Flame Retardant Release from Fabrics During Laundering and Their Toxicity to Fish

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It has been estimated that the use of flame retardant plastics and textiles will grow 35 to 45% a year through 1975--from 800 million pounds in 1970 to 3.5-4.5 billion pounds by 1975 (Chem. and Eng. News, 1971). Flame retardants include many chemical classes such as organic compounds containing phosphorus, sulfur, halogens and nitrogen and inorganic compounds of antimony, boron and others (LYONS 1970). One of the methods used to flame retard textiles is by topical application of the compound. To achieve satisfactory flame resistance, some retardants must be applied at rates equally up to 35% of the weight of the fabric itself (Chem. and Eng. News, 1971). This method is largely applicable only to cotton fabrics.

Organophosphorus compounds are being used to a great extent for this application (BAITINGER 1972). The present study was undertaken to determine if appreciable quantities of these latter compounds might be released from fabrics during laundering and to study their toxicity to fish.

Experimental

Three organophosphorus compounds which are commercially available as flame retardants for textiles (LE BLANC 1973) were studied. They were tris (2,3-dibromopropyl) phosphate (I), Pyrovatex CP (N-methylol dimethyl phosphonopropionamide) (II) and THPOH [tetrakis (hydrosymethyl) phosphonium hydroxide] (III). Fabrics were also obtained which had been commercially treated with these flame retardant finishes. They included a polyester flannel treated with I and cotton cloth treated with either II or III. Three by six inch portions of each was heated in distilled water at 140° F for 20 minutes to simulate a laundering operation. The water solutions were then evaporated to dryness, the residue was hydrolyzed by refluxing with 3 ml of concentrated hydrobromic acid for 4 hours and phosphorus was determined spectrophotometrically as the molybdenum blue complex. (In a study of the effect of the time of refluxing with hydrobromic acid on the completeness of hydrolysis it was found that phosphorus was recovered from these compounds within 4 hours). Non-phosphate detergents, soaps, or common emulsifiers were not used during the simulated laundering operation since it was not possible to find any which did not contain appreciable quantities of phosphorus as impurities.

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The toxicity of these compounds to goldfish (Carassius auratus) was studied. Six goldfish, about 3 inches in length, were placed in each of several glass fish tanks containing 20 liters of well water through which filtered air was continuously bubbled. Four ml of a solution containing 5 mg per ml of I in acetone, II in methanol and III in water were placed in separate tanks with the fish. This resulted in a concentration of 1 ppm of the compounds in the water. Fish were exposed to 4 ml of the solvents themselves (acetone and methanol) in separate tanks. Fresh water containing the respective flame retardant was used to replace that in the tanks when the latter became cloudy (every 3 to 4 days) from the accumulation of metabolic products. The fish were fed daily by addition of a few granules of a commercial goldfish food. The fish were maintained at room temperature in this manner and observed as regards abnormal behavior or death.

Results and Discussion

Based on phosphorus analysis, concentrations of I, II and III were released during the washing step up to 10 micrograms per square inch of fabric. This concentration was found to vary for a given fabric. The cause of this may be the known variations in thickness of flame retardant finishes in different areas of a given sample of fabric. Similar quantities of phosphorus were again released when a given sample of fabric was washed a second and third time. It was realized that some of the measured phosphorus might have been due to traces of inorganic phosphorus in the fabric. An attempt was made to study this possibility by modifying the analytical method so as to obviate inorganic phosphorus impurities. Compound I was soluble in benzene. In several trials the water in which the fabric coated with I had been washed was extracted with two portions of benzene. (The wash water was cloudy and this cloudiness, presumably due to the release of the water insoluble flame retardant (I), passed into the benzene layer upon partitioning). The benzene extracts were combined, evaporated and the residue remaining refluxed with hydrobromic acid and analyzed. It was found that similar amounts of phosphorus were recovered from the benzene extracts thus indicating that the phosphorus was organic in origin.

As described above, the toxicity of I, II and III to goldfish was studied. The data showing the extent of fish survival is illustrated in Figure 1. All of the fish died during the first 5 days of exposure to I. The fish appeared to swim in a completely disoriented manner prior to death. This compound was the only halogenated phosphorus compound. Its anticholinesterase activity was found to be about 16% of that of an equimolar concentration of the insecticide, Tetram (O,O-diethyl-S-(beta diethylamino)ethyl phosphoro thiolate) whereas

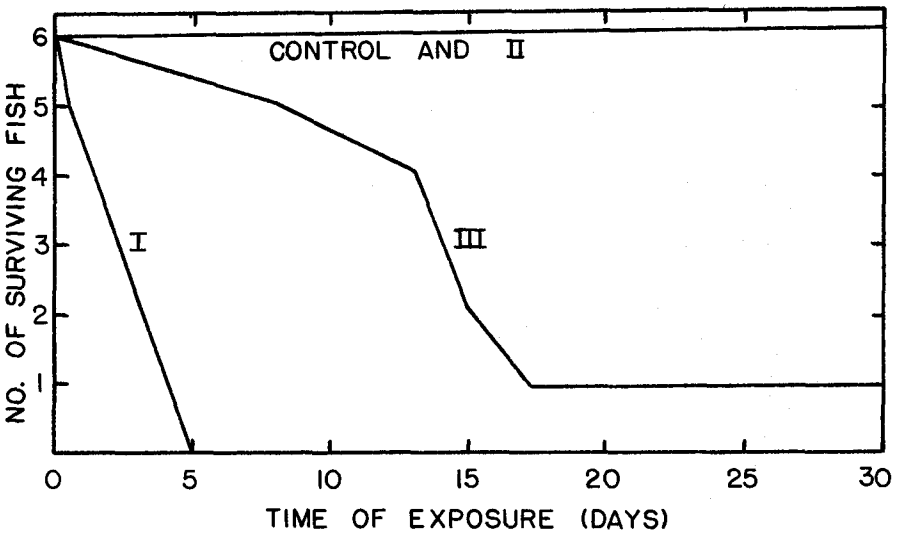

Figure 1. Survival of goldfish exposed to 1 ppm of flame retardant compounds.

II showed an anticholinesterase activity about 25% of that of Tetram. (The anticholinesterase activity of Tetram at a solution concentration of 3 X 10^{-5}M was 0.68 optical density units per minute at 412 mμ). The anticholinesterase activity of III could not be measured due to interference with the colorimetric method (ELLMAN et al. 1961). All of the control fish and those exposed to II survived well and appeared normal throughout the 30 day exposure time. The toxicity of III was intermediate between that of I and II. Perhaps I was more toxic to the fish than II even though its anticholinesterase activity was less because it was more efficiently absorbed by them owing to its greater lipoid solubility.

A concentration of 1 ppm of the compounds was chosen for fish exposure based on the following considerations. A typical home laundering may involve washing the equivalent of six sheets, each 72 X 81 inches, in a total volume of about 30 gallons of water. If all of the sheets were coated with a flame retardant and 10 micrograms per square inch of the compound was removed during laundering a concentration of about 6 ppm would result in the combined wash and rinse water.

There are many other factors which would have to be evaluated before one could rightfully assess the significance of this work. The use of detergents during laundering might accentuate the removal of flame retardants. Whether the rate of release of flame retardants changes when a fabric is repeatedly laundered is unknown. The presence of uncoated

fabrics in the items being laundered might decrease the water concentration of the released compounds by readsorption. The presence of detergents and a flame retardant or mixture of different flame retardants in water as from a typical home laundering operation might either enhance or reduce the overall toxic effect on fish. The species of fish, water temperature, dissolved oxygen content, exposure time and a host of other environmental factors may also greatly affect toxicity. Undoubtedly the greatest factor is the extent to which the laundry water is either purified in a sewage plant or septic system prior to its final release into the environment or the extent of dilution of it by the receiving waters. Owing to the extent of future usage predicted for flame retardants it is important that losses of these compounds during detergent laundering of treated fabrics be studied. This will be possible as specific analytical methods are developed for them.

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