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Cotton Made Flame-Resistant with Bromine-Containing Phosphonitrilates in Combination with THPC Resins

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Abstract

A permanent-type flame retardant based on a bromoform adduct polymer of allyl phosphonitrilate in combination with THPC resin has been developed for use with cotton fabrics. The combination flame retardant is applied to fabrics from aqueous emulsion using conventional textile finishing equipment. The flame retardant is very efficient; 8-oz. twill and sateen are made highly flame-resistant with as little as 13% resin add-on.

A GOOD permanent-type flame retardant for cotton should possess several desirable properties or attributes. No one factor alone can make it a completely satisfactory flame retardant. It should be durable to laundering with either the soap and soda-type wash or with "synthetic" detergents; it should make the textile glow-resistant, which in some cases may be as important as flame resistance; it should not detract significantly from the desirable properties of the fabric; it must not cause dermatitis or be toxic in any way to the person wearing garments treated with it; and it should be efficient as a flame retardant, making the textile adequately flame- and glow-resistant with a low weight increase. Heretofore, permanent-type flame retardants have been commercially acceptable for some uses, even if they increased the weight of the fabric by as much as 50%. The use of THPC * resins [4] has been an important step in reducing the weight increase necessary for adequate flame resistance.

The amount of flame resistance needed in a fabric is dependent upon end use. For some uses, a textile that passes a mild test, such as the Commercial Standards flame test [1], is sufficiently flame-resistant. Many textiles must pass a more severe test, such as the vertical flame test [6], before they are considered adequately flame-resistant. Then for some uses one might want the fabric to be so flame-resistant that it will not burn when a narrow strip is held in an open flame.

THPC resins penetrate cotton fibers. Since only a limited amount can go inside a fiber, surface deposition occurs with high concentration of resin-forming solutions causing loss in strength and flexibility. Therefore, the maximum practical degree of flame resistance that can be obtained with THPC resins is limited. Although most fabrics can be made sufficiently flame-resistant with the resin to pass the vertical flame test, only loosely constructed fabrics such as blanket material or heavy belting materials fail to burn when narrow strips are exposed to an open flame. It has not been possible to make some light-weight or tightly constructed fabrics sufficiently flame-resistant to pass the vertical flame test without imparting excessive stiffness.

The degree of flame resistance of a particular cotton fabric is dependent upon the amount of flame retardant either in the fibers or on the surface of the fibers. Therefore, the degree of flame resistance of THPC-resin-treated fabric should be increased by depositing an efficient flame-retardant polymer on the surface of THPC-resin-treated fibers. If the polymer were flexible, the fabric would not be made excessively weak and stiff. This idea was first tried by applying 2, 3-dibromopropyl phosphonitrilate [2] to a THPC-resin-treated fabric. The fabric was extremely flame-resistant. Narrow strips would not burn. A number of other surface-coating flame-retardant polymers were tried in combination with

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* Tetrakis (hydroxymethyl) phosphonium chloride, $(HOCH_2)_4PCl$.

THPC resins. A bromoform adduct polymer of allyl phosphonitrilate was found to be most efficient. The purpose of the present paper is to report a combination flame retardant based upon THPC resin and a bromoform adduct polymer of allyl phosphonitrilate.

Method

The mechanics of finishing with the combination flame retardant are essentially the same as that for THPC resin alone [4]. The main difference is in the preparation of the treating solution. The THPC-resin-forming solution is made and then the emulsion-containing brominated phosphonitrilate is added to the solution. An emulsion is formed that is stable for several hours, but for optimum effects it should be used immediately after preparation.

The amount of the flame retardant needed on a particular fabric will depend upon the weight and construction of the fabric. The required amount can be established by a preliminary or pilot application. The wet pickup which controls the final resin add-on for the particular fabric should also be established by pilot run. The amount deposited on the textile material can be controlled by varying the concentration of the flame retardant in the emulsion. It is recommended that a tight squeeze roll setting be used for padding the fabrics.

Materials

The preparation of bromoform adduct polymer of allyl phosphonitrilate (PNE-$CHBr_3$) in aqueous emulsion is described in this issue by Hamalainen and Guthrie [3]. The emulsion used most and found to be satisfactory for combining with THPC-resin-forming solution is the emulsion containing 30 to 31% PNE-$CHBr_3$ made from 1 part PNE (allyl phosphonitrilate) per 0.64 part bromoform. Emulsions containing both THPC-resin-forming materials and PNE-$CHBr_3$ are prepared by adding the required amount of PNE-$CHBr_3$ emulsion to the THPC-resin-forming solution. The final emulsions containing both flame retardants are referred to as THPC-PNE-$CHBr_3$ emulsions.

Procedure

No one emulsion is suitable for all textiles, but an adequate emulsion can be prepared by varying the amount of water in the typical emulsion described here.

First, dissolve 124 g. THPC in 124 g. water and add 18 g. triethanolamine to the solution. Then dissolve 78 g. trimethylolmelamine and 78 g. urea in 328 g. water and combine the two solutions to form a clear THPC-resin-forming solution. Stir in 250 g. of an emulsion containing 30% of the bromine-containing phosphonitrilate. This combined emulsion is used in the finishing process. It can be used as is or diluted with water. The fabric is padded through the emulsion using two dips and two nips and then dried at 80° to 90° C. It is cured 5 to 6 min. at 140° to 145° C., washed to remove salts and unused reagents, and dried by any convenient method. A loop dryer is suggested to minimize tension on the fabric during the drying and curing cycles. The drying time will depend upon the weight and construction of the fabric, lightweight material drying in 3 to 4 min., and heavy material requiring up to 12 min. If the fabric is thoroughly dry, curing can be completed in 4 min. for lightweight fabrics and in about 7 min. for heavier fabrics. About 5 to 6 min. are required for 8-oz. twill and sateen.

The drying and curing oven should be well vented to remove formaldehyde and other fumes. A textile softener may be applied in the final rinse. A softener usually improves both the hand and tear strength.

Most Suitable Concentration of the Flame Retardants

Emulsions containing various amounts of each flame retardant were applied to 8-oz. twill and sateen in order to determine the optimum ratio of each in the combination which produced the most flame resistance with the least weight add-on and which was most durable to laundering. In these experiments the THPC-resin-forming solution contained 15.8% THPC, 10% trimethylolmelamine, 10% urea, and 2.5% triethanolamine (TEA). The bromine-containing emulsion contained 30% PNE-$CHBr_3$. The treating emulsions were made to contain 50 to 90 parts THPC-resin-forming solution and 10 to 50 parts PNE-$CHBr_3$ emulsion. For example, a 90:10 ratio was made by combining 90 g. of the THPC-resin-forming solution with 10 g. of the PNE-$CHBr_3$ emulsion. In all cases the fabrics were padded through the solution using two dips and two nips, dried 5 to 6 min. at 85° C., cured 5 to 6 min. at 140° C., and then washed and dried.

The finished fabrics were given the strip flame test ([5] p. 529) and the standard vertical flame test

[6] before laundering and again after they had been laundered 15 times according to Federal Specifications CCC-T-191b, Test No. 5556. The results summarized in Table I show that with an 85–15 emulsion combination a resin add-on of 17% was necessary on 8-oz. twill for it to pass both the vertical flame test and the 180° strip flame test after 15 launderings. With the same emulsion an add-on of 18% was required for the sateen. (The resin add-on values are apparent and not real since they were obtained by weight changes in the equilibrated fabrics before and after resin treatment and not by analysis. Changes in moisture regain would alter the values somewhat.) With an 80–20 emulsion combination, 8-oz. twill and sateen required 16% resin add-on to withstand 15 launderings. About 15.5% resin add-on was the lowest found satisfactory on twill or sateen to withstand 15 launderings and retain its flame resistance. This was obtained with the 70–30 emulsion combination. The 50–50 combination was slightly less effective than the 70–30 combination. At the other extreme, fabric treated with the 90–10 emulsion was just slightly more flame-resistant than when THPC-resin-forming solution was used alone. With the use of either the 80–20 or the 70–30 emulsions, resin add-on as low as 13% was sufficient for both twill and sateen to pass both flame tests before laundering.

Treatment of Fabric

In order to obtain samples large enough for more complete laboratory evaluation, two pieces of sateen (8.5 oz.) about 18 in. wide and 10 yd. long were treated with the emulsions described below.

Emulsion X

A THPC-PNE-$CHBr_3$ emulsion was prepared by mixing 542 g. of 31% PNE-$CHBr_3$ adduct emulsion with 1381 g. of THPC-resin-forming solution containing 18.1% THPC, 11.5% trimethylolmelamine, 11.5% urea, and 2.9% TEA. This is about a 75–25 emulsion combination.

TABLE I. Effects of THPC-PNE-$CHBr_3$ Emulsions on Flame Resistance of 8-oz. Twill and Sateen

		Treating solution composition			Flame resistance			
					Original fabric		After 15 launderings†	
Sample designation	Fabric type	THPC resin-forming solution (wt. %)	PNE-$CHBr_3$ emulsion (wt. %)	Resin add-on (%)	Char length (in.)	Angle*	Char length‡ (in.)	Angle*
1	Twill	85	15	17.1	3.5	180	3.8	180
2				15.1	4.2	180	4.9	135
3				12.9	3.7	135	BEL	90
4	Sateen	85	15	18.5	3.2	180	3.7	180
5				16.5	3.3	180	3.9	135
6				14.2	3.8	180	3.8	90
7	Twill	80	20	17.5	3.6	180	3.0	180
8				14.1	4.0	180	3.4	135
9				11.4	4.1	180	4.5	135
10	Sateen	80	20	18.5	3.2	180	3.0	180
11				15.6	3.2	180	3.8	180
12				14.1	3.8	180	3.7	135
13	Twill	70	30	16.4	3.4	180	3.7	180
14				14.5	3.6	180	4.4	180
15				13.1	3.4	180	4.9	135
16	Sateen	70	30	16.3	3.1	180	3.7	180
17				14.4	3.4	180	3.7	135
18				12.8	4.8	180	4.9	90

* Angle at which 1-cm. strip fails to support combustion when held at angle indicated and ignited at end with match ([4], p. 529).
† After 15 launderings with a detergent as described in Federal Specifications CCC-T-191b, Test No. 5556.
‡ A.A.T.C.C. Standard Test Method 34-52.

TABLE II. Test Results on THPC-PNE-$CHBr_3$ Emulsion-Treated Fabrics before Laundering

Test	Direction of test	Untreated control	Fabric with 18.0% resin	Fabric with 15.7% resin
Elmendorf tear (lb.)	Warp	11.5	5.8	6.2
	Filling	A.C.*	8.8	8.6
Trapezoid tear (lb.)	Warp	13.3	8.4	9.1
	Filling	19.3	13.0	14.3
Breaking strength (lb.)	Warp	110.7	114.8	106.4
	Filling	137.5	126.8	121.0
Stiffness ($\times 10^4$ in. lb.)	Warp	17	65	57
	Filling	16	38	38
Abrasion flex (cycles)	Warp	1225	454	430
	Filling	1786	662	520
Flat (cycles)	—	267	768	580
Crease resistance (% recovery)	Warp	63	59	66
	Filling	51	53	52
Char length (in.)	Warp	—	3.1	3.6
Afterglow (sec.)	—	—	None	None

* A.C. = above capacity of machine.

Emulsion Y

After emulsion *X* had been used to treat one piece of sateen, 10 g. of water was added to each 90 g. of the emulsion remaining to make emulsion *Y*.

A 10-yd. sample of sateen was treated in emulsion *X* and then another 10-yd. sample was treated with emulsion *Y*. In each case the fabrics were padded using two dips and two nips, dried 5 min. at 85° to 90° C., cured 7 min. at 144° C., washed and dried. Emulsion-X-treated fabric contained 18% resin add-on and emulsion-Y-treated fabric contained 15.7% resin add-on. The major part of both of these samples was softened with Triton X-400 * by padding the resin-treated fabric through 4% solution of Triton X-400 to a wet pickup of 50% and then drying.

Properties of the Flame-Resistant Fabric

The results shown in Tables II and III indicate that the tear strength and flex abrasion are the two properties affected most by the flame retardant. However, the amount of tear-strength loss is dependent upon the fabric treated. That is, some fabrics lose considerable tear strength, as exemplified by the 8-oz. sateen, while other materials lose little or no strength. For example, 8-oz. twill generally retains 100% Elmendorf tear strength after softening.

* Mention of trade names is for information and convenience only and does not imply their endorsement over materials not mentioned.

The two pieces of sateen had a good hand and were extremely flame-resistant before and after 15 launderings. Chemical analyses on portions before and after 15 launderings with Igepon T*, showed that an average of 15% of the bromine and nitrogen and 14% of the phosphorus was removed. The flame resistance was less durable to alkaline soap washes. About 25% of the flame retardant, based on analysis, was removed by boiling a piece of the treated fabric in an aqueous solution containing 1% soap and 0.2% sodium carbonate.

Summary

A combination flame retardant based upon THPC resin and a bromoform adduct polymer of allyl phosphonitrilate has been developed. Fabric is treated by padding it through a mixture of the flame retardants, then drying and curing at an elevated temperature. The emulsion of the flame retardants is produced by adding a bromoform-adduct-polymer emulsion to a THPC-resin-forming solution.

The THPC resin penetrates the fibers, and the adduct polymer is deposited on the surface. This combination is especially valuable for treating medium- and lightweight fabrics which are most difficult to make highly flame-resistant. These fabrics can be

TABLE III. Test Results on THPC-PNE-$CHBr_3$ Emulsion-Treated Fabrics after 5, 10, and 15 Launderings

Test	No. of times laundered	Direction of test	Untreated control	Fabric with 18% resin	Fabric with 15.7% resin
Elmendorf tear (lb.)	5	Warp	12.9	6.5	7.1
		Filling	A.C.*	11.1	10.2
	10	Warp	11.7	7.7	7.3
		Filling	A.C.	10.1	9.3
	15	Warp	9.8	7.2	8.2
		Filling	12.5	10.0	9.3
Trapezoid tear (lb.)	5	Warp	13.6	9.0	9.2
		Filling	20.8	12.2	13.2
	10	Warp	13.6	9.0	9.0
		Filling	21.7	13.5	12.8
	15	Warp	12.5	9.1	9.2
		Filling	21.5	13.1	12.0
Char length (in.)	5	—	—	3.4	3.1
	10	—	—	3.6	3.3
	15	—	—	3.7	3.7
Afterflame in strip test (sec.)	5	—	—	0	0
	10	—	—	0	0
	15	—	—	0	0

* A.C. = above capacity of machine.

made so flame-resistant that ½-in. strips of the fabric will not burn when held in the vertical position and ignited at the bottom. The combination flame retardant is more efficient than the THPC resin; that is, fabrics can be made more flame-resistant with less weight add-on.

The flame-resistant finish withstands at least 15 launderings with Igepon T. Treated fabrics have a good hand and appearance. Tear-strength retention is excellent with 8-oz. twill but is only fair with 8-oz. sateen.

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