United States Patent Office 3,829,289
Patented Aug. 13, 1974

3,829,289

PROCESS FOR DECREASING THE FLAMMABILITY OF TEXTILES AND PRODUCT PRODUCED THEREBY

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No Drawing. Continuation-in-part of abandoned application Ser. No. 140,256, May 4, 1971. This application Apr. 7, 1972, Ser. No. 242,237
Int. Cl. D06m *13/28, 13/44, 13/54*
U.S. Cl. 8—115.7 12 Claims

ABSTRACT OF THE DISCLOSURE

A process for decreasing the flammability of textiles comprising a cellulosic fiber component and a nitrogen-free thermoplastic fiber component which comprises treating the cellulosic fiber component with an unsaturated compound (viz, N-methylol phosphono propionamide, N-methylol amide, N-methylol carbamate, or allyl halide) so as to introduce unsaturated groups into said cellulosic component and subsequently halogenating (preferably brominating) the unsaturated groups thus introduced into said cellulosic component. Where the unsaturated compound used does not contain phosphorus, organophosphorus reagents can be introduced in a separate step (before or after halogenation of the unsaturated groups).

This application is a continuation-in-part of Ser. No. 140,256, filed May 4, 1971, now abandoned.

The present invention pertains to a process for decreasing the flammability of textile materials, and more particularly of textiles comprising cellulosic fibers in conjunction with nitrogen-free thermoplastic fibers such as polyester or polyolefins.

The problem of textile flammability has been of interest for many years, and many approaches have been proposed to the solution of this problem. Many processes are known for decreasing the flammability of textile materials, and some among these have attained commercial importance. However, known processes are generally effective for textile materials or fabrics made entirely from one type of fiber—in most instances cellulose. For example, treatment with organophosphorus compounds is known to decrease the flammability of cellulosic textiles, and insolubilization of appropriate phosphorus-containing reagents in or on cellulosic textile can impart flame retardant properties that withstand a great number of launderings, dry cleanings or other cleaning procedures.

In view of the recent commercial importance attained by fabrics made from blend yarns, and particularly of polyester/cellulose fabrics, consideration has also been given to processes intended to decrease their flammability. The problem of imparting flame retardant properties to textile materials containing more than one fiber, and more specifically polyester and cellulose fibers (in blends or mixtures) proved to be of enormous complexity. When flame retardant chemicals known to be effective on celluosic fibers are added to such fabrics, the flammability of the treated material is generally not decreased. In fact, the treated fabric in some instances burns more readily than the untreated one because, after ignition, molten polyester continues to burn in and around the cellulosic fibers (even though these have been rendered non-combustible by the flame retardant treatment) instead of dripping away from the flame, and the entire structure is consumed. Several investigators have documented these observations (e.g.

W. Kruse and K. Filipp—Melliand Textilber, *49*, 203 (1968)

W. Kruse Melliand Textilber, *50*, 460 (1969))

and various interpretations have been proposed for the observed phenomena. It has been postulated that flame retardant polyester/cellulose can be obtained only when appropriate flame retardant chemicals are present in or on both fibers (e.g. G. C. Tesoro & C. H. Meiser Tex. Res. J. *40*, 430 (1970)), and that it would not be possible to obtain flame retardant polyester/cellulose fabrics of adequate performance by modifying the cellulose with flame retardant chemicals while leaving the polyester component essentially unchanged. Other investigators, using different fabric constructions (fiber mats) have reached an apparently opposite conclusion.

P. Linden, L. G. Roldan, S. B. Sello, H. S. Skovronek, Proceedings Annual Meeting I.C.F.F., New York, December 1970; Textilveredlung, 6, No. 10, 651–6 (1971).

The latter concede, however, that the differences probably can be attributed to variations in the flame retardants, fabric structures or testing methods. Attempts to treat fabrics with chemicals or combinations of chemicals that could be insolubilized in or on both fibers have led to unsatisfactory results, primarily because the chemical inertness of polyester necessitates the use of high concentrations of reagents in chemical systems which form polymeric coatings on fiber surfaces, and thus inevitably impair the flexibility, aesthetic properties and hand of the treated textiles. Accordingly, there is a great need in the industry for processes to decrease the flammability of polyester/cellulose fabrics, and more generally of fabrics made from cellulosic fiber in conjunction with non-nitrogenous thermoplastic fibers.

I have discovered that it is possible to impart flame retardant properties to polyester/cellulose yarns and fabrics by processes modifying the cellulosic fiber component while leaving the polyester component essentially unchanged.

The modification of the cellulosic component is carried out by (a) treatment with a reagent containing unsaturation, and (b), in a subsequent step, halogenation (preferably bromination) of the unsaturated groups introduced. The reagent containing unsaturation may also contain, in the same molecule, elements known to have flame retardant effectiveness in cellulosic polymers such as phosphorus (phosphine, phosphonate, phosphonium, etc.) and, optionally, nitrogen (amide, amine, etc.). On the other hand, the incorporation of such "flame retarding elements" can be carried out as a subsequent step (c). When halogen is introduced into the cellulosic component as shown in the process of the present invention, the amount of additional flame retarding compound (e.g. organophosphorus) needed is lower, and its effect on fabric properties is reduced. The overall result is to obtain a polyester/cellulose textile in which the cellulose contains compounds of halogen (bromine), phosphorus, and (optionally) nitrogen in such amounts as to cause the flammability of the textile to be significantly decreased without substantial impairment of other properties. The extent of decrease in flammability will depend on the amounts of flame retardant chemicals present in the cellulose, on the ratios of flame retarding elements introduced, and also on the percentage of cellulose present in the polyester/cellulose substrate and available for modification. In many situations, it is possible to obtain self extinguishing polyester/cellulose fabrics—or fabrics which would pass a severe flammability test (Vertical Test—AATCC–34—1966) with amounts of insolubilized flame retardants comparable to the amounts needed to attain self extinguishing behavior on 100% cellulosic fabrics. The object of the present invention is thus to provide novel processes by which the flammability of polyester/cellulose textiles can be decreased, the effect generally being durable to laundering, dry cleaning, and other conditions of use.

It is a further object of the present invention to decrease the flammability of polyester/cellulose textiles by introducing the flame retardant chemicals solely or primarily into the cellulose component, leaving the polyester fiber essentially unchanged.

The objects of the invention can be attained by reacting cellulose hydroxyl groups in a polyester/cellulose fabric with unsaturated organophosphorus reagents and thereafter halogenating (brominating) the unsaturated groups introduced.

Alternatively, the cellulose hydroxyls in the polyester/cellulose can be reacted with an appropriate unsaturated compound, and organophosphorus reagents can be introduced in a separate step (before or after bromination of the unsaturated groups).

In the case of regenerated cellulose, it is also possible to introduce a flame retardant compound containing unsaturation during the fiber manufacturing step, to use this modified fiber in blends with polyester, and to carry out halogenation of the unsaturated groups after fabric has been manufactured.

The processes of the present invention can be used to obtain flame retardant textiles suitable for many end uses (apparel, furnishings, industrial, military, etc.). The following types of substrates are included among those suitable for practicing the process of the invention:

(a) Woven, knitted, or non woven fabrics made from blended yarns of polyester/cotton in which the cotton content *is at least 20%* (100% cotton fabrics can, of course, also be used);

(b) Fabrics made from blended yarns containing polyester and regenerated cellulose (rayon, modified rayon) in which the regenerated cellulose content is at least 20%;

(c) Woven fabrics made from 100% cellulose yarns (cotton or regenerated cellulose) in the warp or filling direction, and 100% polyester, or polyester/cellulose blend yarns in the other direction;

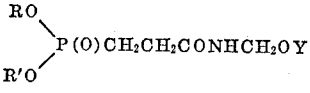
(d) Knitted fabrics made from plied yarns in which cellulose yarns are combined with polyester filaments;

(e) Viscose solutions from which regenerated cellulose fibers are spun (for subsequent blending with polyester fibers).

Generally speaking, the cellulose content of the substrate should be at least 20% and preferably 35% or more in order for the process to be effective.

The chemical systems suitable for carrying out the process of the invention on polyester/cellulose textiles include the following:

(a) Compounds containing at least one unsaturated group, phosphorus, and at least one group capable of reaction with cellulose hydroxyl groups. Examples of these are the N-methylol phosphono propionamides of the formula

(I) 

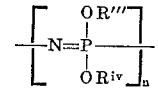
where R is alkenyl, and R′ is selected from the group consisting of alkyl, substituted alkyl and alkenyl, and Y is hydrogen or lower alkyl; and

(b) Compounds containing at least one unsaturated group, and at least one group capable either of reaction with cellulose hydroxyl groups or of blending with alkali cellulose. Examples of these are unsaturated N-methylol amides and carbamates of the formula (II)

$$R''CONHCH_2OH$$

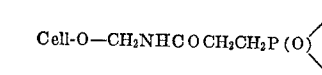
and (III) $R''OCONHCH_2OH$ where R″ is alkenyl; and allyl or substituted allyl halides such as allyl chloride or allyl bromide. When such compounds as these are used, the phosphorus which may be required to reach the desired level of flame retardancy is introduced in a separate treatment with appropriate organophosphorus reagents generally known in the art. Typically the alkenyl and/or alkyl substituents referred to above for R, R′ and R″ are lower alkenyl or lower alkyl, e.g. allyl, methyl, ethyl, propyl, hydroxymethyl and the like. The same is true for the R‴ and R^{iv} substituents referred to below.

(c) Compounds for inclusion in viscose. When it is desired to use the process of the invention in the manufacture of regenerated cellulose fibers specifically designed for blending with polyester, the unsaturated flame retardants used need not contain cellulose-reactive groups, but must withstand the fiber manufacturing process, as outlined, for example, in U.S. Pat. 3,455,713. For example, a water-insoluble liquid phosphonitrilate polymer of the formula (IV)

(IV) 

wherein R‴ and/or R^{iv} is alkenyl may be used. After blending of the modified fiber with polyester fiber, the yarn or fabric made from this blend can be halogenated according to the process of the present invention to obtain the desired flame retardant product.

The methods and conditions employed for obtaining the flame retardant textiles of the present invention depend, in part, on the substrate and chemical system employed, and on the level of performance required. Cellulose/polyester fabrics may be treated with compounds such as those shown in Formulae (I), (II) and (III) by padding from aqueous solution, in the presence of appropriate catalysts, drying, curing and washing. The conditions of catalysis and curing are generally those known in the art and do not constitute a feature of the invention. Under these known conditions, the cellulose in the polyester/cellulose is modified to an ether, schematically shown below in formulae (IV), (V) and (VI) for the products obtained with the compounds of formulae (I), (II) and (III), respectively.

 (IV)

$$Cell\text{-}OCH_2NHCOR'' \quad (V)$$

$$Cell\text{-}OCH_2NHCOOR'' \quad (VI)$$

The pendant alkenyl groups in the cellulose ether are then halogenated by treatment with a solution of elemental halogen under mild conditions. Bromine is the preferred halogen for a number of reasons: it is an effective flame retardant element, it reacts rapidly with the unsaturated groups, and it does not attack, discolor or impair the cellulosic component in the substrate. The bromine may be dissolved in water or in an inert organic solvent. The concentration of bromine, the time and temperature of the bromination reaction and the medium employed are not critical and may be determined in each case by appropriate experiments.

One of the major advantages of the process of the invention is that covalently bound bromine is introduced readily and uniformly throughout the modified cellulose fibers. This cannot be done by employing brominated reagents for the cellulose modification, since limitations in the solubility and penetration of such brominated reagents generally result in the reagent being concentrated on fiber surfaces, with consequent unsatisfactory efficiency, and poor durability of the treatment in laundering, in cleaning and in use.

The evaluation of the flammability of treated textiles is conveniently and accurately carried out by the "Limiting Oxygen Index (LOI) Method" as described in several recent publications (e.g., Isaacs—J. Fire & Flammability I, 36–47 (1970)). The higher the LOI, the lower the flammability. LOI values above .240–.260 are believed to reflect self extinguishing behavior in Vertical flammability tests such as AATCC 34–1966 and are thus indicative of satisfactory flame retardant properties in use.

The durability of flame retardant properties to laundering or other cleaning procedure is easily evaluated by exposing the treated textiles to appropriate washing or cleaning procedures and checking the LOI after exposure. Analytical determination of halogen and of other elements introduced in the cellulose modification can also be used to establish that the desired flame retarding elements are firmly bound to the cellulose molecules, and retained after exposure to laundering and other conditions.

The following examples are illustrative of the invention described.

EXAMPLE 1

3-(Diallyl phosphono)propionamide, when made with sodium methylate catalyst by the procedure of Example III of U.S. Pat. 3,374,292, was found by NMR to contain at least 10% methyl ester groups, the result of exchange between allyl groups and catalyst. This problem was eliminated by effecting the reaction of diallyl phosphite with acrylamide in allyl alcohol and dioxane, with sodium allylate catalyst. The reaction of the intermediate with formalin was catalyzed with triethylamine instead of caustic soda, the preparations being otherwise like those of the reference. A sample of the resulting dried *N-methylol 3-(diallyl phosphono)-propionamide* was analyzed: calcd. 11.8% P, 5.32% N; found 11.64% P, 5.36% N.

EXAMPLE 2

A solution of the intermediate 3-(diallyl phosphono)-propionamide of Example 1 (46.4 g., 0.2 mol) in 200 ml. dioxane was held at −5 to −10° C. while 64 g. (0.4 mol) bromine was added dropwise, with stirring, in 20 minutes. After another hour of stirring at −10° C. and ten minutes at room temperature, the mixture was left standing overnight at room temperature. The heavier of the two resulting layers was dissolved in 65 ml. acetone and treated with 250 ml. pentane. The 86 g. of crude precipitate was separated, dissolved in 50 ml. ethanol, and precipitated with 500 ml. water, giving nearly white solid which weighed 65 g. after drying under vacuum at 60° C. A sample dried over P_2O_5 at room temperature was analyzed: calcd. 2.53% N, 57.87% Br; found 2.38% N, 57.7% Br.

For hydroxymethylation 27.65 g. (0.05 mol) of the brominated amide was mixed with 1.65 g. (0.052 mol) 95% paraformaldehyde and 0.1 ml. triethylamine, and the mixture was placed in a 100° C. oil bath for 10 minutes. After the reaction mixture was evaporated to dryness at 50° C. under reduced pressure, the residue was dissolved in a little acetone and precipitated with 8 ml. water. NMR analysis of the dried precipitate showed it to consist about 95% of the desired *N-methylol 3-(bis-2,3-dibromopropyl phosphono)-propionamide.*

EXAMPLE 3

Procedure Used in Subsequent Examples

In this and following examples the procedure employed was to pad an aqueous solution of additive, 1% curing catalyst (2-amino-2-methylpropanol hydrochloride), and 0.1% detergent (nonylphenylpolyethyleneoxyethanol) onto weighed samples of fabric in a laboratory padder at 30 p.s.i.; dry 4 minutes at 93° C.; cure 3 minutes at 175° C.; process wash 12 minutes with water containing 0.001% detergent in a home washing machine set on "warm"; tumble-dry; and condition overnight at 72° F. and 65% relative humidity in preparation for final weighing and testing. Except when otherwise indicated, test fabrics were 10% cotton sheeting, 3.75 oz./yd.², 95 x 84 count,, and 50/50 polyester/cotton sheeting, 3.68 oz./yd.², 96 x 88 count. Samples for treatment were usually about 10 x 20 inches, weighing before treatment about 18 g. for 50/50 polyester/cotton and 16 g. for 100% cotton. The treatment cycle was repeated more than one time when it was desired to increase the extent of modification (add-on) beyond the maximum obtainable in a single treatment.

EXAMPLE 4

For purposes of comparison, as well as to supply starting material fabrics for the products of this invention, numerous samples of 100% cotton and 50/50 polyester/cotton fabrics were treated by the procedure of Example 3 with solutions of N-methylol 3-(diallyl phosphono) propionamide of Example 1; and some of these were tested. Runs also were made with N-methylol 3-(dimethyl phosphono)propionamide, known commercially as Pyrovatex CP, particularly to establish the effects of changes in reactant solution concentration. Results of typical experiments are listed in Table 1. "Reactant Applied" tells, unless otherwise indicated, the percent of dry reagent on the fabric before cure. "Ad-on" tells the percent of reagent remaining on the fabric (reacted) after curing and process washing. The LOI of the original fabric for all of the examples was 0.168.

TABLE 1

Effect of known reactants on 100% cotton and 50/50 polyester/cotton fabrics

Reactant	Percent: Cotton in fabric	Percent: Reactant applied	No. cycles	Percent add-on	LOI
Pyrovatex CP	100	8.5	1	3.5	0.200
	100	15.2	1	7.5	0.222
	100	23.6	1	10.7	0.260
	50	13.4	1	6.5	0.215
	50	25.1	1	7.9	0.222
	50	34.6	1	8.4	0.225
	50	*40	3	13.3	0.233
N-methylol 3-(diallyl phosphono)propionamide	100	*30	1	9.3	0.220
	100	*30	2	14.2	0.244
	50	*30	1	6.6	0.211
	50	*30	2	8.8	0.215

*Concentration of reactant in applied solution.

It is evident, from these data, that the permanent add-on of each reactant was increased to a degree by increasing both the amount padded on and the number of application cycles. However, further increases beyond those shown did not further increase either the add-on or the LOI.

It is apparent that in the absence of halogen, the LOI of 50/50 polyester/cotton samples treated with either of these known reagents containing phosphorus and nitrogen is too low to indicate self extinguishing behaviour. Pyrovatex CP required high add-ons to achieve LOI levels around 0.260 on 100% cotton, and it fell far short of this on 50/50 polyester/cotton.

EXAMPLE 5

Bromination in the process of my invention was carried out by one of three procedures, the third being preferred from the standpoint of high bromine uptake, product uniformity, and high LOI.

A. Dry samples soaked in chloroform solutions of bromine at room temperature, then washed thoroughly.

B. Samples soaked in aqueous solutions of bromine at room temperature and then washed.

C. Samples padded with water, then soaked in chloroform solutions of bromine at room temperature and then washed.

In typical runs by method A on fabrics of Example 4, 10 x 20-inch specimens derived from 100% cotton and 50/50 polyester/cotton were soaked in 200 g. of chloroform containing varying amounts of bromine for differing periods of time at room temperature. Results of these brominations are shown in Table 2. The phosphorus analyses heading the table are measures of the amount of N-methylol 3-(diallyl phosphono)-propionamide bound to each specimen being brominated.

TABLE 2

Bromination of dry fabrics by method A

Fabric	Percent P in starting fabric	Bromination G. Br_2	Bromination Time, min.	Percent bromine in treated fabric	LOI Before bromination	LOI After bromination
100% cotton	1.67	0.96	10	5.0	.241	.267
	1.62	2.24	10	3.8	.244	.263
	1.69	4.88	10	5.0	.244	.255
	1.70	0.96	30	6.3	.244	.274
	1.65	2.24	30	5.1	.241	.274
	1.73	4.88	30	6.7	.244	.278
	2.27	35.2	30	7.4	.250	.299
50/50 polyester/cotton.	1.04	0.64	10	2.7	.125	.225
	1.03	1.28	10	2.2	.217	.227
	1.04	3.56	10	2.7	.215	.227
	1.08	0.64	30	2.3	.215	.227
	1.03	1.28	30	3.4	.225	.233
	1.02	3.56	30	4.5	.215	.235
	1.23	16.0	30	3.8	.213	.241

The data in this table show that although bromine was added and flame resistance was increased, the effects were less than with the next two methods.

EXAMPLE 6

In the next series of brominations, method B was used, the fabrics of Example 4 being soaked for 30 minutes in 200 g. of water containing indicated amounts of bromine. Higher additions of bromine and high LOI's were achieved, as shown in Table 3, but the treated fabrics were less uniform in appearance than those of Method C.

TABLE 3

Bromination of fabrics with aqueous bromine (method B)

Fabric	Percent P in starting fabric	Grams Br_2 in solution	Percent bromine in treated fabric	LOI Before bromination	LOI After bromination
100% cotton	2.18	18.2	13.9	.253	.313
	2.34	16.0	14.1	.255	.317
	2.31	16.0	14.6	.253	.323
50/50 polyester/cotton	1.23	9.6	8.5	.220	.260
	1.24	9.6	8.5	.222	.255
	1.18	9.6	8.5	.217	.255

EXAMPLE 7

In the next and preferred brominations, using method C, water-padded fabric samples of Example 4 were soaked 30 minutes at room temperature in 200 g. of chloroform containing indicated amounts of bromine. High uptakes of bromine and high LOI's were achieved, and the resulting fabrics were white, soft, and resistant to laundering and dry cleaning, as shown in Tables 4 and 5.

TABLE 4

Bromination in chloroform of water-padded fabrics (method C)

Fabric	Percent P in starting fabric	Grams Br_2 in solution	Percent bromine in treated fabric	LOI Before bromination	LOI After bromination
100% cotton	2.18	16	8.8	.253	.303
	2.36	16	10.9	.250	.308
	2.46	19.2	10.2	.250	.299
50/50 polyester/cotton	1.15	9.6	6.5	.217	.247
	1.18	6.4	7.0	.217	.250
	1.24	9.6	7.3	.220	.255

TABLE 5

Typical properties of fabrics brominated by method C

Property	100% cotton	50/50 polyester/cotton
Crease recovery (W x F)	94 x 93 (control 73 x 77).	113 x 114 (control 111 x 116).
Stoll flex cycles (W x F)	558 x 388 (control 498 x 690).	3,338 x 11,848 (control 5,000+).
Tensile strength (W x F) grab	59 x 51 (control 75 x 63).	81 x 81 (control 89 x 79).
Tear strength (W x F)	865 x 800 (control 1,063 x 813).	1,025 x 925 (control 1,413x 1,100).
LOI of finished sample:		
Process washed	.278	.258.
After 5 launderings	.278	.254.
After 25 launderings	.268	.250.
After dioxane rinse (no weight loss).	.278	.254.

The following test methods were used in determining properties listed in Table 5:

Crease recovery: ASTM–D–1295–60 T
Stoll Flex (Abrasion resistance): ASTM D 1175–44T
Tensile Strength (Grab): ASTM D 1682–64
Tear Strength (Elmendorf): ASTM D 1424–63

EXAMPLE 8

This example demonstrates the disadvantages of using a prebrominated reagent, such as that prepared in Example 2. This reagent, N-methylol 3-(bis-2,3-dibromopropyl phosphono)propionamide, was applied at varying concentrations to 100% cotton and 50/50 polyester/cotton fabrics by the method of Example 3. Since the reagent was so insoluble in water, it was padded onto the fabrics from 1/1 dioxane/water. The results of this work are summarized in Table 6.

TABLE 6

Fabrics Treated with N-methylol 3-(bis-2,3-dibromopropyl phosphono)-propionamide in dioxane/water

	100% cotton		50/50 polyester/cotton	
Sample number	1A	2A	1B	2B
Concentration applied solution (percent reagent)	34	17	34	17
Percent wt. gain	22.9	14.2	16.0	14.2
Percent P found (as finished)	1.1	0.8	1.0	0.7
Percent N found (as finished)	0.6	0.4	0.5	0.4
Percent Br found (as finished)	10.6	6.6	7.8	6.5
Percent Br after dioxane rinse (calc'd from weight loss)	3.0	----------	1.5	----------
Percent Br after 25 launderings (calc'd from weight loss)	4.5	----------	4.8	----------
LOI (as finished)	.286	.243	.256	.242
LOI after dioxane rinse	.198	----------	.200	----------
LOI after 25 launderings	.243	----------	.231	----------

It is obvious from careful evalution of these data that the apparent weight gain from the overall process was high and that the resistance of the additive to laundering was moderate. However, unlike the superior white, soft, and flexible fabrics of Example 7, all samples of Example 8 were yellow and stiff. These undesirable properites persisted through laundering. The high loss of reagent upon simply rinsing with dioxane is taken as evidence that the reagent was actually only a surface deposit, i.e., it had merely coated the fabric rather than reacted with it.

EXAMPLE 9

In this example the reagents and the order of addition of the flameproofing elements were changed. A 40% aqueous solution of N-methylol allyl carbamate (NMAC) was padded by the method of Example 3 onto 10 x 20-inch samples of sheeting. Add-ons, after curing and process washing, ranged 10.2–11.6% on 100% cotton and 8.3–8.9% on 50/50 polyester/cotton. These samples were then padded with water and soaked for varying times at room temperature in 350 g. of chloroform containing 4 times the calculated amount of bromine (method C). The results of these experiments are shown in Table 7.

TABLE 7

Fabrics treated with N-methylol allyl carbamate and then brominated by method C

Fabric	Percent wt. gain of NMAC	Soaking time, mins.	Percent Br
100% cotton	10.6	5	4.54
	10.5	10	5.67
	11.0	30	9.75
	11.6	45	6.58
	11.4	60	5.82
	10.8	75	5.54
	10.2	90	5.36
50/50 polyester/cotton	8.6	5	5.57
	8.6	10	6.90
	8.3	30	7.17
	8.5	45	3.73
	8.8	60	3.26
	8.8	75	1.46
	8.9	90	1.55

It is evident from these results that the optimum soaking time was about 10–30 minutes. The LOI of the brominated samples was about 0.212 for the 100% cotton and 0.208 for the 50/50 polyester/cotton sheetings.

These same samples were then treated with 40% aqueous solutions of Pyrovatex CP by the method of Example 3. The results for these fabrics, now containing nitrogen, phosphorus, and bromine are summarized in Table 8.

TABLE 8

Fabrics treated in turn with N-methylol allyl carbamate, bromine, and pyrovatex CP

Fabric	Percent Br, before pyrovatex	Percent P, after pyrovatex	LOI
100% cotton	5.67	0.91	0.247
	6.58	1.01	0.266
	5.82	0.83	0.256
	5.54	1.24	0.261
	5.36	1.18	0.264
50/50 polyester/cotton	3.73	0.56	0.229
	3.26	0.44	0.225
	1.46	0.83	0.234
	1.55	0.84	0.240

Although not so high as those of the preferred method of Example 7, these LOI values show that the methods of this invention are applicable to a variety of compositions.

EXAMPLE 10

Another variation upon the combination of the bromination method of this invention with other treatments is shown in this example. A number of test samples were made by bromination (method C) of fabrics previously treated with N-methylol allyl carbamate as in Example 9. Aqueous solutions (200 ml.) containing the indicated amounts of tetrakis (hydroxymethyl)phosphonium chloride (THPC), urea, and trimethylolmelamine (TMM), together with 0.025% of nonionic detergent (nonylphenoxypolyethyleneoxyethanol), were adjusted to pH of about 5.8 wth NaOH and were then padded onto the fabrics at 30 p.s.i., giving wet pickups of about 60%. The samples were dried 4 minutes at 93° C., cured at 160° C. for 3 minutes, and process washed. The LOI values and other experimental details are shown in Table 9.

TABLE 9

Fabric samples treated in turn with N-methylol allyl carbamate, bromine, and then THP C/ Urea/Trimethylolmelamine

Fabric	Percent Br before THPC	Percent additives in water			Percent P after THPC	LOI
		THPC	Urea	TMM		
100% Cotton	8.32	17.0	5.0	10.0	1.41	0.266
	9.40	12.2	3.6	7.2	0.92	0.261
	8.30	8.2	2.4	4.8	0.74	0.247
	7.36	4.1	1.2	2.5	0.37	0.220
50/50 polyester/cotton	7.26	17.0	5.0	10.0	1.58	0.264
	6.76	12.2	3.6	7.2	1.12	0.249
	6.06	8.2	2.4	4.8	0.76	0.242
	5.40	4.1	1.2	2.4	0.42	0.225

EXAMPLE 11

In the experiments of this example it was demonstrated that the bromination process of my invention could be applied also to fabrics treated with another unsaturated reagent, N-methylol acrylamide (NMA). The initial reaction was performed by the method of Example 3, modified only by the use of a 4-minute cure at 149° C. Water-padded samples were then soaked for 30 minutes at room temperature in 350 g. of chloroform containing 4 times the calculated amount of bromine. The data in Table 10 clearly show that bromine added well, even if somewhat erratically, to the acrylic group. However, as shown in the final column of this table, the added bromine had only limited resistance to laundering.

TABLE 10

Fabrics treated with N-methylol acrylamide and then brominated by method C

Fabric	Percent			
	Conc'n NMA solution	NMA add-on	Br in fabric	Br after 10 washes
100% Cotton	18	7.2	5.72	1.12
	30	11.1	8.64	0.58
	42	16.0	4.78	0.36
50/50 polyester/cotton	18	4.6	4.82	0.42
	30	7.6	8.76	0.47
	42	10.2	3.70	0.37

EXAMPLE 12

In this example samples of polyester blends of allyl cotton, made by the method of Temin and Liflin (Abstracts of Papers, 162nd National Meeting, American Chemical Society, Washington D.C., Sept. 12–17, 1971, Cell. 002) were first brominated and then subsequently reacted with N-methylol 3-(dimethyl phosphono)propionamide, Pyrovatex CP, this being another of the alternative routes for preparing nitrogen-, phosphorus-, and bromine-containing products of the invention.

The procedure of Temin and Liflin comprised immersing fabrics in 20% sodium hydroxide for one hour and padding to 100% wet pickup, followed by immersion as a loose roll, for 16 hours, in allyl bromide or a 50% solution of it in benzene. After washes in acetone and water, the extent of allylation ws estimated from the net weight gain as about 4% add-on with room-temperature allylation and 6% at 60° C., when using 50% allyl bromide in benzene.

In Table 11 results are summarized wherein allyl cotton blend samples, made by soaking alkali-treated 50/50 polyester/cotton sheeting at room temperature for various times in 80% solutions of allyl bromide in benzene, were benzene rinsed, dried, brominated with 4% bromine in chloroform by Method C, washed, and thereafter treated with 40% Pyrovatex CP by the procedure of Example 3.

The data in the table show that bromination of the allyl cotton was insufficient to raise the LOI of polyester blends to the self-extinguishing range. On the other hand, when combined with subsequent reaction with the nitrogen- and phosphorus-containing Pyrovatex CP, the process provided fabric blends which not only measured above 0.260 in LOI, but also readily passed the aforementioned standard vertical flame test, in which latter tests the flames went out instantly when the test burner was removed. Only a degree of yellowing marred the quality of the final fabric.

TABLE 11

50/50 polyester/cotton sheeting treated in turn with alkali, allyl bromide, bromine, and pryovatex CP

Sample	Allylation time, hrs.	After bromination		After pyrovatex CP			
		Percent Br	LOI	Percent Br	Percent P	LOI	Vertical char length, inches
1	4	0.68	.184				
2	17	8.67	.200				
3	17	10.97		8.29	1.58	.264	4.3
4	20	18.18	.225	15.68	1.83	.278	
5	24	16.86	.223				
6	24	18.42		14.78	1.36	.281	3.9
7	24	19.84	.236	14.12	1.43	.287	
8	*24	19.00			1.26	.315	3.4

*Allylated at 60° C.

EXAMPLE 13

The products of this example were made by bromination of blends of polyester staple with phosphonitrilate-containing viscose staple. Hexaallyloxyphosphonitrilate, the synthesis and structure of which are described by Hamalainen and Guthrie, Textile Research Journal, *26*, 141–4 (1956), was prepared by their method. NMR analysis indicated that 88% of the allyl groups were intact and 12% were crosslinked. A mixed hexa(allyloxypropoxy)phosphonitrilate was made in like manner from an equimolar mixture of allyl alcohol and n-propanol. Its NMR analysis indicated an allyl:propyl ratio of 1.3:0.7. Each of the phosphonitrilates was incorporated at three levels of concentration into viscose by the procedure exemplified in U.S. 3,455,713, and the staple yarns thereby obtained were co-spun with polyester staple to 50/50, 75/25, and 100/0 rayon/polyester blend yarns, which were then kintted to test socks. The intent was to achieve blends each containing 1.5–2.0% phosphorus, but unanticipated losses during the viscose spinning reduced the levels to nearer 1.0%.

Samples of the knit sock specimens were then brominated by Method C. As shown in following Table 12, the retention of the additives, as shown by the phosphorus analyses of test samples before and after bromination, was excellent, as was also the uptake of bromine, which latter was near the theoretical maximum.

TABLE 12

Bromination of phosphonitrilate-containing rayon and rayon/polyester blends

Additive	Blend, rayon/PE	Percent phosphorus		Percent bromine introduced
		Before bromination	After bromination	
A	75/25	1.02	1.00	9.86
A	50/50	1.05	0.95	9.20
AP	100/0	1.07	0.99	5.88
AP	75/25	1.16	1.02	7.75

A=hexallyloxyphosphonitrilate.
AP=hexa(allyloxypropoxy)phosphonitrilate.

Further sock specimens were then brominated for evaluation of their degree of flame retardance. As shown in Table 13, the LOI increases upon bromination were dramatic. Some of the brominated specimens even passed the standard AATCC 34–1966 vertical flame test, a very demanding test for knits; and there was clear indication that, had the percentage levels of additive been as high as planned, even the 50/50 blends would have passed this strenous test.

TABLE 13

Flame-retardance of brominated phosphonitrilate-containing rayon and rayon/polyester blends

Additive	Blend rayon/PE	Percent					Vertical char length, inches
		Phosphorus		Bromine introduced	LOI		
		Before bromination	After bromination		Before bromination	After bromination	
A	100/0	1.14	0.98	7.50	.223	.298	3.1
A	75/25	1.02	1.00	9.54	.214	.271	*BEL
A	50/50	1.05	0.95	8.59	.204	.254	BEL
AP	100/0	1.07	1.02	6.01	.218	.298	3.3
AP	75/25	1.16	1.04	7.17	.214	.266	4.8
AP	50/50	1.00	0.97	7.98	.210	.243	

*Burned entire length.

EXAMPLE 14

The other examples having been performed with woven sheeting, this one applied the combined processes of Examples 4 and 7 to a knit fabric made from 50/50 plied yarn of filament polyester and cotton. The analyses and LOI's of the original knit and of two samples treated with different amounts of N-methyol 3 - (diallyl phosphono) propionamide and bromine are given in Table 11. Results are comparable to those using woven fabrics.

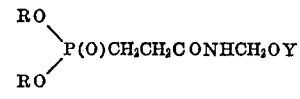
TABLE 14

50/50 polyester/cotton knits treated with N-methylol 3-(diallyl phosphono)propionamide and then bromine by method C

Percent		
P	Br	LOI
		0.169
0.96	4.00	0.236
1.17	6.11	0.249

It will be recognized that various other modifications may be made in the invention in addition to those described above. Hence, the scope of the invention is defined in the following claims wherein I claim:

1. A process for decreasing the flammability of textiles comprising cellulosic and polyester fiber components which comprises reacting hydoxyl groups in the cellulosic component with an N-methylol phosphono propionamide of the formula



wherein R is alkenyl, R' is selected from alkyl, substituted alkyl and alkenyl and Y is hydrogen or lower alkyl so as to introduce unsaturated groups into said cellulosic component and thereafter halogenating the unsaturated groups thus introduced into said cellulosic component, the polyester fibers being essentially unmodified by the reaction of the cellulosic component to introduce unsaturated groups therein and the subsequent halogenation.

2. The process of claim 1 wherein the halogenating is brominating.

3. The process of claim 1 wherein a polyester/cotton fabric is padded with an aqueous solution of an N-methylol alkenyl phosphono propionamide, dried and cured and the alkenyl groups thus introduced into the cotton component of said fabric are then brominated.

4. The process of claim 3 wherein said phosphono propionamide is N-methylol 3-(diallyl phosphono)-propionamide.

5. The process of claim 3 wherein bromination is carried out by impregnating the fabric with a bromine solution.

6. The product produced by the process of claim 1.

7. A process for decreasing the flammability of textiles comprising cellulosic and polyester fiber components which comprises reacting hydroxyl groups in the cellulosic component with an unsaturated phosphorus-free compound selected from the group consisting of compounds having the formula $R''CONHCH_2OY$, compounds of the formula $R''OCONHCH_2OY$ and allyl halides, wherein R'' is alkenyl and Y is hydrogen or lower alkyl, so as to introduce unsaturated groups into said cellulosic component and subsequently halogenating the unsaturated groups thus introduced into said cellulosic component and

reacting said cellulosic component with an organo phosphorus compound selected from the group consisting of N-methylol-3-(dimethyl phosphono) propionamide and tetrakis (hydroxymethyl) phosphonium chloride, the polyester fibers being essentially unmodified by the reaction of the cellulosic component to introduce unsaturated groups therein and the subsequent halogenation.

8. The process of claim 7 wherein the halogenating is brominating.

9. The process of claim 7 wherein the reaction with said organo phosphorus compound is before halogenation.

10. The process of claim 7 wherein the reaction with said organo phosphorus compound is after halogenation.

11. The process of claim 7 wherein the unsaturated compound is N-methylol allyl carbamate or N-methylol acrylamide.

12. The product produced by the process of claim 7.

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RICHARD D. LOVERING, Primary Examiner

U.S. Cl. X.R.

8—116P, 120, 129, 194, DIG. 4; 106—15 FP; 117—136; 252—8.1

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,829,289 Dated August 13, 1974

Inventor(s) Giuliana C. Tesoro

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, line 14, "Ad-on" should be --Add-on--

Column 7, line 12, in the "Before bromination" column, eighth number down, ".125" should be --.215--

Column 7, line 36, in the "Grams Br_2 in solution" column, the first number, "18.2" should be --12.8--

Column 8, line 41, "properites" should be --properties--

Column 9, line 8, add comma after "bromine"

Column 9, line 52, in the "TMM" column, the fourth number down, "2.5" should be --2.4--

Column 9, lines 11 and 13, each occurrence, capitalize the tradename "Pyrovatex"

Column 11, line 2, change "pryovatex" to --Pyrovatex--

Column 11, line 3, capitalize "Pyrovatex"

Claim 1, line 75, the second "RO" should be --R'O--

Signed and sealed this 19th day of November 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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