synergism.

Phosphorus-halogen synergism is not a general phenomenon[12,13] but is measurable in some cases. For example, tris(2,4-dibromophenyl) phosphate outperforms the same % Br and % P in separate additives.[14]

Reactive Phosphate and Phosphonate Ester Oligomers

An ethylene methylphosphonate/methyl phosphate oligomer with 21% P and OH functionality was developed originally for aminoplast-impregnated paper products and is currently sold by Akzo Nobel for paper, textile and urethane uses.[15,17] It is made by reaction of P_2O_5 with dimethyl methylphosphonate to make a mixed methyl metaphosphate/metaphosphonate which is then treated with ethylene oxide. A more-recently introduced diol for flexible foam, made by similar chemistry starting with triethyl phosphate, is Clariant's OP 550, an 18% P diol which is made by reaction of P_2O_5 with triethyl phosphate and ethoxylation of the metaphosphate intermediate.[16]

Red Phosphorus and ammonium polyphosphate in nylon 6

Despite its own flammability, red phosphorus has been found to be a powerful flame retardant additive used in Europe for nylon.[17,18] Mode of action studies by Levchik *et al.* [19] have shown that in nylon 6, red phosphorus is oxidized during fire exposure to an acid which esterifies fragments of the nylon, leading to char with a coating likely to be polyphosphoric acid. A similar mode of action was shown for ammonium polyphosphate.[20]

Efficiency Improvement of Phosphorus Compounds by Synergists

No general synergist is known for phosphorus. Nitrogen-phosphorus synergism is often seen but not always.[12,13] Phospham, $(PN_2H)_x$, performed in nylon 4,6 like the same % P as red phosphorus.[21]

Where nitrogen compounds are found to be synergistic, they may be assisting phosphorylation, perhaps via P-N intermediates. We recently identified P-NH-P and/or P-NH_2 signals by xps in the char of ethylene-vinyl acetate copolymer flame-retarded by a synergistic phosphorus-nitrogen combination not originally having any P-N bonds.[22]

Synergism with phosphorus, but sometimes antagonism, has been found from various metal oxides and salts. For example, in a resorcinol diphosphate plus novolak system in PC/ABS, zinc borate, Fe_2O_3 and MoO_3 were helpful whereas Cu_2O, SnO, PbO and Bi_2O_3 were deleterious.[7] Combinations of phosphates and Sb_2O_3 are often antagonistic.[12,13,23] Levchik *et al.* have shown that talc benefits flame retardancy in an ammonium phosphate formulation in nylon 6, by forming silicophosphates which prevent volatility loss of phosphorus and add to the fire-barrier residue.[24] Scharf *et al.*[25] noted that in a phosphorus intumescent system, TiO_2 reinforced the char and helped flame retardancy, but SnO_2 made less coherent, less protective, char. Researchers at Lille found that a few % of a zeolite synergized an intumescent phosphate system, producing a less-brittle char.[26]

Char-forming Ingredients in Phosphorus-based Intumescent Systems

In flame retarding polyolefins or styrenic polymers which are poor char formers, it is generally necessary to add a char-forming ingredient to obtain efficient performance from a phosphorus additive. The char-forming chemistry of the pentaerythritol systems has been studied at Turin[27] and Lille[28]; the first step is phosphorylation of the polyol, followed by a series of eliminations.

We found a synergistic interaction of Monsanto's (Solutia's) tris-cyclic-neopentyl ester of nitrilotris(methylphosphonic acid (XPM-1000)[29] with melamine pyrophosphate in polyolefins and copolymers. XPM-1000 appears to be a char-former as well as contributing some catalysis.[22]

CONCLUSION

Further progress with phosphorus flame retardants can be expected, especially in view of multiple modes of action, and with insight into means for improving their action.

References

[1] Weil, E. D., Patel, N. and Huang, C.-H., in *4th Ann. BCC Conference on Flame Retardants*, Stamford, CT, May 18–20, 1993.

[2] M.. T. Huggard and P. S. White (to Albright and Wilson Americas Inc.), U.S. Pat. 5,137,937 (1992).

[3] D. A. Bright, S. Dashevsky, P. Y. Moy, and B. J. Williams, *J. Vinyl Add Tech.* **3**, 170 (1997).

[4] D. A. Bright, S. Dashevsky, P. Y. Moy, and K.-M. Tu, in SPE ANTEC, Atlanta, April 1998.

[5] H. Nishihara, S. Tanji and R. Kanatani, *Polym. J. (Tokyo)*(in English) **29**, 399 (1997), **30**, 163 (1998).

[6] J. Carnahan, W. Haaf, G. Nelson, G. Lee, V. Abolins and P. Shank, in *Proc. 4th Intl. Conf. Fire Safety*, Product Safety Corp., San Francisco, CA, 1979.

[7] E. A. Murashko, G. F. Levchik, S. V. Levchik, D. A. Bright and S. Dashevsky, *J. Fire Sciences*, in press (two articles)(1998).

[8] A. B. Boscoletto, M. Checchin, L. Milan, P. Pannochia, M. Tavan, G. Camino and M. P. Luda, *J. Appl. Polym. Sci.* **67**, 2231 (1998).

[9] K. Takeda, F. Amemiya, M. Kinoshita and S. Takayama, *J. Appl. Polym. Sci.*, **64**(6), 1175 (1997).

[10] E. D. Weil, W. Zhu and N. Patel, *Polym. Degrad. and Stability* **54**, 125 (1996).

[11] M. Ravey, I. Keidar, I., E. D. Weil and E. M. Pearce, *J. Appl. Polym. Sci.* **68**, 217, 231 (1998).

[12] E. D. Well, in *Flame Retardancy of Polymeric Materials*, Vol. **3**, W. C. Kuryla and A. J. Papa, eds., Marcel Dekker, Inc., New York, 1975, pp. 186–243.

[13] E. D. Weil, in *3rd Annual BCC Flame Retardancy Conference*, Stamford, CT, May 1992.

[14] J. Green, in *6th Annual BCC Conference on Flame Retardancy, Recent Advances in Flame Retardancy of Polymeric Materials*, Stamford, CT, May 23–25, 1995.

[15] E. D. Weil, R. Fearing and F. Jaffe, *J. Fire Retardant Chem.* **9**, 39 (1982).

[16] M. Sicken, M. (to Hoechst AG), U. S. Pat. 5,608,100 (1997).

[17] E. D. Weil, chapter 14 in *Handbook of Organophosphorus Chemistry*, R. E. Engel, ed., M. Dekker, Inc., New York, 1992, pp. 683–738.

[18] E. D. Weil, in *Encyclopedia of Polymer Science and Engineering*, Vol. **11**, J. Kroschwitz, Ed., Wiley, NY, pp. 96–126 (1988).

[19] G. F. Levchik, S. V. Levchik, G. Camino, and E. D. Weil, in *6th European Meeting on Fire Retardancy ofPolymeric Materials*, Lille, Sept. 24–6, 1997.

[20] S. V. Levchik, G. Camino, L. Costa and G. F. Levchik, *Fire & Materials* **19**, 1 (1995).

[21] E. D. Weil and N. Patel, N., *Fire& Materials* **18**, 1 (1994).

[22] W. Zhu, E. D. Weil and S. Mukhopadhyay, *J. Appl. Polym. Sci.* **62**, 2267 (1996).

[23] P. Moy, *Plastics Engineering*, Nov. 1997, 61.

[24] S. V. Levchik, G. F. Levchik, G. Camino and L. Costa, *J. Fire Sciences* **13**(1), 43 (1995).

[25] D. Scharf, R. Nalepa, R. Heflin and T. Wusu, in *Proc. Int. Conf. on Fire Safety*, **15**, 306 (1990).

[26] S. Bourbigot, M. Le Bras, R. Delobel and J.-M. Tremillon, *J. Chem. Soc., Faraday Trans.* **92**(18), 3435 (1996).

[27] G. Camino, G. Martinasso and L. Costa, *Polym. Degrad. Stabil.*, **27**, 285 (1990).

[28] S. Bourbigot, M. Le Bras, L. Gengembre and R. Delobel, *Appl. Surface Sci.*, **81**, 2997 (1994), **120**, 15 (1997), and references therein.

[29] F. E. Paulik and C. R. Weiss (to Monsanto), U. S. Pat. 5,276,066 (1994).