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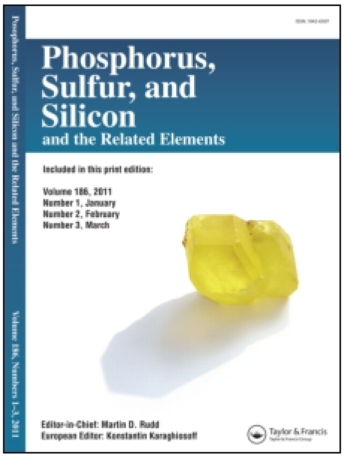

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FLAME RETARDANT ACTIONS OF TRIS(1,3-DICHLORO-2-PROPYL) PHOSPHATE IN FLEXIBLE URETHANE FOAM

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Abstract The flame retardant action of tris(1,3-dichloro-2-propyl) phosphate (TDCPP, widely used to flame-retard flexible urethane foam) appears to result in part from vapor phase physical action and in part from condensed-phase barrier-forming action.

INTRODUCTION

Flexible polyurethane foams, made typically with toluene diisocyanate and aliphatic polyols, often must pass flame retardancy requirements. An economical flame retardant, made on a large scale for this application, is tris(1,3-dichloro-2-propyl) phosphate (hereinafter designated as TDCPP). It is available from Akzo-Nobel as FYROL® FR-2 and from Albright & Wilson as ANTIBLAZE® 195. TDCPP is a liquid containing 49.1% Cl and 7.2% P, made from phosphorus oxychloride and epichlorohydrin.[1] The dichloropropyl groups are almost all 1,3-dichloro-2-isopropyl.

TDCPP is essentially a permanent flame retardant. The advantage of Fyrol FR-2 is that it is chemically very inert and practically does not interact with the tertiary amine and tin compounds used to catalyze the foam formation.

Curiously, despite the major use of TDCPP for over 30 years, little or no study has been made of its mode of action. There were some related studies on tris(2-chloroethyl) phosphate[2,3] and tetrakis(2-chloroethyl) ethylene diphosphate[4] in flexible foams. Briefly, the study on tris(2-chloroethyl) phosphate showed that most of the compound volatilized during burning but some reacted in; the flame retardant mode of action remained rather unclear. The more recent study on tetrakis(2-chloroethyl) ethylene diphosphate pointed to volatilization of the additive, and a gas phase mode of action together with some drip enhancement.[4]

RESULTS AND DISCUSSION

Evidence that all or most of the TDCPP was not bound during the foaming reaction was shown by the fact, not too surprising, that it could be extracted by methylene chloride.

Thermogravimetric analysis (TGA) at 20 /min. and an isothermal (230-5 C) large scale version thereof seemed to show loss of about all of the TDCPP prior to urethane decomposition. However, a fault of TGA as a means for studying flammability is that the rate of heating in TGA is orders of magnitude slower than in the burning process,[5] likewise, the surface to volume ratio is orders of magnitude higher in TGA than under real burning conditions.

Measurement of the fate of the TDCPP during actual burning did not give a simple result - surface tar analysis showed that much of the TDCPP vaporized but some remained behind in a chemically converted form. This still left open the question of the principal mode by which TDCPP flame retards. The vapor phase mode could be significant or could represent wastage of the additive. Furthermore, the vapor phase action could be physical or chemical or both.

A classical test of whether a flame retardant works in the condensed phase or in the flame zone is to generate a curve of oxygen index *vs.* concentration and then to compare this curve to a similarly run "nitrogen oxide index" curve *vs.* concentration.[6] The theory is that if the oxygen index *vs.* concentration and N_2O index *vs.* concentration curves have very different slopes or shapes, then the retardant must be acting as a flame chemistry inhibitor. Conversely, if the curves of oxygen index and N_2O index are very similar, then the retardant probably does not work by means of an effect on the flame chemistry. What we found was that the curves of oxygen index and nitrogen oxide index were quite similar. This is evidence against flame chemistry involvement. However, we want to point out that evidence against involvement in the flame chemistry does not logically prove that the retardant functions in the condensed phase. If the choice of oxidant has little effect and flame chemistry therefore appears not to be involved, there still remains the possibility of a vapor phase mechanism due to heat capacity, endothermic pyrolysis and gas-dynamic effects, independent of the flame chemistry.[7-10]

Further experiments to ascertain whether vaporized TDCPP can act as a flame inhibitor at first seemed to point to no vapor phase action at all. Injection of TDCPP into a flame from a burning non-flame-retarded foam using a syringe or vaporizing TDCPP from a wire loop surrounding the flame showed no evident sign of extinguishment.

However, we than found several simple demonstrations which indicate that there is a vapor phase fire-retardant action specifically when the TDCPP enters from the dark (preheat) zone of the flame. One mode of this demonstration was conducted as follows: small bars of non-flame-retarded foam were carefully painted just on their sharp edges with the TDCPP. Thus, no TDCPP was inside the bars and we estimate that 95% of the lateral area of the bars also did not have TDCPP on it. To have any effect, it would have to evaporate from the treated edges. When these bars are held nearly vertically and ignited from the bottom up by a burner flame, the bars either self-extinguished or burned transitorially with an unstable flame. accompanied by a cloud of white smoke. Thus, when TDCPP is fed into the preheat (dark) zone of the flame, it does show a flame retardant effect. The importance of dark zone (preoxidative zone) endothermic processes in flame retardancy has only occasionally been noted in the literature.[11]

We propose that the effect is caused (1) by endothermic evaporation, absorption of sensible heat by vapors, endothermic pyrolysis (cracking) of the vapors, (2) by the decoupling of heat transfer from the flame as a result of the evident thickening of the dark zone, and (3) partly by the gas dynamic effect of an outgoing poor fuel simultaneously diluting the fuel, slowing the combustion reaction, and shortening the retention time in the combustion zone (the Damköhler number effect[12]). The phosphoric or condensed (*i.e.* dehydrated) phosphoric acid in the whitish smoke could be demonstrated by the classical phosphomolybdate blue color test. It represents nöt only a heat sink but the smoke could also serve as a site for radical recombination.

The question of the possible condensed phase action must now be considered. A tar on the surface of the self-extinguished TDCPP foam was always observed, accompanied by a small amount of sticky flexible char, but never a continuous char layer, contrary to what is usually seen in flame-retarded rigid urethane foams. The infrared spectrum of the tar shows it to be much like the original polyol, with only trace poorly resolved absorption in the carbonyl region characteristic of urethane and urea structures. The infrared spectrum of this tar was surprisingly close to that of the tar from nitrogen-quenched non-flame-retardant foam made with the same polyol. Any phosphorus component present was too weak for us to detect by infraréd.

We had considered the possibility that pyrolysis of TDCPP at or near the surface of the foam might produce a surface film of phosphoric or polyphosphoric acid, which in some other flame retardant systems has been shown to be part of the flame retardant mode of action.[13] However, applying a pH indicator to the self-extinguished surface of a TDCPP-retarded foam showed a weakly-basic surface. Elemental analysis of the tar showed 1.02% Cl and 0.31% P, corresponding to an approximately a 3:1 atom ratio of Cl to P, whereas TDCPP has 6:1 Cl to P.

A ^{31}P nmr analysis of the tar showed that the phosphorus was present as neutral phosphate and as salts of mono- and dialkyl phosphate esters, plus a weak but characteristic signal for a 5-membered cyclic phosphate ester.[14]

The limited amount of reaction which has occurred in the surface of the foam can be reasonably related to the chemistry analogous to reactions reported in the literature for other 2-haloalkyl phosphates, namely cyclization to 5-membered ring phosphates.[15,16]

From analysis of vapors from bulk pyrolysis of TDCPP foam, as others have found from pyrolysis of TDCPP itself,[17] we did identify the 1,2,3-trichloropropane byproduct. The 5-membered ring phosphates readily undergo ring opening. The products, instead of being P-N-bonded, are derived from ring opening with the nucleophile attacking at one of the ring carbons. This chemistry has been demonstrated in the case of the reaction of a tertiary amine with a cyclic 5-membered ring phosphate.[18] We consider that the most likely structures are arylaminopropyl acid phosphates, although zwitterionic structures cannot be excluded.

The question of the flame retardant effect of this surface tar was then examined. It was easy to establish that the surface tar from self-extinguished TDCPP foam had some moderate flame retardant action. By wiping it as smoothly as possible from self-extinguished surfaces of TDCPP foams onto bars of non-flame-retarded foam, self-extinguishing character in the horizontal position was produced at about 110% add-on, based on the weight of the bar. Significantly, a substantial part of the action of this tar was attributable to the polyol component of the polyurethane, since applying a 130% add-on of the phosphorus-free polyol itself produced flame retardancy. The surface tar from non-flame-retardant foam, although mostly polyol by infrared, was less effective, requiring about a 200% add-on to get flame retardancy. The TDCPP tar was observably *less flowable* when produced in massive amounts by continuous application of a burner, and did have some greater amount of coherent black somewhat flexible charry skin. We think that this material may have been responsible for a more coherent and obstructive tar/char layer when TDCPP is present.

Unlike some other polyurethane foam compositions where the flame retardants appear to enhance melt flow,[4] this appears *not* to be the mode of action of TDCPP in flexible foam; to the contrary, TDCPP actually *increases* melt viscosity.

CONCLUSION

Our final conclusion is that the flame retardant effect is produced by a combination of two actions: one, a vapor phase probably dark-zone action caused by endothermic effects and the outward flow of poor fuel, and a second action, the enhancement of the flame retardant barrier character of the tar, probably by physical obstruction of the surface. Both actions relate to the heat and mass flow effects of flame retardants.

Phosphorus flame retardants in general have a surprising number of possible flame retardant modes of action, encompassing several physical and chemical modes, occurring in both the condensed phase and the vapor phase modes, for all of which there are demonstrable examples.[19,20] The present case of TDCPP in flexible urethane foams exemplifies at least two such modes. Quantitative heat and mass balance studies would be needed to assess the relative contributions of each mode.

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