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(54) Treatment of fabrics.

(57) A process for the treatment of fabrics, in particular polyester cotton, which are treated with THP compounds, especially condensates thereof with urea, and heat cured, optionally with ammonia, to give higher fire retardance than corresponding fabrics cured with ammonia alone.

This invention relates to a fabric treatment process, in particular one for rendering fabrics flame retardant with organo phosphorus compounds.

The flame retardant treatment of cotton fabric with tetrakis (hydroxymethyl) phosphonium compounds (hereafter called THP compounds) or precondensates thereof with urea has been described in USP2983623, 4068026, 4078101, 4145463 and 4494951. The treatment processes involved impregnation of the fabric with an aqueous solution of the chemicals, followed by drying, treatment with ammonia to cure the phosphorus compounds in order to insolubilize the phosphorus onto the fabric, finally with oxidation and washing to leave a treated fabric whose flame resistance is retained even after many washes in use.

However the cure efficiency, (which is a measure of the effectiveness of the cure in insolubilizing the phosphorus on the fabric), is not always ideal and a percentage of the expensive phosphorus chemicals applied in the impregnation step is not cured. Thus it is washed off the fabric after the cure and wasted, particularly for cotton polyester fabrics and especially polyester cotton fabrics. In some cases, adequate flame retardant properties cannot be provided to the latter with THP compounds. Furthermore, while some techniques enable the necessary flame retardant properties to be provided to the fabric when first cured, those properties often diminish significantly on repeated washing.

We have discovered a process which can increase the amount of P compound fixed onto the substrate especially one comprising non cellulosic fibres and can enable adequate flame retardant properties to be provided for fabrics comprising non cellulosic fibres such as cotton polyester blends.

The present invention provides a process for the flame-retardant treatment of an organic fibrous substrate containing reactive groups, which process comprises impregnating said substrate with an aqueous solution of an organophosphorus compound, to provide an impregnated substrate which is dried and cured, by heating at a temperature of at least 100° C.

The organic fibrous substrate is especially one comprising or consisting essentially of cellulosic fibres. The cellulosic fibres are preferably natural cotton, but may be ramie, flax, paper or cardboard or regenerated fibres (e.g. viscose or cuprammonium fibres) or partly etherified or esterified cellulose (e.g. cellulose acetate or propionate). The substrate may be substantially completely cellulosic eg 100% cotton or may contain both cellulosic and non cellulosic organic fibres, or just contain non cellulosic organic fibres eg 100% polyester fibres. Inorganic fibres such as glass fibres are usually absent.

The non cellulosic fibres are preferably polyester or polyamide fibres but may also be acrylic. The polyamide may be an aliphatic one, such as copolymers of a polyamine (such as a diamine) preferably an alkylene diamine, eg of 4-12 carbon atoms and a poly carboxylic acid eg a dicarboxylic acid, of 4-14 carbon atoms such as an alkylene dicarboxylic acid (e.g. Nylon 66), or polylactams such as Nylon 6. Alternatively the polyamide may be an aromatic one, such as aramids based on aromatic dicarboxylic acids and phenylene diamines. The acrylic polymer may be polyacrylonitrile homopolymer or copolymer with vinyl chloride, as in modacrylic fibres. The substrate can contain at least 20% of cellulosic fibres and up to 80% of coblendable fibres e.g. 10-80% especially 25-80% of coblendable fibres such as polyamides. However preferably the substrate comprises cellulosic fibres and polyester fibres. The substrate usually contains up to 80% (e.g up to 70%) polyester fibres and from 20% (e.g. from 30%) upwards of cellulosic fibres, e.g. 1-80% or 1-70%, such as 15-70% particularly 22-38% or 45-75% polyester fibres and 20-99% or 30-99% (such as 30-85%), particularly 62-78% or 25-55% cellulosic fibres.

Substrates comprising at least 45% non cellulosic fibres, eg polyester fibres such as 45-100% polyester, are preferred as are ones comprising 30-78% cellulosic fibres and 22-70% polyester fibres, or 30-62% cellulosic fibres and 38-70% polyester fibres. The polyester is usually a condensation product containing structural units from an aliphatic alcohol, e.g. dihydric alcohol, especially ethylene glycol or butane diol (or mixtures thereof) and an aromatic dicarboxylic acid, e.g. terephthalic acid, or a mixture thereof with other dicarboxylic acids, such as isophthalic acid, or sebacic acid.

The substrate fibres may be in the form of thread or non woven fabric, but are preferably as woven fabric. Mixtures of fibres e.g. of cellulosic and other fibres may be an intimate or non intimate mixture but the fibres are preferably in the form of blend of cellulosic fibres and the other fibres e.g. polyester fibres, as in cospun blends such as cotton/polyester or polyester/cotton staple fibre, but may be in the form of core spun yarn with a core of the other fibre e.g. polyester sheathed in cotton fibres. In a fabric, the warp and weft fibres are preferably the same, but may be different e.g. one may be from cotton fibres and the other from e.g. polyester/cotton fibres. Thus in this specification the term "blend" also includes unions and union/blends as well as core sheath fibres. The substrate is preferably a fabric with a weight of 0.05-1.0kg/m^2, e.g. 0.150-0.40kg/m^2, or 0.05-0.20kg/m^2. Examples are polyester/cotton shirting or sheeting or curtain fabric.

The substrate is treated with the organophosphorus compound. In the tetrakis (hydroxyorgano) phosphonium compound, each hydroxyorgano group is preferably an alpha-hydroxyorgano group of 1-9 carbons. Especially said alpha-(hydroxyorgano) group is one of formula HOC-(R^1R^2), wherein each of R^1 and R^2 (these being the same or different) represents hydrogen or an alkyl group of 1 to 4 carbons, e.g. methyl, or ethyl. Preferably R^1 is hydrogen, and R^2 is methyl or especially hydrogen, as in tetrakis - (hydroxymethyl) phosphonium (THP) compounds.

The use of tetrakis hydroxyorgano phosphonium compounds in general will hereafter be exemplified with respect to THP compounds with corresponding molar amounts of the other compounds used instead of the THP compound.

The substrate is treated with an impregnation solution which is an aqueous solution of a THP salt mixed with a nitrogen compound condensable therewith to form a water soluble precondensate, or a solution of a precondensate of said salt and nitrogen compound, or a solution of THP salt, or water soluble self-condensate thereof, or at least partly neutralised THP salt, (e.g. THP hydroxide), with or without the nitrogen compound. The impregnation solution may alternatively comprise a solution of said precondensate and further nitrogen compound (eg urea), as in a solution with a molar ratio of total nitrogen compound (free and combined) to THP group (free and combined) of 0.8-2:1, eg 0.8-1.5:1. The nitrogen compound is preferably one with at least two NH groups (such as 2-4), but advantageously contains two NH or especially two NH_2 groups. The nitrogen compound is usually bifunctional and may be an amine but is especially an amide. Examples of suitable nitrogen compounds are biuret, guanidine, melamine and methylolated melamines, but urea is the preferred species for the purposes of this invention, especially in the absence of melamine or a methylolated melamine. The nitrogen compound is preferably urea whenever it is present in the precondensate.

In a preferred embodiment of this invention, the solution contains a precondensate of THP salt, e.g. chloride or sulphate, and the nitrogen compound in a molar ratio of nitrogen compound to THP of 0.05-0.8:1, e.g. 0.05-0.6:1, or 0.22-0.8:1, such as 0.25-0.6:1, especially 0.4-0.6:1. The pH of said solution is usually 2-7.5, such as 4-6.5, e.g. 4-5. The atom ratio of total N atoms in the nitrogen compound or condensate to the total P atoms from THP salt or condensate in the impregnation solution is usually not greater than 4:1, eg 1-3:1.

In a preferred embodiment of the invention, a fabric comprising non cellulosic fibres, optionally with cellulosic ones, is treated with an impregnation solution comprising a water soluble condensate of the organophosphorus compound and a bifunctional nitrogen compound such as urea. Preferably, these compounds are present in a molar ratio of 1:0.25-0.6. Subsequent curing of said fabric is by means of heat, and preferably also ammonia. In another embodiment, when curing is with heat and ammonia, the impregnation solution contains the organophosphorus compound and the nitrogen compound, unreacted or reacted completely or in part.

The concentration of organophosphorus compound in the aqueous solution may be 5-70% eg 5-35% or 35-70% (expressed by weight as THP^+ ion), but is preferably 20-35%.

If desired the solution may contain a wetting agent such as a nonionic one,eg in amount of 0.05-0.5% by weight of the impregnation solution, a fabric softener such as a polyethylene one and in preferred amount of 0.1-2% by weight, and a salt of a strong acid and weak base (such as an ammonium or alkaline earth metal chloride or nitrate or ammonium acid phosphate) as catalyst for the heat cure, and in amount of 0.1-5% by weight.

The treated substrate is impregnated to give an organo phosphorus pick up of less than 40% e.g. 10-40%; (such as 10-30%), especially 20-30% (as THP ion based on the original weight of the substrate). The substrate can be impregnated with solution and the wet substrate, e.g. fabric-usually squeezed to a wet pick up of 50-130%, e.g. 60-100% (based on the original weight of the substrate). Alternatively, the treated substrate may be impregnated with a concentrated impregnation solution via a minimum add-on, eg foam, technique and a 10-50% wet pick up.

The organophosphorus impregnated substrate is then dried and heat cured either in two separate operations or one continuous operation. Drying may be in a stenter oven or over heated cans, e.g. steam cans and may involve heating at 80-160 °C for 10 min to 10 secs eg at 100 °C to 120 °C for 3 min to 30 secs. Heat curing may be in a stenter or baking oven at a temperature of at least 100 °C e.g. at 100-200 °C or 100-180 °C (such as 130-170 °C) for 10-0.5 minutes e.g. 7-1 minutes. Higher temperature with long curing times should be avoided with substrates containing at least a majority of cellulosic fibres especially 100% cotton.

In a preferred embodiment of this invention, the substrate is further cured by treatment with ammonia, usually gaseous ammonia, which diffuses through the substrate and/or is forced through the substrate e.g. by passage of the fabric over a perforated tube through which ammonia has is emitted. Examples of apparatus and techniques suitable for the ammonia cure are given in USP 4145463, 4068026 and 4494951, the disclosure of which is hereby incorporated by reference. If desired the ammonia cure may precede the heat cure, or the curing may be by heat alone, but preferably the ammonia cure takes place after the heat cure.

The cured substrate usually has solids add-on of 10-50% or 10-40% e.g. 10-30% e.g. 10-25% or 15-30% especially 20-30%, (by weight of the original substrate), based on a total organophosphorus compound pick up of 16-36%, e.g. 20-28% (expressed as THP ion on the same basis).

The cured substrate is then usually subjected to at least one of the following operations: further insolubilization of the cured resin in the treated substrate, oxidation (in order to convert at least some trivalent phosphorus to pentavalent phosphorus in the cured resin), or washing with aqueous base and washing with water.

Alternatively the oxidation may be performed with a gas containing molecular oxygen, preferably air, and particularly with the gas being drawn or blown through the substrate; thus the substrate in the form of fabric can be passed over a vacuum slot or perforated tube though which the gas is blown or sucked.

After the oxidation, or instead thereof, the cured substrate may be washed with an aqueous medium, preferably an aqueous solution of a base, e.g. sodium carbonate, and/or rinsed with water. The oxidation preferably reduces the residual content of formaldehyde on the cured substrate. Alternatively the cured substrate may simply be rinsed with water or submitted to other operations to reduce its content of water soluble materials. Finally the cured fabric is dried, to give a final substrate.

The final substrate, e.g. fabric, can be used for making workwear such as overalls, boiler suits and protective clothing including uniforms, particularly from 30-70% (e.g. 55-70%) cotton and 70-30%, (e.g. 45-30%) polyester, and household fabrics such as sheets and curtains particularly from 30-70% (e.g. 30-60%) cotton and 40-70% polyester.

Processes of the invention with heat and ammonia cure usually give better flammability results, with fabrics comprising non cellulosic fibres, than are obtained with just ammonia cure thereby enabling fabrics to pass more severe flammability tests eg BS6249 (1989) than otherwise. The cured substrates obtained by the process of the invention may also have less reduction in strength.

In this specification unless otherwise noted parts and percentages are by weight.

The invention is illustrated in the following Examples:-

In the Examples were used 4 fabrics A-D details of which were as follows. All had been previously submitted to a desizing treatment.

Fabric	Nature	Weight kg/m^2
A	Polyester	0.140
B	67/33 Polyester cotton	0.095
C	100% Cotton	0.280
D	67/33 Polyester cotton	0.285

The polyester cotton fabrics were cospun intimate blends.

Examples 1-8

Fabrics A, B and C were impregnated to about 55-95% wet pick up with an aqueous solution at pH 4.5 of a precondensate of THP chloride and urea in a molar ratio of 1:0.5, the solution containing an amount of precondensate corresponding to 25.2% by weight THP$^+$ ion. The impregnated fabric was then dried for 1.5 minutes in an oven at 100° C, and then heat cured under conditions specified below. In Ex 8 after the heat cure, the water content of the fabric was returned to normal by equilibration in a humidity controlled room overnight. The heat cured fabric of Ex 8 was then cured further with ammonia gas, which was passed through the fabric in a chamber and in a manner as described in USP 4145463; the cure time was 4 sec. After the heat cure step of Ex 1-7 and ammonia cure step of Ex 8 the fabric was oxidized for 5 min in 5% aqueous hydrogen peroxide solution, washed for 5 mitt at 60° C in 2g/l sodium carbonate solution and rinsed for 5 mins with cold water. The rinsed fabric was then dried to give a final fabric. The final fabric was then analysed for P and N and tested for flame retardancy according to BS 5438 (1989) test 2A; in the case of Ex 1 and 4-6 the fabric was also tested after washing 50 times at 93° C, the washing being as in the manner described in DIN 53920 procedure 1 with soft water. The results were as follows:

Example	Fabric	Heat Cure min	Temp°C	% Solid pick up	Cure Efficiency	Char Length mm	Fabric Final %P	% P Cure Efficiency
1	A	4	150	19.7	62.0	109*	1.34*	53.2
2	B	4	150	12.1	69.5	99	1.93	85.2
3	C	2	150	26.0	36.9	92	1.82	57.6
4	C	3	140	26.0	34.3	63		
5	C	4	140	26.2	35.9	52		
6	C	6	140	26.2	44.7	72		
7	B	2	180	17.0	72.3	110		
8	B	2	180	19.0	74.0	140		

*Denotes figures after 50 washes.

The corresponding char lengths for the final fabrics of Ex 4-6 after 50 washes were 85, 48 and 65 mm respectively.

The cure efficiency was the percentage of final cured solids to the applied solids pick up. The P efficiency was the percentage of P in the final fabric to the P applied to the fabric.

Examples 9 and 10

Fabric D was impregnated with an aqueous solution of 1:2 molar condensate of urea and tetrakis - (hydroxymethyl) phosphonium chloride as described in Ex 1-8 and the excess of liquid squeezed from the fabric.

In Ex 9 and 10 the fabric was then dried and heat cured in a single step at 150° C for 4 minutes. In Ex 10 the heat cured fabric was allowed to stand overnight in a humidity controlled room to equilibrate its moisture content and was then cured further with ammonia gas which was passed through the fabric in a chamber and in a manner as described in USP 4145463.

After the heat cure step of Ex 9 and ammonia cure step of Ex 10, the fabrics were oxidized with 10% hydrogen peroxide solution, rinsed with water, washed with aqueous sodium carbonate and then rerinsed and dried, to give final fabrics.

The final fabrics were then analysed for P and N and tested for flame retardancy. For Ex 10 the testing was done before and after washing 40 times at 93° C, the washing being as in the manner described in DIN 53920 procedure procedure 1 with soft water. The test method used was according to BS 5438 1989 test 2A and the char length was determined. The analysis results were as follows:

EXAMPLE FABRIC	%P	%N	Char length mm
9 Final	1.93	1.36	106
10 Final	2.33	1.97	64
After 40 washes	2.01	1.87	

Examples 11-13

In these Examples fabrics were impregnated with THP precondensate as in Ex 1 but the concentration of precondensate in the aqueous impregnation solution was equivalent to 32.76% THP$^+$ ion by weight, and the impregnated fabric was not dried at 100° C before the heat cure. Otherwise for Ex 11-13 the processes of Ex 1-8 were repeated with heat cure and for Ex 12 and 13, the heat cure was followed by cure with ammonia, which was passed through the fabric in a chamber and in a manner as described in USP 4145463; the cure time was 4 sec. The heat cured fabric of Ex 11 and the ammonia cured fabrics of Ex 12 and 13 were then oxidized, washed, rinsed and dried in Ex 1-8. The final fabrics were then analysed for %P and tested for flame retardancy as described in Ex 1. The results were as follows.

Example	Fabric	Heat Cure min	Temp°C	% Solid pick up	Cure Efficiency	Char Length mm	Fabric Final %P	% P Efficiency
11	A	2	150	27.0	63.0	130	2.53	77.7
12	A	2	150	26.1	71.7	110	2.69	84.8
13	B	2	150	22.5	77.8	108	2.68	95.3

Examples 14 and 15

The process of Ex 9 and 10 was repeated with another 100% polyester fabric (E) of 0.140 kg/m^2 and an intimate blend 60:40 cotton polyester fabric (F) of 0.268 kg/m^2. All the final fabrics and those after 20 washes passed the flammability tests.

Claims

1. A process for the flame-retardant of an organic fibrous substrate containing reactive groups, said process characterised by:
   (a) impregnating the substrate with an aqueous solution of an organophosphorus compound,
   (b) drying the substrate,
   (c) curing the impregnated substrate by heating at a temperature of at least 100 C.

2. A process according to Claim 1, **characterised in that** the curing (c) is achieved before, or especially after, heating by means of ammonia.

3. A process according to Claim 1 or 2, **characterised in that** the organic fibrous substrate consists essentially of cellulosic fibres, e.g. natural cotton, ramie, flax, paper of cardboard, viscose or cuprammonium fibres, or cellulose acetate or propionate.

4. A process according to Claim 1 or 2, **characterised in that** the organic fibrous substrate comprises cellulosic and non-cellulosic, e.g. polyester, polyamide or acrylic, fibres.

5. A process according to Claim 1 or 2, **characterised in that** the organic fibrous substrate consists essentially of non-cellulosic fibres.

6. A process according to any one of Claims 1 to 5, **characterised in that** the impregnation (a) is achieved with a tetrakis -(hydroxyorgano) phosphonium compound, especially where said hydroxyorgano group is an alpha - hydroxyorgano group of 1 to 9 carbons, especially where said alpha - hydroxyorgano group is of general formula HO-C(R^{1}R^2), wherein R^1 and R^2, which are the same or different, are hydrogen or an alkyl group of 1 to 4 carbons, especially a tetrakis (hydroxymethyl) phosphonium (THP) compound, or a water-soluble self-condensate thereof, or a water-soluble condensate thereof with an organic nitrogen compound, e.g. urea, biuret, guanidine, melamine or methylolated melamine, or a mixture of said organic nitrogen compound with phosphonium compound or condensate or self-condensate.

7. A process according to any one of Claims 1 to 6, **characterised in that** the impregnation (a) is achieved by means of a solution comprising a precondensate of THP salt and organic nitrogen compound such that the molar ratio of organic nitrogen compound to THP therein is from 0.05:1 to 0.8:1, especially from 0.25:1 to 0.6:1, especially from 0.4:1 to 0.6:1, and in that said solution has a pH of from 2 to 7.5, especially from 4 to 5, and in that the concentration of organophosphorus compound (by weight expressed as THP^+ ion) in said impregnation solution is from 5 to 70%, impregnation solution also comprise one or more of the following additives:

  (i) a wetting agent, especially where said wetting agent is non-ionic and especially where said wetting agent is present in an amount of from 0.05 to 0.5% by weight of said impregnation solution,

  (ii) a fabric softener, especially where said fabric softener is present in an amount of from 0.1 to 2% by weight of said impregnation solution,

  (iii) a catalyst, especially where said catalyst comprises a salt of a strong acid and a weak base, e.g. an ammonium or alkaline earth metal chloride or nitrate or an ammonium acid phosphate, and especially where said catalyst is present in an amount of from 0.1 to 5% by weight of said impregnation solution.

8. A process according to any one of Claims 1 to 7 **characterised in that** the impregnation (a) is achieved by treating said substrate with said impregnation solution to give an organophosphorus pick -up of less than 40% (as THP^+ ion based on the original weight of the said substrate), especially from 20 to 30% (as THP^+ ion based on the original weight of said substrate).

9. A process according to Claim 8, **characterised in that** the wet substrate is squeezed to a wet pick-up of from 50 to 130% (by weight based on the original weight of said substrate).

10. A process according to any one of Claims 1 to 7 **characterised in that** the treated substrate is impregnated with a concentrated impregnation solution via a minimum add-on technique, especially a foaming technique, and in that the wet pick-up is from 10 to 50% (by weight based on the original weight of said substrate).

11. A process according to any one of Claims 1 to 10 **characterised in that** the curing (c) takes place in a stenter or baking oven at a temperature of from 100 to 180 C and in that the curing time is from 10 to 0.5 minutes.

12. A process according to any one of Claims 1 to 11, **characterised in that** the cured substrate is subjected to further insolubilisation of the cured resin in the treated substrate.

13. A process according to any one of Claims 1 to 12, **characterised in that** the cured substrate is subjected to oxidation, and in that said oxidation is achieved by application of an oxidising agent in excess for from 0.1 to 10 minutes at from 0 to 40 C, and in that said oxidising agent is an aqueous hydrogen peroxide solution of concentration form 0.5 to 15% w/w or an aqueous sodium perborate solution of concentration from 1 to 10% w/w.

14. A process according to any one of Claims 1 to 12, **characterised in that** the cured substrate is subjected to oxidation by means of a gas containing molecular oxygen being drawn or blown through the substrate.

European
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EUROPEAN SEARCH REPORT

Application Number

EP 91 10 5140

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	TEXTILE RESEARCH JOURNAL. vol. 39, no. 4, April 1969, PRINCETON, N.J., USA pages 368 - 374; J.V. BENITATE et al: "AN ECONOMICAL DURABLE FLAME RETARDANT FINISH FOR COTTON" * pages 370 - 374 * – – –	1-3,6-9, 11	D 06 M 15/431 D 06 M 13/285 D 21 H 21/34 D 21 H 25/06
X	AU-B-3 441 6 (AMERICAN CYANAMID COMPANY) * the whole document * – – –	1,3,6-11	
X,Y	FR-A-2 211 558 (AMERICAN CYANAMID COMPANY) * the whole document * – – –	1,3-11,2, 12,13	
Y	FR-A-2 289 661 (AMERICAN CYANAMID COMPANY) * claims * – – –	2,12,13	
A	EP-A-0 248 553 (BURLINGTON INDUSTRIES, INC.) * claims ; figure * – – – – –	1-14	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
D 06 M

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	05 July 91	BLAS V.M.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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