

NOTE

Flexible Polyurethane Foam. III. Phosphoric Acid as a Flame Retardant

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Received 15 March 1999; accepted 24 March 1999

Key words: polyurethane foam; fire retardant; phosphoric acid

INTRODUCTION

Haloalkyl phosphate esters are well-established, effective fire retardants for polyurethane foam.¹ However, in spite of the many studies performed on such systems (a review of the literature is given in ref. 2), little is certain about the mode of action of these materials. One of the more frequently postulated mechanisms is based on the thermal decomposition of these esters to phosphoric acids, which are claimed to be the actual retardants.^{3–9} This postulate is based on two conjectures, that these phosphates decompose thermally to yield free phosphoric or polyphosphoric acids, and that these are effective fire retardants for polyurethane foams.

Regarding the first conjecture, although the alkyl phosphates do tend to yield the free acids on thermolysis,¹⁰ the haloalkyl phosphates tend to condense to haloalkyl polyphosphates, apparently via a different, lower temperature mechanism.^{11,12} In the case of tris(1,3-dichloro-2-propyl) phosphate, free phosphoric acid was not detected in the pyrolysis zone under the flame of a burning polyether-based flexible polyurethane foam containing this material.¹³

Regarding the second conjecture, in spite of the frequent references suggesting that phosphoric acid is the active species when organophosphates act as fire retardants in urethane foams,^{3–9} the actual efficacy of phosphoric acid in this substrate does not seem to have ever

actually been subjected to experimental verification. The latter was the objective of the work reported here.

EXPERIMENTAL

The foam used was a polyether-based water-blown commercial type of flexible polyurethane.¹⁴ It was cut into 100-mm long bars of square cross sections, 15 mm on a side.¹³ These bars were coated with acid using solutions containing various concentrations of 85% ortho-phosphoric acid in acetone. After evaporation of the solvent, the bars were positioned vertically, ignited at their top, and allowed to burn down to self-extinguishment (or total consumption).

RESULTS

Phosphoric acid was found to be quite an effective (although, of course, impractical for direct application) fire retardant for the polyether-based flexible polyurethane foam examined. A linear relation was found between the initial acid content of the foam and the length of burn prior to self-extinguishment. The results are given in Table I as well as in Figure 1.

This leads to the relation:

$$\text{Length of Burn (mm)} = 96 - 17$$

$$\times \% \text{H}_3\text{PO}_4 \text{ (85\% in Foam); } r = 0.97$$

Table I Length of Burn as a Function of H_3PO_4 Content of 100-mm Long Bars of Foam Coated with Various Concentrations of Acid

| % H_3PO_4 in the Foam (as 85% H_3PO_4) | Length of Burn (mm) |
|--|------------------------|
| 0.2 | Totally consumed |
| 0.9 | 82 |
| 1.6 | 73 |
| 3.0 | 45 |
| 3.1 | 32 |
| 4.9 | 18 |

Volatility of phosphoric acid (in the form of P_2O_5) becomes significant above about 700° .¹⁵ Even if such temperatures were achieved in these small, dwindling flames, it would seem unlikely that much of the phosphorus would vaporize out of the pyrolysis zone, which is undoubtedly cooler than the flame. It, therefore, seems fairly safe to assume that most, if not all, of the acid will be retained in the pyrolysis zone. The concentration of the acid in this zone can, therefore, be expected to rise as the bar of foam burns down. A linear relation between the initial acid concentration and the length of burn is, therefore, not unexpected. This also

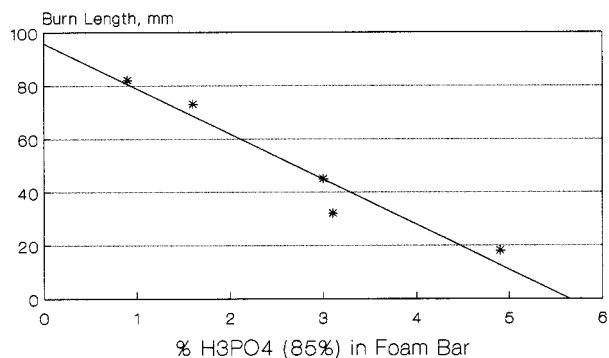


Figure 1 Length of burn as a function of H_3PO_4 content of foam bar.

indicates that the retarding activity of the acid occurs largely in the pyrolysis zone, that is, in the condensed phase.

Figure 2 gives the thermogravimetric (TGA) curve of the nonretarded foam superposed on that of a foam coated with 5.6% H_3PO_4 (85%). It is clear from these curves that the presence of the acid reduces the thermal stability of the polyurethane, which indicates that a reaction occurs between the acid and the polyurethane. The finding that this foam is soluble in hot 85% phosphoric acid is further confirmation of such a reac-

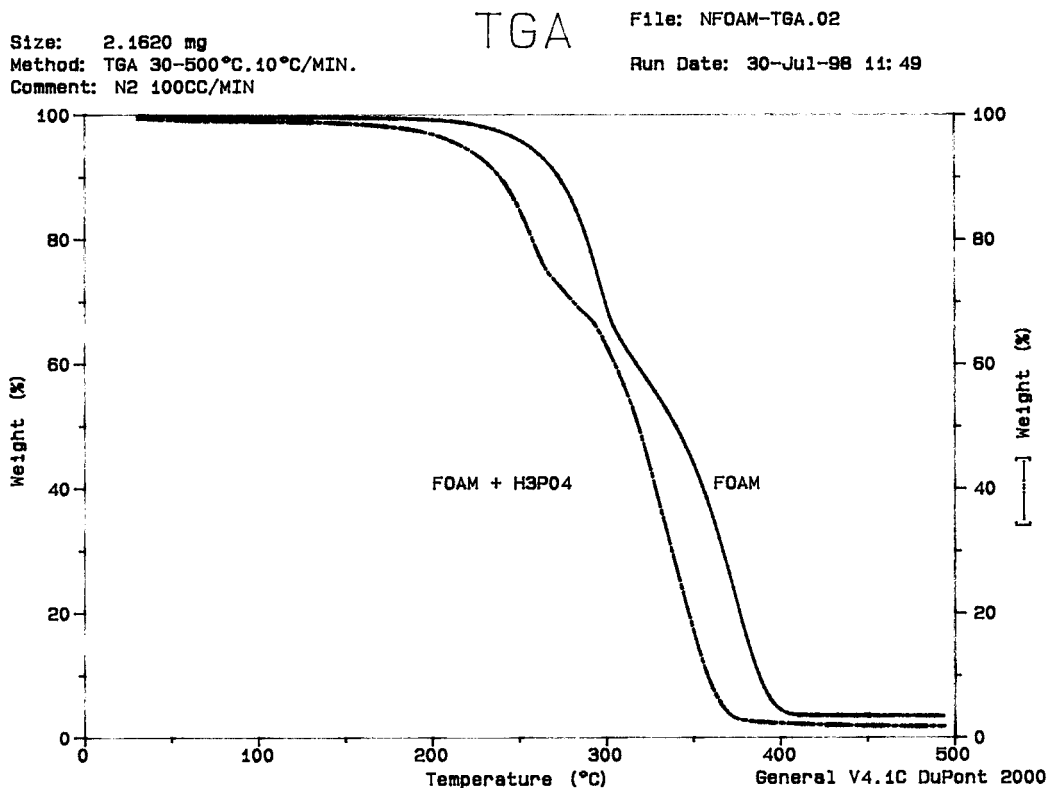


Figure 2 Thermograms of the foam and the phosphoric acid treated foam.

tion; the foam is crosslinked and in order for it to dissolve, the crosslinks have to be broken.

To the best of our knowledge, this is the first time that the oft-proposed hypothesis that phosphoric acid acts as a fire retardant for polyurethanes³⁻⁹ has been confirmed experimentally. As the haloalkyl phosphates do not release the free acid on pyrolysis,¹¹⁻¹³ it would seem unlikely that their mode of action is based on a mechanism involving the acid. It is, however, possible that the reaction of these esters, as well as the acid, with the polyurethane substrate, both lead to the formation of the same material, which is the actual retarding agent or intermediate.

For the foam, the authors thank Barbara Williams, Akzo Research Laboratories, Dobbs Ferry, New York. Part of this study was done on M.R.'s sabbatical at the Polytechnic University's Polymer Research Institute.

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