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Fabric Release, Fish Toxicity and Water Stability of the Flame Retardant, Fyrol FR-2

V. D. Ahrens[1], G. A. Maylin[2], J. D. Henion[2], L. E. St. John, Jr.[3], and D. J. Lisk[3]
[1] *College of Home Economics, University of Delaware, Newark, Del. 19711,* [2] *Equine Drug Testing Research Program, Veterinary Diagnostic Laboratory, Cornell University, Ithaca, N.Y. 14853,* [3] *Pesticide Residue Laboratory, Department of Food Science, Cornell University, Ithaca, N.Y. 14853*

Tris (2,3-dibromopropyl) phosphate (TDBPP) was the major flame retardant having been used on about half of all children's polyester and polyester blend sleepwear up to 1977. It has been estimated that up to 20 million garments with a retail value of nearly $80 million were stocked for sale at that time. TDBPP was soon shown to be released from wetted fabrics in concentrations highly toxic to fish and to rapidly undergo dehydrobromination in water (MAYLIN et al. 1977). TDBPP was also found to be mutagenic by the test of AMES (1971). Other substitute flame retardants have now begun to enter the market. A compound which is now being used on a large scale on children's polyester and polyester blend sleepwear is Fyrol FR-2 (Tris (2,3-dichloropropyl) phosphate). In the work reported, the rate of release of Fyrol FR-2 from children's polyester sleepwear was studied and compared to that of TDBPP. The toxicity of Fyrol FR-2 released from such wetted garments to fish and the stability of this compound in water was also investigated.

EXPERIMENTAL

The rate of release of Fyrol FR-2 from children's 100% polyester sleepwear was determined as a function of the number of launderings and compared to that of TDBPP released from such a polyester garment. One hundred percent polyester fabric untreated with any flame retardant was used as the control. The characteristics of the fabrics studied are listed in Table 1. The entire pajama was laundered by the AATCC test method 135-1973 of the American Association of Textile Chemists and Colorists (1976) using soft water (34.4 ppm hardness) and 60 g of a phosphate detergent containing 3% of equivalent phosphorus.

There has been speculation that if fabrics without a flame retardant finish are laundered with flame retardant garments, a portion of the flame retardant released during the laundering may be absorbed by the unfinished fabric. A separate laundering trial was therefore conducted in which a pair of TDBPP-finished polyester pajamas was laundered successively with polyester fabric having no flame retardant finish.

Prior to and periodically after specific numbers of successive launderings, 5 circular discs, 2.9 cm in diameter, were removed from the fabric or fabrics at random for analysis. Each disc, ranging in weight from 0.1 to 0.15 g, was analyzed individually for

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the quantity of flame retardant remaining based on its total chlorine or bromine content. The method of analysis consisted of burning the entire disc in an oxygen-filled combustion flask (LISK 1960) and absorption of the evolved HCl or HBr gas in 100 mL of water. Determination of chloride or bromide in the solution was then made by the colorimetric method of BERGMANN and SANIK (1957).

An investigation was made of the possible toxic effects to fish from Fyrol FR-2 released into their water from submerged polyester sleepwear. Six goldfish (Carassius auratus) about 7.5 cm long were placed in a glass tank containing 20 L of well water (electrical conductivity, 290 micromhos/cm; 20° C). A 38 x 64 cm area of unlaundered or laundered section of Fyrol FR-2-finished polyester sleepwear was immersed in their water and the effect on the fish was noted with time. The concentration of Fyrol FR-2 was determined in the water using gas chromatography. A column, 1.0 m x 4 mm i.d., packed with 10% DC-200 on Gas Chrom Q and operated at 196° C was used. The retention time of Fyrol FR-2 was 7.3 min. Two tenths ng of the compound produced a 10% full scale deflection using a Tracor Ni-63 detector.

The stability of pure Tris (2,3-dichloropropyl) phosphate (Fyrol FR-2) added to water and that of the compound when released into water from submerged Fyrol FR-2-finished polyester sleepwear was studied. Five ppm of Fyrol FR-2 was dissolved in water and allowed to stand for 24 h. An 11.5 x 16.5 cm section of Fyrol FR-2-finished fabric was immersed in 1.0 L of water and allowed to stand for 24 h. A 10-mL portion of water from each of the above test samples was then extracted with two, 2-mL poritons of diethyl ether. The ether solutions were analyzed by gas chromatography-mass spectrometry (Hewlett Packard Model 5992A operated in the electron impact mode). The gas chromatographic column was 1.0 x 2 mm i.d. and packed with Ultra-bond (KARASEK and HILL 1975) (0.28% Carbowax 20M on 100/120 mesh acid-washed Chromosorb W). Following sample injection, the column was operated isothermally at 150° C for 2 min and was then programmed up to 220° C at the rate of 8°/min. A Finnigan Model 1015 mass spectrometer operated in the conventional chemical ionization mode using methane as the reagent gas was employed to study the stability of Fyrol FR-2 in water by solid probe sample introduction.

RESULTS AND DISCUSSION

Figure 1 shows the rate of release of Fyrol FR-2 and TDBPP from the respectively finished polyester sleepwear. To serve as the control fabric, the ppm of "apparent" flame retardant calculated as equivalent TDBPP resulting from successively laundering 100% polyester containing no flame retardant (see Table 1) is also shown at the bottom of Figure 1. The coordinates in Figure 1 are the average values of analysis of the 5 randomly selected replicate discs of fabric taken after any particular number of launderings. The rate of release of the two flame retardants during 20 launderings did not differ greatly when expressed as a percentage loss (after 20 launderings) of the original load of the flame retardant on the fabric. The percentage loss for TDBPP and Fyrol FR-2 were,

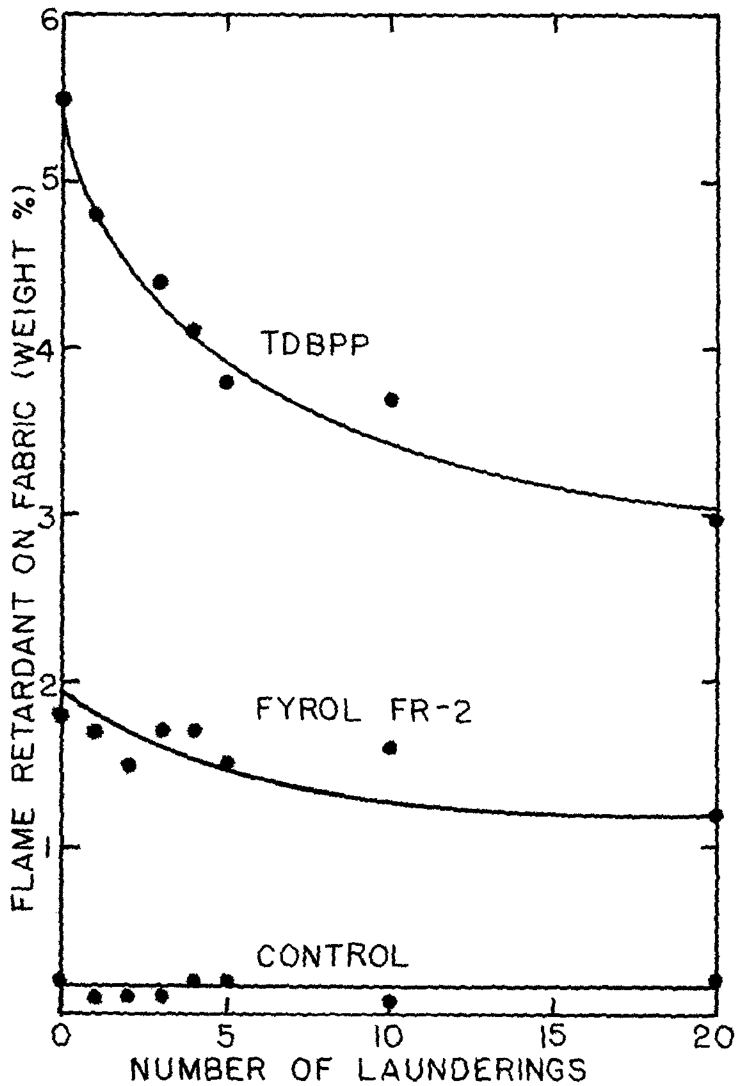

Figure 1. Rate of release of flame retardants from 100% polyester pajama fabrics as a function of the number of launderings (see text).

respectively, 46 and 37. No absorption of released TDBPP by unfinished polyester fabric occurred when the two fabrics were laundered together 20 times successively.

When the 38 x 64 cm portion of unlaundered Fyrol FR-2-finished polyester sleepwear was immersed in their water, the goldfish became progressively more sluggish and all died within 3 h. When this water was analyzed a concentration of 30 ppm of Fyrol FR-2 was found. The above fabric was removed from the fish tank, laundered once and then immersed again in a new tank of water with fish. None of the fish exhibited any toxic symptoms during 96 h of ex-

TABLE 1
Description of the fabrics studied

Construction	Fiber/yarn	Flame retardant finish	Fabric weight (oz/yd^2)[a]
Jersey knit	100% polyester spun yarn	Fyrol-FR-2	6.7
Plain weave flannelette	100% polyester spun yarn	TDBPP	4.9
Plain weave	100% polyester spun yarn	none	4.8

[a] One oz/yd^2 = 33.9 g/m^2.

posure. Apparently sufficient flame retardant was available to dissolve from the immediate surface of the fabric to cause rapid toxicity to the fish. One laundering, however appeared to effectively remove this surface reservoir of the compound. Laundering a fabric with hot water, detergent and agitation followed by hot water rinses would expectedly be far more efficient in removal of the compound than merely dipping the fabric in water at room temperature without agitation. Fyrol FR-2 has a water solubility of about 100 ppm and it was shown earlier that 5 ppm of the compound in water was lethal to goldfish within 24 h (ELDEFRAWI et al. 1977). It is less toxic to fish, however, than TDBPP (ELDEFRAWI et al. 1977).

Fyrol FR-2, whether added to water as a standard or having diffused out of the respectively finished polyester fabric when immersed in water appeared to be stable in water after 24 h. This was indicated by the fact that the molecular weight of the compound was confirmed by chemical ionization-mass spectrometry by observing the quasi molecular ion as the base peak at m/e = 429. Also no quasi molecular ion for the dehydrochlorination product of Fyrol FR-2 was observed at m/e = 392. TDBPP was previously reported to undergo dehydrobromination in water (MAYLIN et al. 1977). Possibly since chlorine forms a stronger (LOVERING and LAIDLER 1960) bond with carbon than bromine does, Fyrol FR-2 is more stable.

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