Toxicity to Fish of Flame Retardant Fabrics Immersed in Their Water. Part I

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The use of flame retardants in textiles, home furnishings, building materials and other applications is estimated to amount to several billion pounds annually (CHEM. AND ENG. NEWS, 1971). Flame retardants at concentrations of at least 3% of the weight of the fabric may typically be used. Childrens sleepwear sold in this country must, by law, be flame retardant. By far, organophosphorus compounds are used most extensively as flame retardants for sleepwear (LE BLANC, 1975). Generally, nitrogen or bromine in the molecule improves the flame resistance offered by phosphorus (REEVES, 1972).

Tris (2,3-dibromopropyl) phosphate (TDBPP) is the flame retardant used in virtually all polyester fabric produced in the United States today for childrens sleepwear. In an earlier study (GUTENMANN and LISK, 1975) it was found that up to 10 micrograms of TDBPP per square inch of polyester fabric was released when the fabric was subjected to a simulated laundering in water without detergent. One ppm of pure TDBPP added to water containing goldfish killed all fish within 5 days, presumably by its demonstrated ability to inhibit cholinesterase (GUTENMAN and LISK, 1975). In the work reported it has been shown that immersion of laundered or unlaundered, flame retardant fabric used in childrens sleepwear in water containing goldfish results in release of TDBPP, metabolism of the compound and dramatic fish death.

EXPERIMENTAL

Fabrics treated with the following flame retardants were studied: Antiblaze 19 (a mixture of cyclic phosphonates), Fyrol 76 (an oligomeric vinyl phosphonate), Pyrovatex CP (N-methylol dimethyl phosphonopropionamide), TDBPP (tris(2,3-dibromopropyl) phosphate), and THPOH (tetrakis (hydroxymethyl) phosphonium hydroxide).

The effect of immersing portions of such flame retarded fabrics in water containing goldfish was investigated. Six goldfish (Carassius auratus) about 3 inches long, were placed in a glass tank containing 20 liters of well water (electrical conductivity, 290 micromhos/cm, temperature 20° C). A 7 x 15 inch area of an unlaundered or home-laundered fabric which had been commercially treated with a specific flame retardant was immersed in the water and the effect on the fish was noted with time.

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Mass spectrometric analysis (electron impact mode using 70 electron volts and an emission current of 500 microamperes) for TDBPP in water was conducted using a Finnigan Model 1015 gas chromatograph mass spectrometer with a Systems Industries Model 150 data system. Twenty five ml of the water in which the TDBPP-finished fabrics had been immersed was extracted with diethyl ether. The ether was concentrated by rotary evaporation and a portion of the ether solution was evaporated to dryness in a glass capillary tube and introduced via the solids probe, direct inlet which was heated from ambient to 100° C over a 5-minute period.

RESULTS AND DISCUSSION

Table 1 lists the observed fish mortality as a function of the immersion time of a specific flame retardant fabric in their water. It is obvious that the TDBPP-finished fabrics consistently caused fish mortality. Death was preceded, in turn by hyperactivity, fading of their gold color, anorexia, bulging eyes, head and body, extended scales, disoriented swimming, sluggishness, rapid gill movement and finally attempts to occupy a position close to the air sparger in the tank. The symptoms were identical when the fish were maintained in water to which 1 ppm of pure TDBPP was added. Certain of these symptoms would tend to support the reported anticholinesterase activity of TDBPP (GUTENMANN and LISK, 1975). The ultimate cause of death from anticholinesterase agents is generally believed to be asphyxiation (O'BRIEN, 1960). Histopathological examination of the fish showed subcutaneous and intramuscular edema and focal necrosis in liver and kidney. When fish showing bulgy body parts were removed and placed in fresh water they became lethargic, would not eat and finally died with a few days.

It is evident that when the various TDBPP-finished fabrics were laundered the time required for fishkill generally increased indicating that TDBPP was being released from the fabric more slowly. It is also possible that laundering makes TDBPP progressively less available owing to slow deposition of carbonate deposits on the fibers. In this regard, when the polyester flannel, polyester broadcloth and polyester knit (the third listed fabric) were removed after fishkill and immediately immersed in tanks containing fresh water and 6 new fish the times required for death of all of the fish were, respectively, 96, 118 and 70 hours. It was considered that toxicity may also have been caused by hydrolysis in water of TDBPP to 2,3-dibromopropanol (DBP). However, exposure of goldfish to 1 ppm of DBP in water for 7 days had no observable effect even though 1 ppm of TDBPP in water killed all of the goldfish in 5 days (GUTENMANN and LISK, 1975).

Based on total phosphorus analysis about 75 to 140 micrograms of TDBPP were released per square inch of immersed fabric surface after the various 100% polyester fabrics (unlaundered) had been submerged in the tanks of water (without fish) for 24 hours. The magnitude of flame retardant release

Table 1. Toxicity to goldfish of flame retardant chemicals released from commercially treated fabrics immersed in their water.

Flame retardant finish	Fabric	No. of launderings prior to immersion*	No. of hours of immersion	No. of dead fish**
TDBPP	100% polyester flannel***	0	36	6
TDBPP	100% polyester (broadcloth or nonwoven)***	0	24	6
TDBPP	100% polyester knit****	0	64	6
TDBPP	100% polyester knit****	0	24	6
		1	24	6
		2	53	6
		3	76	6
TDBPP	50% polyester-50% triacetate knit****	0	96	6
		1	144	6
TDBPP	60% polyester-40% flame retarded acetate knit***	0	96	2
		1	168	1
TDBPP	50% polyester-50% cotton gingham***	0	96	6
		1	168	6
Antiblaze 19	100% polyester gingham***	0 or 1	168	0
Fyrol 76	50% polyester 50% cotton double knit***	0 or 1	168	0
Fyrol 76	100% cotton (flannel or flannelette)***	0 or 1	168	0
Pyrovatex CP	100% cotton flannelette***	0 or 1	168	0
THPOH/NH_3*****	100% cotton (broadcloth or denim)***	0 or 1	168	0
none	100% polyester (flannel, knit or nonwoven)***	0 or 1	168	0
none	90% acetate-10% nylon knit***	0 or 1	168	0
none	50% polyester-50% cotton broadcloth***	0 or 1	168	0
none	100% cotton (flannel, denim or muslin)***	0 or 1	168	0

* Full agitation for 12 minutes in 16 gallons of well water at 71° C containing 1 cup of granular carbonate detergent and 1/2 cup Calgon followed by a rinse in 16 gallons of cold water.

** A total of six fish were exposed

*** Fabrics obtained from commercial mills

**** Childrens pajamas purchased locally

***** Ammonia is added to neutralize the weakly acidic phosphonium ion.

Table 2. Table of relative abundances (ra) in the mass spectrum of authentic TDBPP.

m/e	ra*	m/e	ra	m/e	ra
38	3.5	199	14.	534	5.0
39	100.	200	7.0	535	5.0
40	8.8	201	16.	536	6.8
41	93.	202	3.3	537	5.3
47	2.2	203	8.0	538	5.0
55	4.5	216	2.0	539	2.0
57	48.5	217	35.	540	1.5
65	1.5	218	5.0	612	2.0
92	1.6	219	36.	613	6.0
93	11.	259	1.5	614	9.3
94	2.2	280	2.0	615	14.
95	7.5	281	3.5	616	19.
98	3.1	334	5.0	617	20.
99	24.	335	4.0	618	19.
105	3.0	336	6.0	619	15.
106	3.2	337	6.5	620	11.
107	4.4	338	5.0	621	5.0
108	2.8	339	3.2	622	2.1
118	16.	414	8.0	694	1.5
119	65.	415	8.5	695	2.9
120	7.0	416	21.	696	3.5
121	58.	417	22.	697	5.5
136	9.5	418	22.	698	5.0
137	56.	419	17.	699	5.5
138	4.0	420	8.0	700	3.5
145	1.5	421	5.5	701	3.5
198	4.0	533	2.5	702	1.5

* Relative abundances less than 1% were omitted.

would expectedly vary depending on the solubility of the compound in the fibers, the weight and physical texture of the fabric and the weight percent of the compound which may vary considerably over various portions of a given fabric and operating conditions during the flame retarding process. Mass spectrometric analysis of the water indicated that within 24 hours TDBPP underwent loss of HBr following its release from fabrics into water or when pure TDBPP was added to water. Hydrolysis or photolytic degradation of TDBPP may have occurred with production of 2-bromo-2-propenyl bis(2,3-dibromopropyl)

Table 3. Table of relative abundances (ra) in the mass spectrum of an ether extract of water in which unlaundered 100% polyester pajama material commercially flame retarded with TDBPP had been immersed for 24 hours.

m/e	ra*	m/e	ra
38	2.5	201	6.3
39	86.	203	4.0
40	7.6	217	18.
41	100.	219	21.
42	1.3	281	1.8
47	2.0	335	1.5
55	4.0	337	1.5
57	52.	339	1.7
79	6.4	414	3.5
80	9.0	415	3.0
81	6.5	416	9.4
82	12.	417	7.3
93	7.2	418	8.8
95	5.5	419	5.8
98	1.4	420	3.8
99	35.	421	2.0
106	1.5	421	2.0
107	2.0	536	2.7
108	1.5	538	1.6
118	2.1	613	2.2
119	56.	614	5.0
120	3.5	615	6.0
121	50.	616	10.
122	1.5	617	8.3
135	1.3	618	10.
136	1.5	619	6.3
137	54.	620	5.0
138	3.0	621	2.1
139	1.3		
199	7.0		

* Relative abundances less than 1% were omitted.

phosphate. This was indicated by the disappearance of the characteristic molecular ion (M/E = 698) in the mass spectrum of authentic TDBPP and appearance of the molecular ion of a new species at M/E = 618 when 1 ppm of TDBPP had remained in water for 24 hours (12 hours each of daylight and darkness). The relative abundances versus m/e for these mass spectra are shown in Tables 2 and 3. It is therefore possible that this metabolite is the piscicidal agent.

There were no visible toxic effects in any of the fish exposed up to 7 days to the fabrics finished with flame retardants other than TDBPP (Table 1). Whereas flame retardation of cellulosic materials typically involves the formation of chemical bonds between the flame retardant and cellulose hydroxyl groups or polymer deposition within cellulose (BAITINGER, 1972), a compound such as TDBPP may commonly be "melted" into the polyester fibers after topical application of the compound as an emulsion to the fabric. Release of TDBPP by diffusion out of fibers upon immersion of the treated fabric in water would expectedly be easier than with flame retardants bonded to cellulosic fabrics. Chemical bonding of flame retardants such as Fyrol 76, Pyrovatex CP and THPOH to cellulosic fabrics and the lower toxicity of these compounds (and Antiblaze 19) as compared to TDBPP probably accounted for fish survival.*

SUMMARY

A number of commercial and candidate flame retardants were studied with regard to their toxicity to fish when released from fabrics immersed in their water. Immersion of laundered or unlaundered flame retardant 100% polyester or polyester blend fabrics used in children's sleepwear in water containing goldfish resulted in release of the anticholinesterase flame retardant TDBPP (tris(2,3-dibromopropyl) phosphate) and death of all fish within 24 hours. TDBPP undergoes loss of HBr in water and production of a metabolite.

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*reported in Part II of this study.