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PROCESS FOR PREPARING DURABLE FLAME-RETARDANT SYNTHETIC-CELLULOSIC FABRIC BLENDS

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ABSTRACT OF THE DISCLOSURE

Fabric blends of cellulosic and polyester fibers are rendered durably flame-retardant by impregnating with

(A) tetrakis(hydroxymethyl)phosphonium chloride and urea (or a precondensate of these reactants),
(B) a reaction product of melamine with either formaldehyde or formaldehyde and methanol, and
(C) a fatty acid ester of polyethylene glycol,

and forming insoluble reaction products on said fabric. The fatty acid ester of polyethylene glycol serves both to soften the fabric and to carry fireproofing reaction products onto the polyester component.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to an improved process for treating textile materials which are blends of cellulosic and polyester fibers so as to cause fibers of both those classifications to be flame retardant concurrently.

Description of the prior art

Although polyester-cotton blends are one of the more common types of fabrics in current use, there is a paucity in the art of conferring fire resistance to such blends.

The situation regarding blended polyester-cotton is unusual, inasmuch as fabrics solely of polyester fiber normally meet specifications for flame retardancy, such as the "Vertical Test" of the American Association of Textile Chemists and Colorists, AATCC 34–1966, without the addition of a fire retardant finish. However, when only the cotton fibers of a blended fabric are rendered flame retardant, the resulting product is quite flammable and does not meet flame retardancy specifications. This is due to the fact that when 100 percent polyester fabric is exposed to a flame, the polyester melts and drips away largely unburned, while on exposure of a blended fabric of polyester and flame-resistant cotton to a flame, the cotton prevents the polyester from dripping away.

Satisfactory flame retardancy is obtained only when both polyester fibers and cotton fibers are rendered individually flame retardant. Heretofore, one proposal for rendering both types of fibers individually flame retardant in a blended fabric has been to combine two treatments, one designed to treat polyester and the other cotton fibers. In work described in American Dyestuff Reporter, vol. 57, page 373 (May 6, 1968), samples of blended fabric were treated with compositions containing tetrakis(hydroxymethyl)phosphonium chloride, a known fire retardant for cellulosic fabric and then other samples were treated with tetrakis(hydroxymethyl)phosphonium chloride formulations plus tris(2,3-dibromopropyl) phosphate, a known polyester fire retardant. Only one of the treating procedures, which did not include tris(2,3-dibromopropyl) phosphate, gave satisfactory flame retardancy. In this procedure, the fabric was padded at 80° F. with a formulation containing tetrakis(hydroxymethyl)phosphonium chloride, trimethylolmelamine, urea, sodium hydroxide, polyethylene emulsion and nonionic wetting agent at a wet pickup of 80 percent. The fabric was dried at 200° F. and then cured for three minutes at 320° F. While this procedure gives satisfactory initial flame retardancy, the physical properties of the fabric are severely damaged, the fabric is unduly stiffened, and the flame retardancy is not sufficiently durable to withstand repeated washings. The addition of tris(2,3-dibromopropyl) phosphate to the above-described treatment gives a slight improvement in flame retardancy, but the problems of physical property deterioration and undue stiffness remain.

SUMMARY OF THE INVENTION

In accordance with the present invention, excellent flame retardancy of cellulosic-polyester blends is obtained without the necessity of applying a separate polyester flame retardant such as tris(2,3-dibromopropyl) phosphate and without unduly deteriorating physical properties or imparting objectionable stiffness. The cellulosic-polyester blended fabrics are rendered durably flame retardant by impregnating with

(A) tetrakis(hydroxymethyl)phosphonium chloride and urea or a precondensate of these reactants,
(B) a reaction product of melamine with either formaldehyde or formaldehyde and methanol, and
(C) a fatty acid ester of polyethylene glycol and forming insoluble reaction products on said fabric. It is essential that the reaction product containing melamine be insolubilized in the presence of moisture such as by steam curing.

DETAILED DESCRIPTION OF THE INVENTION

This invention provides a method of rendering a polyester cellulosic blend fabric flame retardant by impregnating the fabric with the following chemical systems:

System A: Tetrakis(hydroxymethyl)phosphonium chloride and urea or a precondensate of these reactants,
System B: Melamine-formaldehyde reaction product or a melamine-formaldehyde-methanol reaction product, and
System C: An ester derived from polyethylene glycol and a higher aliphatic carboxylic acid,

and forming insoluble reaction products on said fabric from the above-described chemicals.

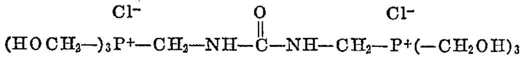
The chemicals of Systems A and B form insoluble products on curing, which are essential to the desired flame retardancy, while the polyethylene glycol ester of System C must be present on the fabric during the formation of insoluble products from the chemicals of System B. The presence of the polyethylene glycol ester assists in carrying insoluble products to the polyester component and also prevents the insoluble products from making the fabric unduly stiff.

All of the components of Chemical Systems A, B and C can be applied and then the desired insoluble products formed simultaneously, thus, for instance, all of the chemicals can be applied from a single bath such as by padding from an aqueous dispersion, and then the desired insoluble products formed simultaneously in a single curing step. Alternatively, the polyethylene glycol ester of System C can be added to the fabric, along with the chemicals of System B, an insoluble product formed by curing and then the chemicals of System A added and insolubilized. Additionally, the chemicals of System A can be added and insolubilized and then the polyethylene glycol ester of System C can be added to the fabric along with the chemicals of System B, and insoluble products formed by curing.

The compounds of System A form an insoluble product containing bound phosphorus and bound nitrogen. The insoluble product can be formed by the reaction on the fabric of tetrakis(hydroxymethyl)phosphonium chloride and urea. Alternatively, there can be applied to the fabric a precondensate of tetrakis(hydroxymethyl)phosphonium chloride and urea which is subsequently further reacted. Procedures for preparing such precondensates are described by Reeves et al. U.S. Pat. 2,812,311 and Coates U.S. Pat. 2,983,623. The following equation illustrates the formation of a suitable precondensate:

$$2(H_2N-)_2C{=}O + (HOCH_2-)_4P^+Cl^- \longrightarrow$$

(urea) tetrakis(hydroxymethyl)phosphonium chloride



$$(HOCH_2-)_3\overset{Cl^-}{P^+}-CH_2-NH-\overset{\overset{\displaystyle O}{\|}}{C}-NH-CH_2-\overset{Cl^-}{P^+}(-CH_2OH)_3$$

Ureylenedimethylene)bis[tris(hydroxymethyl)phosphonium]dichloride

The use of a precondensate minimizes objectionable odor during formation of an insoluble product on the fabric. The compounds of System A can be reacted to form an insoluble product by heating at a temperature of about 60–250° C. or by the wet fixation procedures described below.

The component of System B is an N-methylol derivative of melamine having from two to six methylol groups or a methyl ether derived from such an N-methylol compound wherein the sum of $-CH_2OH$ groups and $-CH_2OCH_3$ groups is from two to six. The N-methylol compounds can be prepared by reacting melamine with two or more moles of formaldehyde according to known procedures. The methyl ethers can be prepared by known procedures by reacting the N-methylol compounds with methanol or coreacting melamine, formaldehyde and methanol.

To avoid unduly deteriorating the physical strength of the fabrics, the components of System B cannot be insolubilized by dry heat, but rather wet fixation procedures must be used. In such wet fixation, the components of System B are formed into an insoluble product while the moisture content of said fabric is at least 20 percent based on the weight of the fabric. Wet fixation is preferably accomplished by contacting the impregnated fabric with steam. Alternatively, wet fixation can be carried out at lower temperatures by maintaining the fabric in a moist environment at a temperature and for a period of time sufficient to form an insoluble product. For instance, the fabric can be impregnated with an aqueous solution of N-methylolmelamine, the fabric wrapped in polyethylene while a substantial amount of water remains in the fabric, and the wrapped fabric stored at a temperature of at least 20° C. until the desired degree of insolubilization is reached. Use of wet fixation, rather than dry curing, greatly reduces the amount of crosslinking of the N-methylol-type compound with cellulose, thus eliminating undue loss of fabric strength.

System C represents a critical feature of the invention, and stems from the discovery that a particular type of adjunct makes it possible to impart flame retardancy simultaneously to both cellulosic and polyester fibers without causing objectionable stiffness of the treated fabric, the adjunct being a higher aliphatic carboxylic ester derived from polyethylene glycol.

Suitable polyethylene glycol esters have the formula

$$A(-OCH_2CH_2-)_mOA'$$

wherein

A is an acyl group derived from a saturated or unsaturated aliphatic monocarboxylic acid of 8–24 carbon atoms;
A' is hydrogen or an acyl group derived from a saturated or unsaturated aliphatic monocarboxylic acid of 8–24 carbon atoms, and
m is an integer of from about 4 to 80.

Oleic acid is the preferred acid for making the esters, which include both di-esters as well as mono-esters. Particularly outstanding results are obtained with polyethylene glycol monooleate. Illustrative of other suitable acids are palmitoleic, lauric, myristic, palmitic, stearic, and arachidic acids.

Useful polyethylene glycols for making the esters have the formula

$$H(-OCH_2CH_2-)_mOH$$

wherein *m* is 4 to 80.

A conventional way in which various commercial compositions of closely related polyethylene glycols are named is by appending to the term "polyethylene glycol" a round number approximately the average molecular weight. This is illustrated in Table A.

TABLE A.—ILLUSTRATIVE POLYETHYLENE GLYCOLS

Conventional name of commercial product	Molecular weight, M	Number of oxyethylene units, *m*, in $H(-OCH_2CH_2-)_mOH$
Polyethylene glycol 200	194	4
Polyethylene glycol 300	282	6
Polyethylene glycol 400	414	9
Polyethylene glycol 600	590	13
Polyethylene glycol 1000	986	22
Polyethylene glycol 1540	1,558	35
Polyethylene glycol 4000	3,406	77

Blends of two or more of such products as are illustrated in Table A may be used in making the ester which is to serve in System C of the process of this invention. For instance, a blend of equal parts of polyethylene glycols 300 and 1540 is particularly useful. Major species in that particular blend (conventionally designated as polyethylene glycol 1500) are

$$H(-OCH_2CH_2-)_6OH$$

and

$$H(-OCH_2CH_2-)_{35}OH$$

An important feature of the present invention is that the nonreactive fatty esters of polyethylene glycol are key factors in accomplishing the following two crucial objectives:

(1) They make possible the flame retardancy of the synthetic fiber component of the fabric blend (and with the same agents which are effective in imparting flame retardancy to the cellulosic fiber component).

(2) They keep fabric stiffness at an acceptably low level for a flame-resistant fabric.

Hence, incorporation of the soluble ester composition of this invention into a pad bath of one or more of the flame-retardant ingredients, and the subsequent formation of the flame-retardant finish, provides an effective durable flame-retardant treatment for blends without the problem of excessive stiffness. The nonreactive fatty esters of polyethylene glycol make it possible to attain desirably high add-ons of bound nitrogen (4 to 7 percent) and phosphorus (2 to 4 percent) with a balanced distribution on both cellulosic and noncellulosic components of the synthetic-cellulosic fabric blend.

Heretofore, the high add-ons of the composition supplying bound nitrogen which were required to attain a practical degree of flame retardancy in conjunction with a compound of phosphorus characteristically resulted in too much stiffening. That was even the situation when nitrogen-rich compositions, such as melamine-formaldehyde addition reaction products were used.

Not only do the nonreactive esters of polyethylene glycol improve flame retardancy of fabric blends, but stiffness is kept at a level which is but a fraction of the stiffness which normally would result with blends which are otherwise difficult to make flame retardant.

Another surprising aspect of the nonreactive esters of polyethylene glycol is that they are quite specific in bringing about the beneficial effects discussed above. Closely related derivatives, such as polyethylene glycols or their monoesters, having a methoxy group in place of a terminal hydroxy group are hardly effective in meaningful control of stiffness.

The results obtained are particularly remarkable in view of the fact that the nonreactive fatty esters of polyethylene glycol which make possible the improved process of this invention are not per se durable additives. On the contrary, they are water-soluble, and are substantially removed in the rinsing operations of the process, their beneficial effect on flame retardancy being unexpected.

The present invention can be used with cellulose-polyester blended fabrics containing from 10 to 90 percent cellulose and from about 90 to 10 percent polyester.

Illustrative of suitable commercial blended fabrics are: polyester 20% and cotton 80%, polyester 35% and cotton 65%, polyester 50% and cotton 50%, polyester 65% and cotton 35%, polyester 80% and cotton 20%, and polyester 65% and regenerated cellulose (as viscose rayon) 35%. The invention is applicable likewise to other ratios, and to blends having fiber types in addition to cellulosic and polyester types, such as the blend consisting of polyester 37%, cotton 35%, and spandex 28%. Cellulose fibers include those made from (a) seed hairs, e.g., cotton, (b) bast fibers such as flax (linen), and (c) rayon and modified rayons.

The following examples are given to further illustrate the invention, but it is to be understood that the invention is not to be limited in any way by the details described therein. Examples 1–3 illustrate the ability of the polyethylene glycol esters employed in the present invention to prevent undue stiffening of the treated cellulose-polyester blended fabrics, while the remaining examples illustrate the methods of the present invention for rendering such blended fabrics flame retardant. In the examples percents and parts are by weight unless otherwise specified.

Analytical and test methods employed in the examples

Bound Nitrogen, N: Determined Kjeldahl digestion followed by titration of distilled ammonia.

Bound Phosphorus, P: Determined by Kjeldahl digestion followed by colorimetric analysis employing acetone-water to intensify the phosphomolybdate color (Bernhart et al., Anal Chem., vol. 27, 440 (1955)).

Flame Retardancy (Semicircular Test), burning in seconds (to a recorded angle in degrees): G. Schon, Melliand Textilber., vol. 48, 215 (1967).

Flame Retardancy (Vertical Test), char length in inches: AATCC 34–1966. A char length of about 6 inches or shorter is passable.

Flex Abrasion Resistance, in cycles: ASTM D 1175–44T (0.5-pound head weight and 2-pound toggle tension on Stoll Flex Abrader).

Laundering: AATCC 88A–1964T, Test III, home-type

washer, 5-pound load, full cycle, 60° C., synthetic detergent; tumble drying.

Stiffness (Cantilever), in mg.-cm.: ASTM D 1388–64.

Tear Strength (Elmendorf), in pounds: ASTM D 1424–59.

Whitness Rating: AATCC 110–1964T.

Abbreviations used in the examples

OWB: On the weight of the bath used for padding, in percent.

OWF: On the weight of the fabric, in percent.

Wet pickup (in percent) times OWB/100%=OWF.

PEG: Polyethylene glycol.

THPC: Tetrakis(hydroxymethyl)phosphonium chloride, $(HOCH_2—)_4PCl$.

TMM: Trimethylolmelamine, (s-triazine-2,4,6-triyltriimino)trimethanol.

EXAMPLE 1

This example provides a comparison of the extents to which various additives derived from polyethylene glycols affect stiffness of a polyester-cellulose blend on which trimethylolmelamine is insolubilized by steaming.

The substrate fabric was 50–50 polyester-cotton poplin suiting weighing 6.24 ounces per square yard, and having a thread count (warp by filling) of 129 by 49 per inch. Its stiffness was 550 milligram-centimeters in the warp direction. Samples were padded with an aqueous solution of trimethylolmelamine (28%), hydrogen peroxide (0.3%), and an additive (polyethylene glycol derivative) present in the percentage shown in the accompanying table. (For the control sample, only the additive was omitted.) The wet pickup was 72–81%. Then the samples were dried at room temperature (approximately 21° C.) to a moisture content of 20%. While on a frame, samples were steamed for 8 minutes. They were then washed in warm water, framed to original dimensions, dried in an oven at 105° C., and reweighed. Results of observations and calculations are shown in the accompanying table.

TABLE FOR EXAMPLE 1

Additive (PEG derivative): $X(—OCH_2CH_2—)_mOX'$						
Polyethylene gylcol derivative	X	X'	Major values of *m*	Percent in pad bath	Weight gain percent on poplin suiting	Stiffness, mg.-cm. (ward direction)
Control (no additive)	None	None	None	None	19.3	10,000
Methoxy PEG 750	H	$CH_3—$	16	7.5	21.5	>10,000
Methoxy PEG 750 monooleate	Oleoyl	$CH_3—$	16	10.1	19.9	7,000
PEG 1500 dioleate	do	Oleoyl	6:35	10.7	22.9	6,750
PEG 1000 monoostearate	Stearoly	H	22	12.6	21.1	3,800
PEG 1500 monooleate	Oleoyl	H	6:35	4.0	19.6	2,060
PEG 1500 monooleate	do	H	6:35	8.1	19.6	1,050
Blank (untreated poplin suiting)	Not even treated with TMM			None	None	550

By comparing the weight gains with that of the control (19.3%), it is evident that insolubilization of trimethylolmelamine on the fabric blend was not impaired by the presence of any of the additives. Note that the additives were derived in a variety of ways from polyethylene glycols of representative molecular-weight ranges.

EXAMPLE 2

This is a variation of Example 1 using less trimethylolmelamine.

The procedure of Example 1 was repeated, but trimethylolmelamine was applied from a 20% solution (instead of 28%). Results of measurements are shown in the accompanying table.

TABLE FOR EXAMPLE 1

Additive (PEG derivative): $X(—OCH_2CH_2—)_mOX'$						
Polyethylene gylcol derivative	X	X'	Major values of *m*	Percent in pad bath	Weight gain percent on poplin suiting	Stiffness, mg.-cm. (warp direction)
Control (no additive)	None	None	None	None	13.4	8,000
Methoxy PEG 750	H	$CH_3—$	16	7.5	15.8	10,100
Methoxy PEG 750 monooleate	Oleoyl	$CH_3—$	16	10.1	16.4	4,110
PEG 1500 dioleate	do	Oleoyl	6:35	10.7	19.6	3,500
PEG 1000 monostearate	Stearoly	H	22	12.6	16.8	1,430
PEG 1500 monooleate	Oleoyl	H	6:35	4.0	13.8	1,650
PEG 1500 monooleate	do	H	6:35	8.1	16.7	850
Blank (untreated poplin suiting)	Not even treated with TMM			None	None	540

Conclusions are similar to those of Example 1. In addition, stiffness was less because less trimethylolmelamine had been applied to the fabric blend from the more dilute pad bath.

EXAMPLE 3

This example provides evidence that significant amounts of trimethylolmelamine are insolubilized on polyester fibers, and that ester-polyethers reduce stiffness of those synthetic fibers.

In order to show the magnitude of the effectiveness of both insolubilized trimethylolmelamine and esterpolyethers specifically on synthetic (as distinguished from cellulosic) fibers, the following procedure was carried out. Taffeta samples of 100% polyester, having a stiffness of 600 milligram-centimeters, were padded with an aqueous solution of trimethylolamine (34%), hydrogen peroxide (0.3%), and an additive (polyethylene glycol derivative) present in the percentage shown in the accompanying table. The wet pickup was 37%. Then the samples were processed in the manner described in Example 1. Results are shown in the accompanying table.

TABLE FOR EXAMPLE 3

Additive (PEG derivative): $X(—OCH_2CH_2—)_mOX'$

Polyethylene glycol derivative	Formula of major species in closely related series	Percent in pad bath	Weight gain, percent on polyester taffeta	Stiffness, mg.-cm. (warp direction)
Control (no additive)	Omitted	None	11.8	800
Methoxy PEG 750 acetate	$CH_3CO(—OCH_2CH_2—)_{16}OCH_3$	3.9	12.2	1,410
Do	$CH_3CO(—OCH_2CH_2—)_{16}OCH_3$	7.9	12.6	1,160
PEG 1000 dioleate	$C_{17}H_{33}CO(—OCH_2CH_2—)_{22}OCOC_{17}H_{33}$	12.7	11.1	720
PEG 1500 monooleate	$C_{17}H_{33}CO(—OCH_2CH_2—)_6OH$ and $C_{17}H_{33}CO(—OCH_2CH_2)_{35}OH$	4.0	8.0	330
Do	$C_{17}H_{33}CO(—OCH_2CH_2—)_6OH$ and $C_{16}H_{33}CO(—OCH_2CH_2)_{35}OH$	8.1	5.1	310
Blank (untreated polyester taffeta)	Not even treated with TMM	None	None	600

EXAMPLE 4

The fabric used was 50–50 polyester-cotton sheeting in a plain weave, weighing 3.56 ounces per square yard, and having a thread count (warp by filling) of 102 by 80 per inch. Its stiffness was 84 milligram-centimeters in the warp direction. The fabric was padded with an aqueous solution of trimethylolamine (20%), hydrogen peroxide (0.3%), and polyethylene glycol 1500 monooleate (8.0%), $C_{17}H_{33}CO(—OCH_2CH_2—)_mOH$ having 6 and 35 as major values of *m*.

The pressure of the pad rolls was adjusted to give a wet pickup of 71 to 74%.

The padded fabric was partially dried in air to a moisture content of (25±5)%. Then it was wrapped in polyethylene foil to prevent loss of moisture, and stored at 41° C. for 72 hours to effect wet fixation. Next, the fabric was rinsed in hot water, then in cold water, and dried in a forced-air oven at 105° C. Results are in the accompanying table.

TABLE A FOR EXAMPLE 4

Trimethylolmelamine				Stiffness, mg.-cm. (warp)	
OWB, percent	OWF, percent	Weight gain, percent	N, percent found	Before laundering	After one laundering
20	14.2	9.2	4.0	140	96
Blank [1]				84	

[1] Untreated sheeting.

Samples of the fabric pretreated with trimethylolmelamine were padded with a precondensate of tetrakis(hydroxymethyl)phosphonium chloride and urea (2:1 ratio by moles). (In one instance, pH was left at 2.8, and in another series, pH was raised to 6.1 by N,N',N''-nitrilotriethanol, commonly called triethanolamine. See the accompanying table.) The samples were dried on frames at 82° C., and cured at 163° C. for 5 minutes in a forced-air oven. The cured samples were rinsed in 2.8% ammonium hydroxide solution for 5 minutes at approximately 21° C., and then for 5 minutes at 50° C. in an aqueous solution containing 0.06% hydrogen peroxide and 0.5% of a nonionic detergent (a mixture of closely related compounds having the formula

$$(CH_3)_3CCH_2C(CH_3)_2(p\text{-}C_6H_4)(—OCH_2CH_2)_nOH$$

with the average value of *n* being about 10). Next, the samples were rinsed for 5 minutes in water at 90° C. Then the samples were dried on frames at 105° C. Results, both prior to laundering and after numerous cycles of laundering and drying, are in the accompanying table.

TABLE B FOR EXAMPLE 4

	Pad bath pH	
	2.8	6.1
2:1 THPC:Urea precondensate, percent OWF	25.2	23.0
Weight gain, percent, after rinsing and drying	13.1	12.2
Bound P, percent, after rinsing and drying but before laundering	2.37	2.0
Bound N, percent, after rinsing and drying but before laundering	4.78	4.46
Char length, inches (vertical flame test)	5.1	4.2
Stiffness, mg.-cm. (warp direction):		
Before laundering	1,440	1,150
After 1 laundering	960	1,080
Bound phosphorus, percent:		
After 25 launderings	2.27	1.6
After 50 launderings	2.27	1.6
Bound nitrogen, percent:		
After 25 launderings	4.41	4.5
After 50 launderings	3.80	4.5
Char length, inches (vertical flame test):		
After 10 launderings	5.5	5.5
After 25 launderings	7.3	7.2
After 50 launderings	7.5	7.3

EXAMPLE 5

This example describes the single-step process with a 30-second steaming period to impart durable flame retardance to a synthetic-cellulosic fabric blend.

The fabric used was 50–50 polyester-cotton suiting in a plain weave, weighing 6.71 ounces per square yard, and having a thread count (warp by filling) of 74 by 37 per inch. It was padded (to a wet pickup of 78%) using an aqueous pad bath having respectively 14.4%, 7.0%, and 28.9% of each of the following components: trimethylolmelamine, polyethylene glycol 1500 monoleate, and (ureylenedimethylene)bis[tris(hydroxymethyl)phosphonium] dichloride. The latter compound had been made by a condensation reaction involving tetrakis(hydroxymethyl)phosphonium chloride (2 moles) and urea (1 mole). Prior to padding, the pH of the pad bath had been raised to 6 by the addition of a relatively small quantity of N,N',N''-nitrilotriethanol.

The fabric was dried at approximately 71° C. on a pin frame. Then the pin frame with the fabric on it was placed horizontally in a chamber designed for steaming. Steam at approximately 102° C. was introduced, and the fabric was exposed to it for 30 seconds. Next, the fabric was rinsed according to the rinsing procedure described in Example 4. Then the treated fabric blend was dried on a frame at 105° C. Data in the accompanying table demonstrate that this suiting fabric had durable flame retardance. Note that the fabric had been impregnated with (ureylenedimethylene)bis[tris(hydroxymethyl)phosphonium] dichloride, trimethylolmelamine, and polyethylene glycol monooleate in the relative amounts by weight of approximately 4, 2, and 1, respectively.

TABLE FOR EXAMPLE 5

Trimethylolmelamine, percent OWF	11.2
PEG 1500 monooleate, percent OWF	5.45
2:1 THPS:urea precondensate, percent OWF	22.4

TABLE FOR EXAMPLE 5—Continued

Weight gain, percent, after rinsing and drying	25.3
Char length, inches (Vertical Flame Test):	
Before laundering	4.3
After 10 launderings	4.5
After 25 launderings	5.0

EXAMPLE 6

This example consists of a variation of Example 4.

The steps of Example 4 were applied to 50–50 polyester-cotton sheeting in a plain weave and weighing 3.67 ounces per square yard. The warp-by-filling count was 101 by 81 threads per inch. In the first step, a sample was padded with an aqueous solution of trimethylolmelamine (20%), hydrogen peroxide (0.3%), and polyethylene glycol 1500 monooleate (8.0%), and processed by wet fixation as in Example 4. In the second step, the same precondensate as in Example 4 was used (the pad bath having been adjusted to pH 6 by a relatively small quantity of N,N′,N″-nitrilotriethanol). The sample was processed as in Example 4. Results are in the accompanying table.

TABLE FOR EXAMPLE 6

N, percent, from TMM pretreatment	4.2
2:1 THPC:urea precondensate, percent OWF	22.0
Weight grain, percent, after curing, washing and drying	11.9
Bound phosphorus, percent	2.59
Bound nitrogen, percent	5.55
Char length, inches (Vertical Flame Test)	3.8
Tear strength, pounds:	
Warp	1.9
Filling	1.2
Flex abrasion resistance, cycles	1500+
Stiffness, mg.-cm. (warp direction):	
Before laundering	1230
After 1 laundering	870
Whiteness	+77

EXAMPLE 7

In this example the order of the two steps of Example 6 is reversed.

Another portion of the synthetic-cellulosic blend fabric used as the substrate in Example 6 was processed with the ingredients of that example, but the order of the two steps was reversed. That is, this time Step 1 consisted of padding on the precondensate of Example 4 (after the pad bath had been adjusted to pH 6 by addition of N,N′,N″-nitrilotriethanol), followed by curing as in Example 4. This time, Step 2 consisted of padding with an aqueous solution of trimethylolmelamine (20%), hydrogen peroxide (0.3%), and polyethylene glycol 1500 monooleate (8.0%), and processing by wet fixation as in Example 4. Results are in the accompanying table.

TABLE FOR EXAMPLE 7

2:1 THPC:urea precondensate, percent OWF	24.5
Weight gain, percent, after curing, washing and drying in Step 1	11.1
Trimethylolmelamine, percent OWF	18.5
Weight gain, percent after wet fixation, washing and drying in Step 2	12.2
Tear strength, pounds:	
Warp	1.7
Filling	1.4
Flex abrasion resistance, cycles	900
Whiteness	+37
Stiffness, mg.-cm. (warp direction):	
Before laundering	730
After 1 laundering	430
Percent P:	
Before laundering	1.9
After 10 launderings	1.9

TABLE FOR EXAMPLE 7—Continued

Percent N:	
Before laundering	4.8
After 10 launderings	4.5
Char length, inches:	
Before laundering	7.0
After 10 launderings	7.9

EXAMPLE 8

This is a variation of Example 6 using a 2:1.25-by-moles precondensate of tetrakis(hydroxymethyl)phosphonium chloride and urea.

The synthetic-cellulosic blend fabric and the first step were the same as those of Example 6. The second step was similar to that of Example 6, except the precondensate had been made from tetrakis(hydroxymethyl)phosphonium chloride and urea in the ratio of 2:1.25 by moles. Results are in the accompanying table.

TABLE FOR EXAMPLE 8

N, percent from TMM pretreatment	5.2
2:1.25 THPC:urea precondensate, percent OWF	23.6
Weight gain, percent, after curing, washing and drying	13.9
Char length, inches (Vertical Flame Test):	
Before laundering	5.0
After 10 launderings	5.1
After 25 launderings	5.1
After 50 launderings	5.5

EXAMPLE 9

This example provides a comparison of the relative effectiveness of polyethylene glycol monooleate and tris(2,3-dibromopropyl)phosphate in the single-step process involving brief steaming to impart durable flame retardance on a synthetic cellulosic blend.

The single-step padding process was applied to the 50–50 polyester-cotton suiting described in Example 5. The compositions of the pad baths (and other variables) are shown in the accompanying table. Tris(2,3-dibromopropyl)phosphate was in emulsified form. Prior to padding, the pH of each pad bath was raised to 5 by the addition of a relatively small quantity of N,N′,N″-nitrilotriethanol. The wet pickup of the ingredients was 70 to 73%. The padded samples were dried at approximately 71° C. on a pin frame and then the pin frame with the fabric on it was placed horizontally in a chamber designed for steaming. Steam at approximately 102° C. was introduced, and the fabric was exposed to it for 4 minutes. Next, the fabric was rinsed according to the rinsing procedure described in Example 4 and then dried on a frame at 105° C. Data in the accompanying table demonstrate that this suiting fabric had durable flame retardance.

TABLE FOR EXAMPLE 9

PEG 1500 monooleate:		
Percent OWB	3.3	None
Percent OWF	2.3	None
Tris(2,3-dibromopropyl) phosphate:		
Percent OWB	None	6.7
Percent OWF	None	4.9
Trimethylolmelamine:		
Percent OWB	14.7	14.7
Percent OWF	10.3	10.7
2:1 THPC: urea precondensate:		
Percent OWB	29.4	29.4
Percent OWF	20.6	20.6
Weight gain, percent, after rinsing and drying	18.8	23.0
Char length, inches (vertical flame test):		
Before laundering	4.5	3.3
After 10 launderings	4.5	3.0
After 25 launderings	4.5	4.5

Based on char lengths in the vertical flame tests, particularly after numerous launderings, polyethylene glycol monooleate is comparable in effectiveness with tris(2,3-dibromopropyl) phosphate, a commonly used brominated additive to augment the flame retardancy of such blends. Moreover, when polyethylene glycol 1500 monooleate was used, the weight gain (after rinsing and drying) was

18.8%, definitely less than the weight gain of 23.0% when tris(2,3-dibromopropyl) phosphate was used. Inasmuch as polyethylene glycol 1500 monooleate is a nonreactive additive, it is not insolubilized on the fibers. Nevertheless it significantly assists in rendering both fiber components flame retardant in the fabric.

EXAMPLE 10

This example illustrates wet fixation of bound nitrogen in the pretreatment step, and insolubilization of bound phosphorus-nitrogen by ammonia in the next step.

The fabric used was 50–50 polyester-cotton sheeting in a plain weave, weighing 3.67 ounces per square yard, and having a thread count (warp by filling) of 101 by 81 per inch. Samples were padded with an aqueous solution of trimethylolmelamine (28%), hydrogen peroxide (0.3%), and polyethylene glycol 1500 monooleate (8.0%). The pressure of the pad rolls was adjusted to give a wet pickup of 71 to 74%. The padded sample was partially dried and subjected to wet fixation as described in Example 4. Next, another step was carried out to add bound phosphorus and additional bound nitrogen. In order to accomplish this, the sample was padded with a precondensate of tetrakis (hydroxymethyl)phosphonium chloride and urea (2:1 ratio by moles), namely (ureylenedimethylene)bis[tris(hydroxymethyl)phosphonium] dichloride. (The pad bath was at pH 2.2.) The sample was partially dried and then exposed to ammonia vapor for 10 minutes at approximately 21° C. Next, the sample was rinsed by the multiple rinsing procedure described in Example 4. Results are in the accompanying table.

TABLE FOR EXAMPLE 10

N, percent, from TMM pretreatment	5.2
2:1 THPC:urea precondensate, percent OWF	19.5
Weight gain, percent, after washing and drying	10.9
Stiffness, mg.-cm. (warp direction)	890
Char length, inches (Vertical Flame Test):	
Before laundering	4.4
After 10 launderings	4.4
After 25 launderings	7.0
Semicircular Flame Test, seconds (angle):	
Before laundering	5 (30°)
After 10 launderings	5 (30°)
After 25 launderings	25 (20°)

EXAMPLE 11

This is a variation of Example 5 in which the reactive derivative of melamine is different.

Example 5 is repeated with the exception that trimethylolmelamine is replaced by a melamine-formaldehyde reaction product made from substantially 6 moles of formaldehyde and 3 moles of methanol per mole of melamine. The result is that a desirable degree of durable flame retardance is imparted to the suiting fabric.

EXAMPLE 12

The procedure of Example 5 was repeated using as the fabric a series of polyester-cotton sheet fabrics having different polyester to cotton ratios. The results are given in the following table.

TABLE FOR EXAMPLE 12

Polyester-cotton sheeting	THPC: Urea precondensate, percent OWF	TMM, percent OWF	PEG 1500 monooleate, percent OWF	Percent weight gain *	Char length		
					Orig.	10 L	25L
80/20	21.8	10.9	4.9	23.8	6.1	6.1	6.5
65/35	22.1	11.0	5.0	24.5	5.1	4.7	3.9
50/50	21.4	10.7	4.9	24.2	5.0	5.0	4.9
20/80	22.9	11.5	5.2	26.3	4.4	4.0	4.4

* After rinsing and drying.

It will be apparent that many modifications and variations may be effected without departing from the scope of the novel concepts of the present invention, and the illustrative details disclosed are not to be construed as imposing undue limitations on the invention.

We claim:

1. A process for treating cellulose-polyester blended fabric to render said fabric flame retardant, said process comprising

(a) impregnating said fabric with component A comprising tetrakis(hydroxymethyl)phosphonium chloride and urea or a precondensate of these reactants and forming on said fabric an insoluble reaction product form component A;

(b) impregnating said fabric with a melamine derivative prepared by reacting melamine with either formaldehyde or formaldehyde and methanol, said melamine derivative having attached to its nitrogen atoms from 2 to 6 substituents of the formula $—CH_2OZ$ wherein

Z is hydrogen or $—CH_3$

and forming an insoluble product on the fabric from said melamine derivative while maintaining the moisture content of said fabric at a minimum of 20% by weight based on the weight of said fabric, and

(c) impregnating said fabric with a polyethylene glycol ester of the formula $A(—OCH_2CH_2—)_mOA'$ wherein

A is an acyl group derived from an aliphatic monocarboxylic acid of from 8—24 carbon atoms;

A' is hydrogen or an acyl group derived from an aliphatic monocarboxylic acid of from 8–24 carbon atoms, and

m is an integer of from 4 to 80,

said polyethylene glycol ester being impregnated into said fabric prior to the insolubilization of said melamine derivative, in an amount sufficient to reduce the stiffness of the treated fabric and said fabric being dried after the insolubilization of the melamine derivative in the presence of moisture.

2. A process as claimed in claim **1** wherein said component A and said melamine derivative are simultaneously insolubilized while maintaining the moisture content of said fabric at a minimum of 20 percent by weight based on the weight of said fabric.

3. A process as claimed in claim **1** wherein said component A is insolubilized on said fabric prior to impregnating said fabric with said melamine derivative and said polyethylene glycol ester.

4. A process as claimed in claim **1** wherein said melamine derivative is insolubilized on said fabric in the presence of said polyethylene glycol ester prior to impregnating said fabric with component A.

5. A process as claimed in claim **1** wherein said component A is a precondensate of tetrakis(hydroxymethyl)-phosphonium chloride and urea.

6. A process as claimed in claim **1** wherein said melamine derivative is trimethylolmelamine.

7. A process as claimed in claim **1** wherein said polyethylene glycol ester is polyethylene glycol monooleate.

8. A process as claimed in claim **1** wherein said melamine derivative is insolubilized on said fabric by contacting the fabric with steam.

9. A process as claimed in claim **1** wherein said component A is a precondensate of tetrakis(hydroxymethyl) phosphonium chloride and urea, said methylol derivative is trimethylolmelamine and said polyethylene glycol ester is polyethylene glycol monooleate.

10. A process as claimed in claim **8** wherein said component A is a precondensate of tetrakis(hydroxymethyl) phosphonium chloride and urea, said methylol derivative is trimethylolmelamine and said polyethylene glycol ester is polyethylene glycol monooleate.

11. A flame retardant cellulose-polyester blended fabric produced by the process of claim **1.**

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