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(71) Applicant: **Albright & Wilson Limited  
210-222 Hagley Road West  
Oldbury Warley West Midlands B69 4PR(GB)**

(72) Inventor: **Zakikhani, Mohsen  
9 Brooklands Drive  
Kidderminster DY11 5EB(GB)**

(74) Representative: **Savidge, Roger Gordon  
Madgwick et al  
c/o Albright & Wilson Limited, P.O. Box  
2098,7 Stars Road  
Oldbury, Warley, West Midlands B69  
4PR(GB)**

(54) **Treatment of fabrics.**

(57) Fabrics, in particular cotton polyester fabrics, are treated with a reactive silicon compound such as an aminotrimethoxysilane and then subsequently treated with a THP compound and cured with heat and/or ammonia, to give higher fire retardance than corresponding fabrics without the pretreatment step.

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This invention relates to a fabric treatment process, in particular one 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  
 5 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  
 10 phosphorus on the fabric, is not always ideal and a percentage of the expensive phosphorus chemicals applied in the impregnation step is not cured, and is washed off the fabric after the cure and wasted. The cure efficiency for cotton fabrics is higher than for cotton polyester fabrics and especially polyester cotton fabrics and in some cases adequate fire retardant properties cannot be provided to the latter with THP compounds. Furthermore, while some techniques enable the necessary fire retardant properties to be  
 15 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 retained on the substrate after washing, and can enable adequate fire retardant properties to be provided for fabrics comprising non cellulosic fibres such as ones of cotton and polyester fibres.

The present invention provides a process for the flame retardant treatment of an organic fibrous  
 20 substrate containing reactive groups, which process comprises impregnating said substrate with a silicon compound having at least two active-hydrogen-reactive groups (or precursor therefor), then subsequently with an aqueous solution of an organophosphorus compound, to provide a second impregnated substrate which is dried and cured heat and/or ammonia, to give a cured substrate.

The silicon compound is applied in a first step to give a first impregnated substrate and then the  
 25 organophosphorus compound is applied in a second step. The first impregnated substrate is usually maintained to allow the silicon compound to interact or react in the substrate before the second step.

The silicon compound (or a hydrolysis product thereof) contains at least two groups capable of reaction or interaction with active hydrogen groups especially in hydroxyl, amide or amine groups (including ammonia). Preferably the silicon compound contains at least one group designated R in the formula below  
 30 which, as is or after hydrolysis, is capable of reaction or interaction with a hydroxyl group in an insoluble polymer, e.g. cellulosic hydroxy groups or polyester terminal hydroxyl groups or with an amide group in an insoluble polymer, e.g. a polyamide such as a nylon; and at least one group, designated R<sup>1</sup> in the formula below, which is capable of reaction or interaction with hydroxymethyl groups e.g. ones which are attached to nitrogen, oxygen or especially phosphorus atoms, and/or ammonia or amide NH<sub>2</sub> groups. The conditions  
 35 of the reaction or interaction are usually under the influence of heat, and may be under acid, neutral or basic conditions, and are preferably such that when R (or a group formed by hydrolysis thereof) reacts or interacts, R<sup>1</sup> will not so react.

Preferably the silicon compound is of formula



wherein each of a and b, which is the same or different, is 0, 1, 2, 3 or 4 c is 0, 1 or 2 and a+b+c is 4. R and R<sup>1</sup> are as defined above, while R<sup>2</sup> is an inert organic group, e.g. one inert under the conditions of the first and second steps. Preferably a is 1, 2 or 3 especially 3, b is 3, 2 or 1 especially 1 and c is preferably  
 45 0. Group R may be hydrogen, halogen (e.g. chlorine or bromine), hydroxyl or an ether, acetal, ketal or ester thereof. Alternatively two groups R may together be divalent ether, acetal, ketal or ester groups, or three groups R may together form a trivalent ether or ester group. Preferably R is a hydrolyzable group. Examples of ether groups for R are alkoxides and alkoxy-alkoxides and aryloxides and aralkoxides e.g. of formula R<sup>3</sup>O wherein R<sup>3</sup> is an alkyl e.g. of 1-10 or 1-6 carbon atoms (such as methoxide and ethoxide or 2-ethylhexoxide), or an alkoxy alkoxylene group, with 1-8 carbon atoms in each of the alkoxy and alkylene groups, (such as 2-butoxy-ethylene or 2-methoxy-ethylene). R<sup>3</sup> may also be an aryl group, e.g. an aromatic hydrocarbyl group of 6-19 carbons (such as phenyl, tolyl and xylyl), or an aralkyl group, such as an aralkyl hydrocarbyl group of 7-20 carbon atoms (such as benzyl and naphthylmethyl). Examples of ester groups for R are carboxylate ones, e.g. of formula R<sup>3</sup>COO- where R<sup>3</sup> is as defined above, especially acetoxymethyl. Preferred  
 55 groups R are hydroxyl and especially alkoxide, such as methoxy, ethoxy, propoxy, isopropoxy and butoxy. Preferably the silicon compound is a tri alkoxy silane of formula R<sup>1</sup> Si(OR<sup>3</sup>)<sub>3</sub>. Thus group R is usually such that the silane is hydrolysed in the impregnation medium or as a prior step to the reaction or interaction, e.g. during the first step to a hydroxy silane (or a cyclized product therefrom with the silanol and any amino

group in R<sup>1</sup>). The use of hydroxy silane itself or cyclic product therefrom or the precursor therefor is also included. The impregnation medium is usually an aqueous solution, so the silicon compound (as is or after hydrolysis) is usually water soluble, e.g. with a solubility of at least 10g/l.

Group or groups R<sup>1</sup> may be an organic group e.g. of 1-12 carbon atoms (such as 1-6 carbon atoms) containing at least one substituent or group which contains at least one e.g. 1-4 and especially 2-4 active hydrogen atoms attached to one or more nitrogen, sulphur, oxygen, or silicon atoms, or a substituent or group which is an unsaturated or 3 atom ring group formed from a carbon atom and a carbon, nitrogen, sulphur or oxygen atom, said unsaturated group being electrophilic and capable of being attacked by nucleophiles, (such as a -CH<sub>2</sub>-OH group or ammonia). The substituent may also be a halide (e.g. chloride or bromide). Group R<sup>1</sup> preferably contains a basic group or quaternary derivative thereof, so the silicon compound in the impregnation medium is advantageously a Zwitterion. Examples of the substituents are -OH, Cl, -NH<sub>2</sub>, -NH-, SH, Si-H, CH<sub>2</sub>=CH-, CH<sub>2</sub>=C(CH<sub>3</sub>)-, epoxy, -CN, and C=O. Examples of group R<sup>1</sup> are ones of formula -R<sup>4</sup>-X, wherein R<sup>4</sup> is an alkylene group e.g. 1-6 carbon atoms (such as methylene, ethylene, 1, 3- propylene), or an arylene group, e.g. of 6-13 carbon atoms (such as o, m, p-phenylene, tolylene or xylylene), or an aralkylene group, e.g. of 7-13 carbon atoms (such as benzylene) R<sup>4</sup> may also be a cyclo alkylene-alkylene or cycloalkenylene alkylene group, each of the latter groups being e.g. of 6-10 carbons (such as 2 cyclohexyl ethyl or 2-(cyclohexenyl) ethyl) or cycloalkylene, e.g. of 5-7 carbons such as cyclohexylene. X is one of the above substituents, especially Cl, -NH<sub>2</sub>, CN, -NHR<sup>5</sup> (wherein R<sup>5</sup> is an alkyl group of 1-6 carbon atoms, an aromatic or aralkyl group, eg of 6-18 carbons, or of formula -R<sup>4</sup>NH<sub>2</sub>. -R<sup>4</sup>NHR<sup>5</sup>, e.g. an amino alkylene group, e.g. of 2-10 carbon atoms (such as 2-aminoethyl, 6-aminoethyl), or an optionally substituted (e.g. vinyl substituted) benzylamino alkylene group with 2-6 carbon atoms in the alkylene group, (such as 2[p vinyl benzyl amino] ethyl or an amino carbonyl group). Amino functional silanes e.g. where X is an NH<sub>2</sub> or NHR<sup>5</sup> group are preferred; such silanes preferably have at least one NH<sub>2</sub> group, and especially one NH<sub>2</sub> and one or two -NH- groups in the molecule.

The olefinic substitution or group - which may be an alkenyl or alkenylene group e.g. of 2-8 carbon atoms, (such as vinyl, or propenylene) or an aryl substituted alkenylene group e.g. of 8-14 carbons (such as vinyl-phenyl or 2-phenyl or 2-phenyl ethenylene) or a cycloalkenyl group, e.g. of 5-7 carbons, (such as cyclohexenylene), may be group R<sup>1</sup> itself or group X itself or may be part of a group X, as when R<sup>1</sup> represents R<sup>4</sup>X e.g. as in the vinyl substituted benzylamino group above, or as in a 2, 1 unsaturated carboxylic ester group such as a methacryloxy or an acryloxy group, attached for example to an alkylene group such as 1, 3 propylene. Examples of the 3 atom ring substituents are cyclopropane, epoxide, episulphide and optionally substituted ethylene imine groups. These groups may form R<sup>1</sup> or part of X or X (as in R<sup>4</sup>X) wherein X and R<sup>4</sup> are as defined above, so R<sup>1</sup> may be for example a 3- (glycidyoxy) propyl group or a 2- (3, 4-epoxycyclohexyl) ethyl group. However preferably the group R<sup>4</sup> contains only saturated C-C bonds.

Most preferred groups R<sup>1</sup> are 1, 3 propylene with a 3-substituent of formula X which is glycidyoxy, methacryloxy, acryloxy, chlorine, amine, cyano, ureido and 2-(amino ethyl) amino, especially when 3 R groups represent three methoxy or ethoxy groups in a molecule of formula R<sup>1</sup> Si (OCH<sub>3</sub>)<sub>3</sub> or R<sup>1</sup> Si (OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>. Thus preferred silicon compounds are N-(2 aminoethyl) - 3-amino propyl trimethoxy silane and 3-amino propyl trimethoxy silane. Vinyl tri alkoxy silanes are also preferred.

Group R<sup>2</sup> is an inert organic group e.g. one of 1-19 carbon atoms such as one given above in relation to R<sup>3</sup>, preferably methyl, and is non reactive and non hydrolyzable.

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. 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.

If desired the fibrous substrate may be one of the above non cellulosic ones having groups capable of interaction with the silicon compound. Thus the substrate may be a polyester, with the silicon compound reacting with hydroxyl or ester groups, or a polyamide with the silicon compound reacting with amide or amine or carboxyl or a polyacrylonitrile with reaction of the silicon compound with nitrile groups. The polyester may be described above, while the polyamide may be a reaction product of a polyamine e.g. a diamine e.g. 4-12 carbons with a polyarboxylic acid e.g. a dicarboxylic acid of 4-14 carbon atoms. The polyacrylonitrile may be a homopolymer or copolymer with vinyl chloride as in modacrylic fibres.

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<sup>2</sup>, e.g. 0.150-0.40kg/m<sup>2</sup>, or 0.05-0.20kg/m<sup>2</sup>, such as polyester cotton shirting or sheeting or curtain fabric.

Usually before the silicon compound treatment the fabric is substantially free from size or other finishing agents, such as softening agents and resins; thus size that may have been on the fabric is usually removed, eg by washing.

The silicon compound may be applied undiluted to the substrate but is preferably applied in aqueous solution, e.g. of 0.1-10%, especially 0.5-7% w/w, and a pH 2-9. A weak acid such as acetic or phosphoric acid may be present also in the solution in amount of 0.1 - 1% by weight, to aid hydrolysis of the silicon compound if required. Preferably the solution is at pH 2-4. The weight of silicon compound applied is usually 0.01-10%, e.g. 0.1-5%, especially 0.5-4%, based on the weight of the untreated fabric. The silicon compound is usually impregnated into the fabric with a wet pick up of 40-150% and then, after initial drying if desired, (e.g. with the impregnated fabric heated at 80-100 °C for 0.1-5 minutes), the impregnated fabric is then treated by heating at 90-150 °C (e.g. 90-130 °C) for 0.5-10 minutes (e.g. 1-5 minutes). Instead of the heating step, the impregnated fabric may be kept, e.g. at ambient temperature for 10-60 hours (e.g. 10-30 hours). If desired, the silicon compound may be impregnated by a minimum add-on technique to provide eg a 10-50% wet pick up. Thereafter the fabric may be dried or kept with a dwell time of, eg, 2-24 hours before the second step. A foam minimum add-on technique may be used, with a cationic or amphoteric foaming agent and a stabilizer. The silicon compound may be hydrolysed in the aqueous solution, or may be hydrolysed during the drying or heat treatment step to form a reactive silicon compound. In this treatment or fixing step, the silicon compound or reactive silicon compound is believed to react with the substrate, especially hydroxyl amide or ester groups thereon, in particular via the reactive group R or a hydrolysed version thereof (e.g. hydroxyl), to give a treated substrate which carries a silicon containing group, especially one with group R<sup>1</sup>, as defined above, intact. Thus the treated substrate preferably contains pendant -SiR<sup>1</sup><sub>3</sub>R<sup>2</sup><sub>3</sub> groups especially SiR<sup>1</sup> groups, attached usually to cellulosic hydroxy groups or terminal hydroxy groups of a polyester. Alternatively active hydrogen containing groups in R<sup>1</sup> can react with ester or amide or nitrile groups in polyester or polyamides or polyacrylonitrile respectively. Unsaturated or 3 ring groups in R<sup>1</sup> can react with the fibres by addition of hydroxyl or N-H groups on the fibres to the silicon compound.

In the second step of the process, the silicon treated substrate is then treated with the organophosphorus compound. In the tetra (hydroxyorgano) phosphonium compound, each hydroxyorgano group is preferably an alpha hydroxyorgano group of 1-9 carbons especially one of formula HOC- (R<sup>5</sup>R<sup>6</sup>) wherein each of R<sup>5</sup> and R<sup>6</sup> which is the same or different represents hydrogen or an alkyl group of 1 to 4 carbons e.g. methyl or ethyl. Preferably R<sup>5</sup> is hydrogen, and R<sup>6</sup> is methyl or especially hydrogen as in tetra kis (hydroxymethyl) phosphonium (THP) compounds. The use of tetra 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<sub>2</sub> 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.

The concentration of organophosphorus compound in the aqueous solution maybe 5-70%, eg 5-35% or 35-70% (expressed by weight at THP<sup>+</sup> 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 e.g. to a moisture content of 0-20%, e.g. 5-15%, (such as about 10%) for subsequent ammonia cure and to substantial dryness for subsequent heat cure, the percentage being derived from the increase in weight of the substrate, eg fabric, and the weight of chemicals impregnated. The drying may be in a stenter oven or over heated cans, e.g. steam cans and may involve heating at 80-120 °C for 10 to 1 min. The dried substrate is then cured. The cure may be 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. Alternatively or preferably prior to the ammonia cure, the dried organophosphorus impregnated substrate may be heat cured, 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 temperatures with long curing times should be avoided with substrates containing at least a majority of cellulosic fibres especially 100% cotton. While a dried substrate may then be heat cured, preferably the drying and heat curing steps are combined in a single step with heating under the heat cure conditions. When heat cured fabric is subsequently to be cured with ammonia, the heat cured fabric is preferably submitted to a humidity equilibration step to allow the fabric to recover its moisture content before the ammoniation.

The cured substrate usually has solids add-on (derived from the THP impregnation and cure stages) of 10-50% or 10-40%, e.g. 10-30%, such as 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. The oxidation is preferably by contact with an aqueous solution of an oxidising agent, preferably a peroxy compound, such as aqueous hydrogen peroxide solution e.g. of 0.5-15% concentration, such as 1-5% strength, or sodium perborate solution, e.g. of 1-10% concentration, usually applied in excess, and usually for 0.1-10 mins at 0-40 °C. 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 through 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 base, e.g. sodium carbonate solution 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.

If the process of the invention is compared to the corresponding one without the silicon treatment step, the initial uptake of THP compound by the substrate in the impregnation may be increased, the cure efficiency may be increased, and the loss of cured P compound from the final substrate during washing in use may be reduced. Thus for a constant total weight phosphorus chemical applied to the substrate, the cured substrate of the invention usually has a higher percentage of bound phosphorus, and may also have a better handle than the corresponding cured substrate without the initial treatment with the silicon compound. There is thus less wastage of phosphorus chemical. The flame retardant properties e.g. the char length, are usually improved enabling fabrics to pass more severe flammability tests than without the pretreatment.

The final substrate obtained by the process of the invention may also have enough cured and bound phosphorus containing resin to enable it to reach exacting flame retardancy standards e.g. BS6249 Part I 1984 Index B, which may not be passed by the same original substrate cured without the initial treatment with silicon compound. The final substrate obtained by the process of the invention may also have less reduction in strength compared to corresponding substrates without the initial treatment.

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

The invention is illustrated in the following Examples in which all the fabrics had been previously submitted to a denizing treatment.

### **Example 1**

(a) A 67:33 intimate blend polyester cotton fabric of 0.246kg/m<sup>2</sup> was impregnated with a 2% w/w aqueous solution of 3- (2 amino ethyl) amino propyl trimethoxy silane, sold by Dow Corning under the trademark Z6020. The excess of liquid was then separated from the fabric, which was allowed to dry at room temperature overnight to leave a treated fabric comprising about 1.6% of silane.

(b) The treated fabric was then impregnated with an aqueous solution of 1:2 molar condensate of urea and tetrakis (hydroxy methyl) phosphonium chloride containing 25.2% solids (expressed by weight as THP<sup>+</sup> ion) and the excess of liquid squeezed from the fabric to give a wet pick up of about 50%.

(c) The fabric was then heat cured at 150 °C for 3 minutes, and then its water content returned to normal by equilibration in a humidity controlled room overnight. The heat cured fabric was then cured further with ammonia gas which was passed through the fabric in a chamber as described in USP 4145463.

(d) After the ammonia cure, the fabric was washed with 10% hydrogen peroxide solution, rinsed with water, washed with aqueous sodium carbonate and then rerinsed and dried, to give a final fabric.

The final fabric was then analysed for P and N and tested for flame retardancy before and after washing 40 times at 93 °C, the washing being as in the manner described in DIN 53920 procedure 1 with soft water. The test method used was according to BS 5438 (1989) Test 2A. In all cases the fabrics met the flammability requirements of BS 6249 Index B. The analysis results were as follows:

	<b>FABRIC</b>	<b>%P</b>	<b>%N</b>
5	Final	2.39	2.19
	After 40 washes	2.34	2.12

10 The fabric passed the ignition test even after 40 washes.

#### Examples2-6

The process of Ex1 was repeated with 2 separate fabrics and 3 types of cure step (c). The fabrics were  
 15 (A) a 100% print cotton of 0.240 kg/m<sup>2</sup> fabric weight (B) the 67:33 polyester cotton fabric of Ex1.

In each case the treated fabric was impregnated and treated as in steps (a), (b) of Ex 1 with wet pick ups in step (b) of 74.1%, 74.7%, 53.7% and 61.9% for Ex 2, and Ex 4-6 respectively. After step (b) fabric A was then cured by (i) heat cure at 150 °C for 4 minutes or (ii) ammonia cured by drying the fabric for 2 minutes at 100 °C and then passing ammonia through the fabric in a chamber as described in USP  
 20 4145463 or (iii) heat curing at 150 °C for 4 minutes followed by ammonia cure by passing ammonia through the fabric in a chamber as described in USP 4145463. In each case after step (b) with fabric B, the cure step (c) was by (i) or (ii) only.

After cure steps (i), (ii) or (iii) the operations of step (d) were performed. The flame retardancy and analyses test were done on the final fabric and the fabric after 40 washes at 93 °C. The results were as  
 25 follows.

<b>Final Fabric</b>					
<b>Ex</b>	<b>Cure Technique</b>	<b>Fabric</b>	<b>%P</b>	<b>%N</b>	<b>Char Length mm</b>
30					
35	2 Heat (i)	A	1.99	1.54	96
40	3 Heat (i)	B	2.17	1.64	50
45	4 Ammonia (ii)	A	3.00	3.07	74
50	5 Ammonia (ii)	B	2.12	2.09	60
55	6 Heat and Ammonia (iii)	A	2.82	2.84	78

The analyses of the fabric after 40 washes were as follows:-

	EX	%P	%N
5	2	1.66	1.35
	3	1.55	1.17
	4	2.90	2.86
10	5	2.19	2.12
	6	2.77	2.61

#### 15 Example7-9

The processes of Ex 2-6 were repeated with the same 3 types of cure (i), (ii) or (iii) but with another fabric, namely a 67:33 polyester cotton intimate blend fabric of 0.095kg/m<sup>2</sup>. The final fabrics of Ex 7-9 and those on the corresponding final fabrics of Comp Ex A-C without the silicon pretreatment were analyzed for  
20 %P and %N. The results were as follows.

	Ex	Cure	%P	%N
25	8	Heat (i)	2.38	2.04
	9	Ammonia (ii)	2.23	2.45
30	10	Heat and Ammonia iii	2.53	2.47
	A	(i)	1.78	1.56
	B	(ii)	1.96	2.18
35	C	(iii)	2.00	2.11

#### Examples10-13

40 The process of Ex1 was repeated with a different fabric namely an intimate blend 60:40 cotton polyester fabric of weight 0.268 kg/m<sup>2</sup> and 4 concentrations of the silane in the first step. All the fabrics before and after washing passed the flammability tests. The other results were as follows:

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Ex	% Silane	Final % P	Fabric % N	Char Length mm	Fabric after 40 washes % P	% N	Char Length mm
11	1	2.94	2.88	43	2.36	2.20	55
12	2	3.14	3.08	60	2.56	2.41	52
13	3	3.04	3.18	50	2.47	2.35	60
14	5	2.97	3.33	40	2.72	2.56	55

#### Example 14

The process of Ex 1 was repeated with a 50:50 intimate blend polyester cotton fabric of weight 0.095 kg/m<sup>2</sup> and a silane concentration in the solution of 5% by weight. The final fabric and that after 20 washes passed the flammability tests. The results were as follows. The final fabric had 3.09%P, 2.82% N and gave a char length of 84 mm, while after 20 washes the fabric had 2.58%P, 2.23%N and 95 mm char length.

#### Example 15-17

The process of Ex 1 was repeated with 3 different silanes in the aqueous solution in step (a) namely (i) a 2% solution of 3-chloropropyl-trimethoxy silane (ii) a 1% solution of 3-[2-[p-vinylbenzylamino]ethyl]-aminopropyl trimethoxy silane. (iii) (iv) a 0.25% solution and a 2% solution of 3-glycidyloxy propyl trimethoxy silane, the silanes being sold by Dow Corning under the trademarks Z6076, Z6032 and Z6040 respectively. All the final fabrics passed the flammability tests. The char lengths in mm for the final fabrics were as follows (ii) 74 mm (iii) 69 mm and (iv) 65 mm respectively.

#### Claims

1. A process for the flame retardant treatment of an organic fibrous substrate containing reactive groups, said process characterised by:
  - (a) impregnating the substrate with a silicon compound having at least two active-hydrogen-reactive groups, or precursor therefor, then subsequently with an aqueous solution of an organophosphorus compound.
  - (b) drying the substrate.
  - (c) curing the substrate by heating at a temperature of at least 100° C and/or treating with ammonia.
2. A process according to Claim 1, **characterised in that** the organic fibrous substrate consists essentially of cellulosic fibres, e.g. natural cotton, ramie, flax, paper or cardboard, viscose or cuprammonium fibres, or cellulose acetate or propionate.
3. A process according to Claim 1, **characterised in that** the organic fibrous substrate comprises cellulosic and non-cellulosic, e.g. polyester, polyamide or acrylic, fibres.
4. A process according to Claim 1, **characterised in that** the organic fibrous substrate consists essentially of non-cellulosic fibres.
5. A process according to any one of Claims 1 to 4, **characterised in that** said silicon compound is of general formula



wherein (i) each of a and b, which may be the same or different, is 0, 1, 2, 3 or 4, c is 0, 1, or 2, such that a + b + c is 4, (ii) R, or its hydrolysis product, is capable of reaction of interaction with a hydroxyl or an amide group in an insoluble polymer, (iii) R<sup>1</sup> is capable of reaction in interaction with hydroxymethyl groups and/or ammonia or amide NH<sub>2</sub> groups, and (iv) R<sup>2</sup> is an inert organic group, especially where said silicon compound has the general formula R<sup>1</sup> Si(OCH<sub>3</sub>)<sub>3</sub> or R<sup>1</sup> Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub> wherein R<sup>1</sup> is 1, 3-propylene with a 3-substituent selected from the following groups: glycidyloxy, methacryloxy, acryloxy, chlorine, amine, cyano, ureido and 2-(aminoethyl) amino, especially where said silicon compound is N-(2 aminoethyl)-3-aminopropyl trimethoxysilane, 3-aminopropyl trimethoxy silane or a vinyl trialkoxysilane.

6. A process according to any one of Claims 1 to 5, **characterised in that** said silicon compound is applied to the substrate in aqueous solution, and in that said aqueous solution has a concentration of from 0.1 to 10% w/w, especially where said aqueous solution also comprises a weak acid, e.g. acetic or phosphonic acid, especially where said weak acid is present in said aqueous solution in an amount of from 0.1 to 1% by weight.
7. A process according to any one of Claims 1 to 6, **characterised in that** the impregnation (a) is achieved by treating the substrate with a solution comprising a silicon compound, or precursor thereof, such that the wet pick-up is 40-150%, especially where the impregnated substrate is then subjected to one or more of the following treatments:
  - (i) drying by means of heating at from 80 to 100 °C for from 0.1 to 5 minutes.
  - (ii) heating at from 90 to 150 °C for from 0.5 to 10 minutes.
  - (iii) keeping at ambient temperature with a dwell time of from 10 to 60, especially where said impregnation substrate is concomitantly allowed to dry.
8. A process according to any one of Claims 1 to 7 **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<sup>1</sup>R<sup>2</sup>), wherein R<sup>1</sup> and R<sup>2</sup>, 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.
9. A process according to any one of Claims 1 to 8 **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<sup>+</sup> 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.
10. A process according to any one of Claims 1 to 9, **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<sup>+</sup> ion based on the original weight of the said substrate), especially from 20 to 30% (as THP<sup>+</sup> ion based on the original weight of said substrate).

11. A process according to Claim 10, 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).
- 5 12. A process according to any one of Claims 1 to 9, 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).
- 10 13. A process according to any one of Claims 1 to 12, characterised in that the heat curing of (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.
- 15 14. A process according to Claim 13, characterised in that said heat curing takes place prior to curing with ammonia.
- 15 15. A process according to any one of Claims 1 to 14, characterised in that the cured substrate is subjected to at least one of the following treatments:
  - (i) further insolubilisation of the cured resin in the treated substrate;
  - (ii) oxidation;
  - 20 (iii) washing with aqueous base and washing with water, and in that the oxidation (ii) 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 from 0.5 to 15% w/w, or an aqueous sodium perborate solution of concentration from 1 to 10% w/w, or in that the cured substrate is subjected to oxidation by means of a gas containing molecular oxygen being  
25 drawn or blown through the substrate.

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## EUROPEAN SEARCH REPORT

Application Number

**EP 91 10 5142**

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	US-A-4 052 158 (E.D.WEIL) * column 5, line 55 - column 10 * - - -	1-3,5,7-9, 13,15	D 06 M 13/285 D 06 M 13/513 D 06 M 15/431
Y	AU-B-3 441 6 (AMERICAN CYANAMID) * the whole document * - - -	1-5,7-11, 13-15	D 21 H 21/34 D 21 H 25/06
Y	US-A-4 207 071 (J.LIPOWITZ ET AL) * the whole document * - - -	1-5,7-11, 13-15	
A	EP-A-0 313 227 (TAKEMOTO) * the whole document * - - - - -	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			D 06 M
The present search report has been drawn up for all claims			
Place of search  The Hague		Date of completion of search  04 July 91	Examiner  BLAS V.M.
<div>CATEGORY OF CITED DOCUMENTS</div> <div>X: particularly relevant if taken alone</div> <div>Y: particularly relevant if combined with another document of the same category</div> <div>A: technological background</div> <div>O: non-written disclosure</div> <div>P: intermediate document</div> <div>T: theory or principle underlying the invention</div> <div>E: earlier patent document, but published on, or after the filing date</div> <div>D: document cited in the application</div> <div>L: document cited for other reasons</div> <div>&amp;: member of the same patent family, corresponding document</div>			