

Review of Three Recent Developments in Flame-Retardant Treatments for Cotton

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Bromine-Containing Phosphonitrilates as Flame Retardants* for Cotton

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Abstract

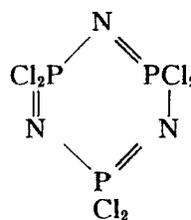
Bromine-containing derivatives of phosphonitrilic chloride were investigated as possible durable flame retardants for cotton fabrics. These, including brominated allyl phosphonitrilate, 2, 3-dibromopropyl phosphonitrilate, and the bromoform adduct polymer of allyl phosphonitrilate, were applied to cotton fabrics as polymeric products from organic solvent or from aqueous emulsions. Evaluation tests on tear strength and the durability of the flame resistance to laundering were made.

SOME of the durable flame retardants for cotton fabric that have been proposed in recent years are polymeric materials containing phosphorus, along with either nitrogen or bromine, or both. It seemed possible that flame retardants of this type might be developed from phosphonitrilic chloride (PNCl_2)_n, as a starting material. This compound itself has been shown to act as a flame retardant. For example, Kauth [4] suggested the use of its polymers to make flame-resistant electrical insulation. The chief disadvantage of the polymeric phosphonitrilic chlorides as flame retardants for cotton fabrics is the ease with which they hydrolyze to yield acids that degrade the cellulose. Consequently, it was thought that some derivatives of the phosphonitrilic chloride in which the chlorine was replaced by other groups should be tried. This paper reports experiments on the preparation and application of flame retardants made by replacing most of the chlorine of phosphonitrilic chloride with bromine-containing groups.

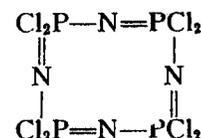
Preparation and Application of Phosphonitrilate Flame Retardants

The phosphonitrilic chloride used to prepare the esters was made by reacting phosphorus pentachloride with ammonium chloride by refluxing in tetrachloroethane as described by Schenck and Roemer [6]. The product used was a mixture containing the trimer and tetramer, which have the structures shown below.

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Trimer



Tetramer

The trimer probably predominated in the mixture. Some of the later experiments were made with the pure trimer, obtained from a commercial company.

The esters described below were formed by substituting $\text{CH}_2=\text{CHCH}_2\text{O}-$ and $\text{CH}_2\text{BrCHBrCH}_2\text{O}-$ groups for most of the chlorine atoms. Chemical analyses of the various ester products formed, see Table I, were in approximate agreement with the assumption that not more than one chlorine atom of the trimer or tetramer remained after esterification. The analytical values indicated that the products were complex mixtures, and that some polymerization and hydrolysis had occurred.

Allyl Ester

The allyl ester, abbreviated PNE, was made by reacting the phosphonitrilic chloride with sodium allylate by a procedure similar to that used by Smith and Elliott [7]. The product was a yellow syrup. Details of a typical preparation follow.

Forty-nine grams of sodium metal was sliced thin and suspended in $1\frac{1}{2}$ liters of benzene in a 3-liter flask equipped with stirrer, reflux condenser, and separatory funnel. Allyl alcohol, 275 ml., was added dropwise with stirring until the sodium had gone

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into solution. Heating on a water bath was necessary to force the reaction to completion. After cooling, 120 g. of the mixed trimeric and tetrameric PNCl_2 dissolved in 250 ml. of benzene was added dropwise with stirring and with external cooling to moderate the exothermic reaction which took place. The reaction mixture was set aside for several days to allow the salt to settle. The supernatant liquid was decanted and the salt layer filtered and washed once with fresh benzene. The combined benzene solutions were flash distilled under reduced pressure leaving a residue of yellowish syrupy liquid which was stored under vacuum for an additional two days. The final weight of the crude PNE was 118 g. (yield 74% of theory).

The crude PNE contained traces of salt and allyl alcohol. It could be purified by dissolving in a solvent such as carbon tetrachloride, washing with dilute aqueous calcium chloride solution, drying over anhydrous calcium chloride, and then stripping off the solvent.

The PNE was brominated or reacted with bromoform and the products applied to fabrics as described below. The PNE itself also showed some flame-retardant action when applied to cotton fabric.

Brominated Allyl Ester

The allyl ester product was brominated to various degrees by adding liquid bromine to PNE dissolved in benzene. The products, viscous liquids obtained by evaporation of the solvent, could be dissolved in benzene and emulsified in an aqueous solution of polyvinyl alcohol. Fabric was padded with these emulsions, air-dried until free of solvent, cured for 10 min. at 140°C ., washed and dried. An 8-oz. twill sample, processed with a 34% emulsion of partially brominated PNE, had a 12.7% dry add-on and was highly flame-resistant.

2, 3-Dibromopropyl Ester

This product was made by reacting the phosphonitrilic chloride with 2, 3-dibromopropanol in pyri-

dine. Details of its preparation and application to cotton fabric have been described in a patent by Hamalainen [3]. Application of the 2, 3-dibromopropyl ester from acetone solution to 8-oz. twill gave good flame resistance that was durable to boiling in soap and soda. Since application from solvent would have practical disadvantages, the ester was emulsified by dissolving in chloroform and dispersing in water containing polyvinyl alcohol, forming a 31% emulsion. An 8-oz. twill sample with a 16.7% add-on was prepared by padding and air-drying. It showed good original flame resistance but failed in the standard vertical test after five detergent launderings. Attempts to obtain durability by curing resulted in lowered tear strength.

Since fabric treated with the 2, 3-dibromopropyl ester product had a very rubbery hand which would be objectionable for many uses, work on improving this by combination with crease-proofing resin treatments was explored. The hand and flame resistance of the fabric was improved, but tear strength was adversely affected.

Bromoform Adduct of the Allyl Ester

The bromoform adduct of the allyl ester PNE was prepared by a procedure similar to that described by Frick and Weaver [1, 2] for the preparation of a flame retardant made by telomerization of triallyl phosphate with bromoform. Details of a typical preparation follow.

The following materials were used.

- 15.9 g. PNE
- 10.2 g. bromoform
- 30.0 g. of 2% polyvinyl alcohol in water
- 1.5 g. sodium bicarbonate
- 0.5 g. potassium persulfate
- 28.6 g. water

The PNE and bromoform were added to the reaction flask and stirred until homogeneous. The polyvinyl alcohol solution was then added with continuous stirring, followed by the sodium bicarbonate dissolved in most of the water and the potassium

TABLE I. Analyses of Various Phosphonitrilate Products

Type of product	Percentage						Mol. wt.
	N	P	Br	Cl	H	C	
Phosphonitrilic chloride (trimer)	12.1	26.7		61.2			348
Allyl ester	9.27	22.0		4.94	5.69	38.6	772
Partially brominated allyl ester	4.56	10.8	43.9	0.45	2.83	19.3	2115
Fully brominated allyl ester	3.67	8.3	50.7	0.28	2.47	17.6	1946
2,3-Dibromopropyl ester	4.54	10.0	47.5	2.83	2.16	14.9	2281

TABLE II. Evaluation of Fabric Treated with PNE-Bromoform Adduct Flame Retardant

Wt. ratio PNE/CHBr ₃	Add-on (%)	Flame tests		Tear strength retention (%)		Chemical analyses (%)		
		Angle* (deg.)	Char length† (in.)	Elmendorf	Trapezoid	N	P	Br
1:0.96	12.9	180	4.8	74	83	0.65	1.37	4.19
1:0.64	11.5	180	4.7	81	94	0.64	1.38	3.52
1:0.32	10.1	135	4.6	84	89	0.65	1.38	2.15
PNE only	8.5	90	4.7	119	84	0.71	1.50	—

* Angle at which 1-cm. strip fails to support combustion when held at the angle indicated and ignited at the end with a match ([5], p. 529).

† A.A.T.C.C. Standard Test Method 34-52.

persulfate added with the rest of the water. The mixture was stirred for 1 hr., holding the temperature at 80° to 85° C. and the pH between 6 and 7 with additional bicarbonate, if necessary. Heating longer than 1 hr. usually resulted in a curdy emulsion that was unsatisfactory for application to fabric.

The emulsion just described, containing 30% by weight of the monomers, was padded on 8-oz. twill using two dips and two nips to a wet add-on of about 69%. The fabric was then dried for 10 min. at 110° C., cured for 6 min. at 140° C., washed and air-dried. The dry add-on was about 11%. The char length in the standard vertical test by A.A.T.C.C. Standard Test Method 34-52 was 3.9 in., and this was maintained through six detergent launderings by the method described in Federal Specifications CCC-T-191b, Test No. 5556. The trapezoid tear strength was essentially unchanged by the treatment,

while the Elmendorf tear strength was 77% of that of the untreated fabric. The six launderings did not appreciably alter the tear strength.

A series of adduct emulsions were prepared having different ratios of PNE to bromoform and applied to 8-oz. twill. A control treatment with PNE alone was also applied. The evaluation data for these fabric samples are given in Table II. The results show that a very high degree of flame resistance, as indicated by the strip test [5], may be obtained with about 12% dry add-on of the PNE-bromoform adduct.

The possibility of using chloroform instead of bromoform in the emulsion telomerization of PNE was explored, but the fabrics produced did not pass the standard vertical test owing in part to a low add-on of 7% or less. Analyses of the fabrics for chlorine indicated little reaction with the chloroform.

TABLE III. Comparison of Bromine-Containing Phosphonitrate Flame-Retardants on 8-oz. Twill

Treatment	Add-on (%)	Laundering	Tear strength retained		Flame tests	
			Elmendorf (%)	Trapezoid (%)	Angle‡ (deg.)	Char length§ (in.)
Partially brominated PNE	12.7	None	56	65	180	4.3
		Alk. soap*	70	63	0	B.E.L.
		Detergent†	54	67	180	5.3
2,3-dibromopropyl ester	14.8	None	79	90	180	5.5
		Alk. soap	103	124	45	B.E.L.
		Detergent	82	123	180	7.0
PNE-CHBr ₃ Adduct Wt. ratio 1:0.96	14.7	None	77	90	180	3.9
		Alk. soap	107	116	135	B.E.L.
		Detergent	84	109	135	5.4

* Boiled for 3 hr. in water containing 1% soap and 0.5% sodium carbonate.

† After 15 launderings with a detergent followed by fluoride sour as described in Federal Specifications CCC-T-191b Test No. 5556.

‡ Angle at which 1-cm. strip fails to support combustion when held at angle indicated and ignited at end with match ([5], page 529).

§ A.A.T.C.C. Standard Test Method 34-52.

Comparison of Bromine-Containing Phosphonitrilate Flame Retardants

A comparison of the partially brominated PNE, the 2, 3-dibromopropyl ester, and the bromoform adduct of PNE was made on 8-oz. twill. The partially brominated allyl ester was prepared by adding liquid bromine to PNE in benzene in an amount sufficient to react with half of the allyl groups and applied from 34% emulsion. The 2, 3-dibromopropyl ester was applied by padding with a 31% emulsion and the fabric air-dried, cured 10 min. at 140° C., washed and dried. The bromoform adduct of PNE was applied from a 30% emulsion, followed by drying for 10 min. at 110° C., curing for 6 min. at 140° C., washing and drying. The resulting three fabric samples were evaluated for flame resistance, tear strength, and durability of the flame resistance to laundering. The results are given in Table III.

It will be noted that although the flame resistance of none of the samples was durable to boiling in an alkaline soap solution for 3 hr. on the basis of the standard vertical test, all three samples behaved satisfactorily after 15 detergent launderings. On the basis of angle strip test, the PNE-bromoform adduct showed the best resistance to the alkaline soap boil and good resistance to detergent laundering.

Summary

Various bromine-containing phosphonitrilate materials, namely brominated allyl phosphonitrilate, 2, 3-dibromopropyl phosphonitrilate, and the bromoform adduct polymer of allyl phosphonitrilate, have been prepared and shown to be effective, durable

flame retardants for cotton fabric. Laboratory experiments with these materials indicate that the bromoform adduct polymer of allyl phosphonitrilate might be suitable for trials on a larger scale.

Acknowledgment

The authors wish to thank the various members of the Textile Testing and Analytical Unit, of the Analytical, Physical-Chemical and Physics Section, for the textile evaluation tests and chemical analyses, respectively. We also wish to thank Howard V. Moore for the preparation of phosphonitrilic chloride.

Literature Cited

1. Frick, J. G., Jr., and Weaver, J. W., *Suspensions of Polymeric Flameproofing Compositions Containing Phosphate and Halomethyl Groups*, U. S. Pat. 2,686,768 (1954).
2. Frick, J. G., Jr., and Weaver, J. W., *Flameproofing Aqueous Suspensions of Halomethylated Phosphates*, U. S. Pat. 2,686,769 (1954).
3. Hamalainen, Carl, *Process for Flameproofing Textiles with Polyphosphonitrilic Ester*, U. S. Pat. 2,681,295 (1954).
4. Kauth, Henry J., *Insulated Electrical Conductor*, U. S. Pat. 2,334,710 (1943).
5. Reeves, W. A., McMillan, O. J., Jr., and Guthrie, J. D., "Chemical and Physical Properties of Aminized Cotton," *TEXTILE RESEARCH JOURNAL* 23, 527 (1953).
6. Schenck, R., and Romer, G., *Über die Phosphonitrilchloride und ihre Umsetzungen*, Ber. 57B, 1343 (1924).
7. Smith, A. E., and Elliott, P. M., *Phosphonitrilic Compounds as Resin Constituents*, Research Contract N8-onr-504, Technical Report 1, 1950.

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A Compounded Flame Retardant for Cotton Fabrics¹

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Abstract

A combination of two existing flame retardants, THPC and the bromoform-triallyl phosphate polymer, produces a flame-retardant finish for cotton which is superior to that of either finish alone. Fabrics 8 oz. or heavier are made highly flame-resistant. The finish is durable and employs a single treating bath with a simple finishing procedure.

MUCH work has been done at the Southern Regional Research Laboratory on the development of an efficient flame-retardant finish for cotton fabric which will remain effective after an indefinite number of dry cleanings or launderings. Two such finishing processes have been developed and announced previously. One of these, called the THPC method, is based on a copolymer made from tetrakis (hydroxymethyl) phosphonium chloride and methylolmelamine [2, 3]. The other, called the BAP method, uses a polymer prepared from bromoform and triallyl phosphate [1]. The first finish is applied from aqueous solution and the latter from aqueous emulsion.

Both of these methods give fabric with good resistance to burning, as judged by the vertical flame test [6], but the THPC method gives a much shorter char length for an equal add-on. The BAP method gives better results when comparable fabrics are ignited along an exposed edge, but the flame resistance is still far from ideal. For some uses, and particularly for materials needed for military requirements, it would be desirable for the fabric to withstand a more rigorous test, such as exposure of a narrow strip to a flame. It was found that results varied with different flame retardants on cotton with (1) width of strip, (2) angle of strip from vertical, (3) type of flame used for ignition, (4) time of ignition,

(5) ambient conditions, and (6) operator. However, for practical use, a strip of fabric, $\frac{1}{4} \times 10$ in., hung vertically in a draft-free area, and ignited with an ordinary match, gave reproducible results.

Using this "match test" method, fabrics treated with the THPC and the BAP methods were compared. Whereas the first had a char length of 3 in. and the second of 5 in. in the vertical flame test, the $\frac{1}{4}$ -in. strip treated with THPC would burn completely, while that treated with BAP would start to burn vigorously and suddenly go out.

To explain this phenomenon, consideration was given to the theoretical aspects of making cotton flame-resistant as given by Schuyten, Weaver, and Reid [4, 5]. Application of their conclusions to the two materials under consideration may be summarized as follows: The main reaction involved in preventing the cotton from burning is a dehydration of the cellulose brought about by decomposition of the flame retardant at flaming temperatures to form a phosphorus-containing acid, probably metaphosphoric acid. This acid acts as a dehydration catalyst; through a carbonium ion mechanism, to produce carbon and water from the cellulose. This dehydration is not complete; only 80% dehydration occurs on about 75% of the cellulose, leaving about 25% of the cellulose to decompose mainly to flammable gases mixed with products of the pyrolytic decomposition of the flame retardant itself. The char length obtained in the vertical flame test is not necessarily closely related to flammability of the cloth under conditions of practical usage but is approximately inversely proportional to the temperature of decomposition of the reagent. For example, the THPC resin decomposes between 350° and 400° C., while

¹ This is a report on one phase of a program of research, on the flame-resistance treatment of cotton textiles, being conducted at the Southern Utilization Research Branch with funds supplied by the Office of the Quartermaster General, Department of the Army, and conducted under the general supervision of the Research and Development Center, Natick, Massachusetts.

² One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U.S. Department of Agriculture.

the BAP decomposes between 200° and 250° C. It is suggested that decomposition of the resin at the lower temperatures is attended by more extensive decomposition of the cellulose. A long tear results which is interpreted as a long char length; however, the tear may well be due to decomposition of the cloth by the heat and action of the agent rather than to actual burning. Although the amount of cellulose decomposing to form gases is about the same in both cases, the rate of production and composition greatly affect the flammability of the gas mixture and therefore the propagation of the flame. Both of these factors influence the limits of flammability of the gaseous mixture, but probably more important is the production of active radicals to react with radicals from the oxidizing gaseous mixture and prevent propagation and end the chain. It was proposed that the production of bromine compounds (as from BAP) is instrumental in reducing flammability of the evolved gases [5]. Probably with THPC, nitrogenous compounds are formed which will reduce the flammability of the gases.

From careful consideration of the above facts, it was believed possible to obtain from a mixture of the two polymers, BAP and THPC, a compounded finish that would have the advantages of

both without excessively raising the add-on required.

Preliminary work, in which a BAP finish was applied over a THPC finish, proved that this was the case. Further work showed that the treatment could be applied from a single impregnating bath by mixing the BAP emulsion with the usual THPC formulation. The most effective results have been obtained by a finish containing about 65% of the THPC resin and 35% of the BAP polymer. The method of application and curing is the same as that used in the THPC process. Add-ons of about 18% are required on 8- to 9-oz. fabrics for a high degree of permanent flame resistance. Lighter fabrics, however, require a higher add-on to obtain maximum flame resistance.

Possibly the cloth so obtained is more resistant toward burning than would be needed for many purposes. Figure 1 shows strips which have been treated by both the THPC and BAP methods as well as by the combined method, before laundering and after 12 laundings. The synergistic effect of the combination treatment is evident.

Experimental

Materials Used

A THPC solution was prepared in the usual manner [2, 3] but at a higher concentration. The BAP emulsion was prepared as previously described [1]. Either the 33 or 40% emulsion may be used provided the concentration is adjusted accordingly. The combination single-bath, THPC-BAP emulsion was prepared in the following manner: 286 g. of tetrakis (hydroxymethyl) phosphonium chloride was dissolved in 125 ml. of water, and 54 g. of triethanolamine was added to the solution. A separate solution of 175 g. of urea dissolved in 375 ml. of water was made, and then 173 g. of Resloom HP* was dissolved in this solution, and the two solutions were mixed. To the mixture was added 810 ml. of 33% BAP emulsion [1] to which 12 g. of Flexol TWS* (tetrabutyl thiodisuccinate) had been added as a plasticizer. The use of triethanolamine as a stabilizing agent keeps the treating bath usable for a period of about 8 hr. at room temperature.

Vat-dyed 8.2-oz. twill and 8.5-oz. sateen were used for the heavier cotton fabrics, and kier-boiled and bleached 5.6-oz. 48 × 48 sheeting and 4-oz. 80 × 80 print cloth were used for the lighter cotton fabrics.

* The mention of trade products and firms does not imply their endorsement by the Department of Agriculture over similar products or firms not mentioned.

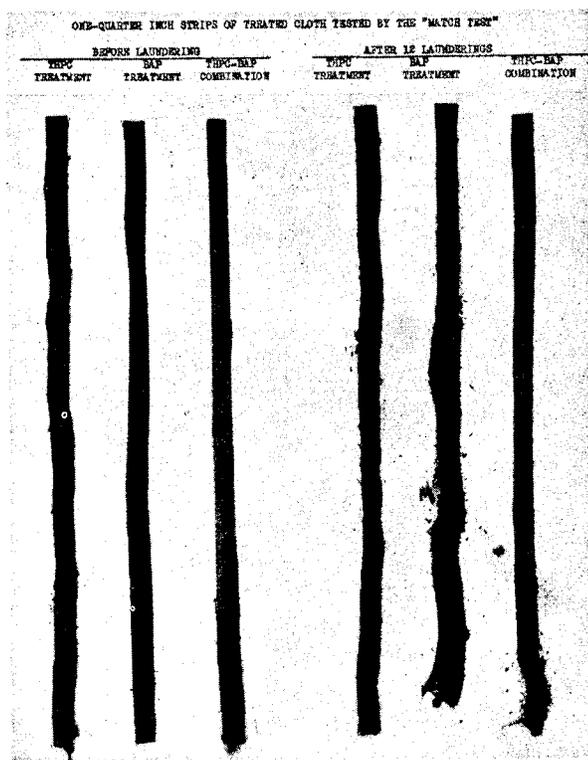


Fig. 1.

Treatment of Fabric

The emulsion was padded onto 4 yd. of half-width twill and sateen using two dips and two nips to obtain an average wet add-on of 67%. The cloth was dried 5 min. at 100° C. (212° F.) and cured 5 min. at 140° C. (284° F.) in a vented hot-air oven. Excess resin was removed by a jig wash consisting of a cold rinse, a wash with 0.01% Igepon T* at 60° C. (140° F.), two rinses at the same temperature, and a cold rinse, using 10 ends in each step. After drying, the cloth was softened by applying a 3% solution of Triton X-400* to a 70% wet add-on and drying again. (This step could be eliminated by adding the softener to the final rinse of the jig wash). Resin add-on was 22% on the sateen, 19% on the twill.

The sheeting and print cloth were treated similarly with resin add-ons of 18 and 25% to each.

Properties of Treated Fabrics

Testing Methods

The treated fabrics were laundered according to Federal Specifications [6] by the Army Mobile Laundry Procedure, Method 5556, using Igepon T as the detergent and an acid fluoride sour following washing. Char length was determined by the vertical flame test, Method 5902, and tear strength by Pendulum (Elmendorf), Method 5132. Results given in the match test were determined in the following manner: A strip of cloth $\frac{1}{4}$ in. wide and 10 in. long was suspended vertically in a draft-free area. Attempts were made to ignite it by a match or other small flame, the flame being held for a time judged by the operator to be optimum for lighting the sample (usually about 6 sec.). If the strip did not burn on removal of the flame, it was classed as "excellent." If it flickered and burned but went out in the bottom 3 or 4 in., it was classed as "good." Strips which burned approximately half the length of the strip and those which burned completely were classed as "fair" and "fail," respectively. Figure 1 shows the appearance of the strips after being subjected to this test.

Properties of Fabrics

The tear resistance and resistance to burning of the treated samples are given in Table I. Tests were made before laundering and after 1, 6, and 12 launderings to determine the durability. Tear resistance before laundering was compared with the original untreated and unlaundered fabric; subsequent comparisons were made with the untreated fabric after laundering the indicated number of times.

The durability of the flame-retardant finish on the heavier fabrics is good in the laundering test. After a more rigorous test, a two-hr. boil in a solution containing 1% standard laundry soap and 0.5% sodium carbonate, the sateen with 19% add-on still has a char length of only 3.7 in. in the vertical flame test. The fabric, however, will no longer pass the match test. Hydrolytic conditions in this test are believed to be much more severe than those involved in ordinary laundering.

Discussion

Cotton fabrics treated by this combination process have a very high degree of flame resistance. The match test already described appears to be a very rigorous test. In fact the flame resistance required to pass this test is probably much more than is needed for many textile uses. Accordingly a treatment of lower add-on may be applied by using more dilute solutions with corresponding savings in cost and with better textile properties in the product.

With the lighter weight fabrics, a durable finish to pass all tests, including the match test, could not be obtained even with 25% add-on. It will be noted, however, from Table I, that the sheeting which failed the match test gave satisfactory results when tested by the vertical flame test. Such results are difficult to obtain with durable flame-retardant finishes. In Table I, only the flame resistance and tear resistance of the fabrics are listed because these are the two properties which undergo marked change. Breaking strength is unaffected by the treatment. The hand of the fabric shows the added weight but is pleasant and seems somewhat better than that obtained with either the THPC or BAP alone.

It may be noted that the effect on tear resistance varies with the type of fabric treated. The tear resistance of the 8-oz. twill is practically unaffected by the treatment. On the other hand, the sateen of about the same weight shows a marked loss initially when compared with the original untreated fabric. When both fabrics have been laundered a number of times, this difference decreases, and after 12 launderings the tear resistance of the treated sateen is 90% of the untreated. The sheetings also show considerable loss of tear strength, particularly at the higher add-ons.

Summary

A durable flame-retardant finish for cotton fabrics has been developed from a combination of two existing finishes, namely the THPC resin and the bromo-

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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

¹ One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U.S. Department of Agriculture.

* Tetrakis (hydroxymethyl) phosphonium chloride, $(\text{HOCH}_2)_4\text{P}^+\text{Cl}^-$.

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 lightweight 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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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-CHBr₃) 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-CHBr₃ made from 1 part PNE (allyl phosphonitrilate) per 0.64 part bromoform. Emulsions containing both THPC-resin-forming materials and PNE-CHBr₃ are prepared by adding the required amount of PNE-CHBr₃ emulsion to the THPC-resin-forming solution. The final emulsions containing both flame retardants are referred to as THPC-PNE-CHBr₃ 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-CHBr₃. The treating emulsions were made to contain 50 to 90 parts THPC-resin-forming solution and 10 to 50 parts PNE-CHBr₃ 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-CHBr₃ 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-CHBr₃ emulsion was prepared by mixing 542 g. of 31% PNE-CHBr₃ 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-CHBr₃ Emulsions on Flame Resistance of 8-oz. Twill and Sateen

Sample designation	Fabric type	Treating solution composition			Flame resistance			
		THPC resin-forming solution (wt. %)	PNE-CHBr ₃ emulsion (wt. %)	Resin add-on (%)	Original fabric		After 15 launderings†	
					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-CHBr₃ Emulsion-Treated Fabrics before Laundering

Test	Direction of test	Untreated control	Fabric with	
			18.0% resin	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 (×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
Char length (in.)	Filling	51	53	52
	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 phosphonitrate 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-CHBr₃ Emulsion-Treated Fabrics after 5, 10, and 15 Launderings

Test	No. of times laundered	Direction of test	Untreated control	Fabric with	
				18% resin	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 1/2-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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Literature Cited

1. "Flammability of Clothing Textiles," Commercial Standard 191-53, U. S. Government Printing Office, Washington, D. C. (1953).
2. Hamalainen, C., *Process for Flameproofing Textiles with Polyphosphonitrilic Ester*, U. S. Pat. 2,681,295 (1954).
3. Hamalainen, C., and Guthrie, J. D., "Bromine-Containing Phosphonitrilates as Flame Retardants for Cotton," *TEXTILE RESEARCH JOURNAL* 26, 2 (1956).
4. Reeves, W. A., and Guthrie, J. D., *U. S. Dept. Agr., Agr., Ind. Chem. Bull.*, AIC 364 (1953).
5. Reeves, W. A., McMillan, O. J., Jr., and Guthrie, J. D., "Chemical and Physical Properties of Aminized Cotton," *TEXTILE RESEARCH JOURNAL* 23, 527 (1953).
6. *1952 Technical Manual and Yearbook of the American Association of Textile Chemists and Colorists* 28, 122 (1952).

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