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(54) Apparatus and process for the flame-retardant treatment of textiles

Verfahren und Vorrichtung, um Textilmaterial feuerfest zu machen

Procédé et appareil pour rendre ignifuge un matériau textile

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Description

This invention relates to an apparatus for use in the flame-retardant treatment of textiles, in particular cellulosic textiles, and to a process employing said apparatus.

Cellulosic textiles are generally rendered flame-retardant by impregnation with an aqueous solution of a **tetrakis** (hydroxyorgano) phosphonium (THP) composition. The THP composition may be a THP salt, a partly-neutralized derivative thereof or a condensate with a nitrogen-containing compound such as urea. Impregnation with the THP composition is followed by drying and curing with ammonia gas to produce a cured, water-insoluble polymer in association with the textile. The ammonia gas may be passed directly into a chamber through which the textile fabric passes, or, preferably, the ammonia gas is forced through the fabric inside the chamber. In our earlier patents GB-A-1439608 and GB-A-1439609, there are described preferred apparatus, which consists of a closed chamber, entry and exit seals thereto through which the fabric moves, a duct located in the chamber and having one or more orifices through which gaseous ammonia issues and subsequently passes through the fabric passing over each orifice, the chamber having means to prevent condensed water from dripping on to the fabric.

The apparatus has several disadvantages, notably it is not capable of giving a satisfactory cure at processing speeds in excess of about 20 metres/minute; the level of curing can sometimes be less than ideal so that retreatment of the fabric may be necessary; and the relatively large amounts of ammonia which are used result in the loss of ammonia to the atmosphere, with resultant atmospheric pollution.

US-A-3846155 describes an apparatus and process for the flame-retardant treatment of fabrics in which an attempt is made to minimise atmospheric pollution by the reduction of the level of ammonia used to cure the fabric. This process has the disadvantage that adequate levels of curing may not be achieved.

The present invention provides an improved apparatus which is capable of operating at higher processing speeds; which gives a consistently high level of curing efficiency which is not susceptible to variation with wide variations of processing parameters such as fabric speed, fabric moisture content, ammonia concentration, and curing temperature; and which utilizes an optimal amount of ammonia for achieving the cure so that the quantities of ammonia employed are considerably reduced and environmental pollution is minimised.

Accordingly, the present invention provides a process for the flame-retardant treatment of a cellulosic fabric, said process comprising the following stages:

(i) impregnating the fabric with an aqueous solution of a tetrakis (hydroxyorgano) phosphonium (THP) composition, said aqueous solution containing from 5% to 50% (especially 15% to 25%) by weight of THP⁺ ion and at least partly drying the impregnated fabric;

(ii) treating the impregnated fabric with a gas including ammonia in an apparatus including a chamber, the initial concentration of ammonia in said gas being from 70% to 90% and the ratio of ammonia in the gas to the THP composition being at least 1.2 to 1;

(iii) removing the treated fabric from the apparatus, together with at least some of the gas including ammonia, characterised in that said gas is recycled back into the apparatus during the course of the process.

The present invention also provides apparatus for carrying out the process described in the immediately-preceding paragraph, said apparatus comprising a chamber (1), entry (12) and exit (13) points, sealed relative to the chamber in a substantially gas-tight manner, for the fabric respectively into and out of the chamber (1), at least one duct (3) located within the chamber (1) and having at least one orifice which (or the totality of which) extends over the width of said fabric, means to close any portion of said orifice not covered by said fabric, means to cause the fabric to travel in contact with the duct (3) and over the orifice, characterised by recycling means (6; 7; 8) to remove at least some of said gas from said chamber (1) and to return said gas thereto, sampling means (15) for analysing the ammonia content of the gas, means for measuring the rate of ammonia fed into the chamber (1), and means for measuring the temperature within the chamber (1).

The present invention also provides a fabric which has been treated in the apparatus, and a fabric which has been rendered flame-retardant according to the process, both as hereinabove described.

The essential features of the process are that the ammonia feed rate is precisely controlled relative to the amount of fabric being processed and that the curing chamber is pre-filled with ammonia to provide a reservoir of ammonia to allow for any slight variation in the ammonia usage relative to the ammonia input. Under these conditions the temperature in the chamber gradually increases and the concentration of ammonia in the chamber gradually decreases until they both reach a steady-state condition. When this steady state is reached the ammonia usage is in balance with the ammonia input, which has been adjusted to ensure complete polymerisation of the THP compound with minimal carry-over of unreacted ammonia.

It is not essential to control the precise ammonia concentration or the chamber temperature at the steady-state condition. By always starting from a lower temperature and a higher concentration of ammonia we ensure that at the steady-state, i.e. until a balance is achieved we ensure that curing is complete although this means that there is a slight carry-over of excess ammonia.

5 Each of the exit and entry points for the fabric is preferably sealed, in a substantially gas-tight manner, by means of flexible (e.g. rubber) seals or flaps. In the chamber there is at least one duct for conveying ammonia gas into the chamber, the duct having at least one orifice or perforation through which the ammonia passes into the atmosphere of the chamber, by way of the fabric moving over the orifice or perforation. Each perforation may be of round, square, rectangular or elliptical shape, and may be, for example, in the form of a series of slots or a single slot. Preferably, the
10 orifices extend across substantially the whole width of the fabric, whereby substantially all the ammonia passes through the fabric.

In order to process fabrics of different widths, it is thus preferred to have suitable plates or covers to close those portions of the orifices not covered by the narrower fabrics. The chamber may contain from one to four ducts, each with one or more orifices emitting ammonia through the fabric. Preferably, means are provided to maintain the contact-angle between fabric and orifice at less than 60°. While the duct or ducts may be located anywhere in the chamber, they are preferably at a location such that the ammonia is forced through the fabric shortly after the fabric enters the chamber. As well as treatment with ammonia forced through the fabric at the ducts, the fabric also preferably passes through the atmosphere of ammonia gas and water vapour which will be present in the chamber. The chamber is preferably fitted with a plurality of rollers, which may be powered or idling, so that the fabric can pass in a serpentine configuration over the rollers. After passage through the atmosphere in the chamber the cured fabric leaves the chamber via the exit point.

The fabric entering the chamber generally contains some moisture and the curing reaction also produces water as a by-product; this water, together with that entering in the fabric, volatilize in the chamber as steam, owing to the heat of the curing reaction. The steam concentration in the chamber is preferably kept to a minimum, and this may be
25 achieved by allowing condensation of the steam on the internal walls of the chamber, preferably associated with means to prevent condensed water from dripping on to the fabric. This prevention means may comprise a sloping roof to the chamber, together with means for collecting the condensed water at the bottom of the chamber without contact with the fabric, such as a circumferential gully or drain. The condensed water may be retained within the chamber but is preferably continuously removed from the chamber. The gases in the chamber, comprising ammonia and steam, may
30 be passed outside the chamber by way of an exhaust pipe and subsequently returned to the chamber at a position remote from the exhaust pipe, preferably in the lower portion of the chamber.

The return may be by way of a perforate duct over which the fabric passes, but preferably by way of a perforate pipe emitting the gases into the atmosphere of the chamber. Advantageously the exhaust pipe is located in the chamber near one or more of the ducts carrying the orifices through which fresh ammonia is forced through the fabric, as this
35 is the location of the maximum heat and steam emission.

The ammonia duct and exhaust pipe are preferably both located in the upper portion of the chamber, while the return pipe is preferably located in the lower portion of the chamber. Alternatively, the ammonia duct or the exhaust pipe may be located in the lower portion of the chamber. The exhaust and return of gases may be in association with means to condense water in the chamber, but in addition (or alternatively) the exhaust gases may be passed through
40 a cooler to reduce their water content prior to return of the gas to the chamber. The gas returning to the chamber may be at about the same temperature as that leaving via the exhaust pipe but is preferably cooler. When the gases are cooled externally, the chamber may be fitted with a heated jacket to reduce condensation in the chamber.

A cooling jacket may also be used to increase condensation on the chamber walls, thereby reducing or eliminating the need for external condensation means. However, the recycle exhaust and return line for the ammonia would still
45 be present in order to render more uniform the ammonia concentration within the chamber. The apparatus of the present invention also contains means for sampling the atmosphere within the chamber, in order that appropriate adjustments may be made to the input feed rate for ammonia, to ensure that a steady ammonia concentration is maintained.

The chamber is preferably mounted on a base which defines a lower compartment, with which the chamber fabric entry and exit points are in substantially gas-tight contact. This lower compartment is also provided with fabric entry and exit points, together with a compartment exit vent, which preferably is under the reduced pressure of an external suction fan.

To use the apparatus the cellulosic fabric is first impregnated with a **tetrakis** (hydroxyorgano) phosphonium composition. The cellulosic fabric is preferably substantially all cellulosic but may comprise cellulose fibres and other fibres coblendable or coveaveable therewith. The non-cellulosic fibres are preferably polyester or polyamide fibres but may
55 also be acrylic (especially modacrylic fibres). The polyamide fibres may be aliphatic, such as copolymers of alkylene diamines and alkylene dicarboxylic acids (eg. nylon 66) or polyactams (such as nylon 6), or may be aromatic, such as aramid, based on aromatic dicarboxylic acids and phenylene diamines.

The fabric can contain at least 30% of cellulosic fibres and up to 70% of coblendable fibres (e.g. 10-70% and

especially 25-60% of coblendable fibres), such as polyamide fibres. Particularly important blended fabrics are those containing cellulosic fibres and polyester fibres. The blended fabric suitably contains up to 70% (e.g. up to 60%) of polyester fibres and from 30%, e.g. from 40% upwards, of cellulosic fibres (e.g. 1-70% or 1-60%, such as 15-60%, particularly 22-38% or 38-60% polyester fibres and 30-99% or 40-99% such as 40-85%, particularly 62-78% or 40-62% cellulosic fibres).

Blended fabrics comprising 40-78% cellulosic fibres and 22-60% polyester fibres or 30-62% cellulosic fibres and 38-70% polyester fibres are preferred. The cellulosic fibres are preferably natural cotton, but may be ramie, flax or regenerated fibres e.g. viscose or cuprammonium fibres. The polyester may be a condensation product containing structural units from an aliphatic alcohol (e.g. a dihydric alcohol such as ethylene glycol) and an aromatic dicarboxylic acid (e.g. terephthalic acid).

The fabric may be non-woven, but is preferably woven. The cellulosic and other fibres may be an intimate or non-intimate mixture, but the fibres are preferably in the form of a blend of cellulosic fibres and other fibres (e.g. polyester fibres), as in a copun blend such as cotton/ polyester staple fibre. Alternatively, the fibres, may be in the form of core spun yarn, with a core of, for example, 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 of cotton fibres and the other of polyester/ cotton fibres. Thus in this specification the term "blend" also includes unions and union/blends as well as core sheath fibres. The fabric is preferably one with a weight of 100-1000g/m² e.g. 150-400g/m², such as cotton polyester shirting or sheeting or curtain fabric.

In the **tetrakis** (hydroxyorgano) phosphonium compound, each hydroxyorgano group is preferably an alpha-hydroxyorgano group having from 1 to 9 carbon atoms, especially one of formula HOC(R¹R²) - wherein each of R¹ and R² (which may be the same or different) represents hydrogen or an alkyl group having from 1 to 4 carbon atoms, e.g. methyl or ethyl. Preferably R¹ is hydrogen and especially both R¹ and R² are hydrogen, as in **tetrakis** (hydroxymethyl) phosphonium compounds.

The use of **tetrakis** (hydroxyorgano) phosphonium compounds in general will hereafter be illustrated with respect to **tetrakis** (hydroxymethyl) phosphonium (THP) compounds, but corresponding molar amounts of other **tetrakis** (hydroxyorgano) phosphonium compounds may be used.

The THP composition is preferably a THP salt mixed with a nitrogen-containing compound condensable therewith, such as melamine, methylolated melamine or urea, or a precondensate of said THP salt and said nitrogen-containing compound, or a THP salt or at least partly neutralized THP salt, e.g. THP hydroxide, with or without said nitrogen-containing compound.

The THP composition is preferably a precondensate of a THP salt, (e.g. THP chloride or THP sulphate and urea, in a molar ratio of urea to THP of 0.05 to 0.8:1, e.g. 0.05 to 0.6:1, such as 0.05 to 0.35:1 or 0.35 to 0.6:1, and is in aqueous solution, usually with a pH of 4 to 6.5 e.g. 4 to 5.

The concentration of organophosphorus compound in the aqueous impregnating solution may be 5 to 50% (expressed by weight as THP⁺ ion), e.g. 15 to 35%, especially 15 to 25%. If desired, the solution may contain a wetting agent, e.g. a nonionic or anionic wetting agent.

The fabric is impregnated with the THP solution and the wet fabric squeezed to a wet-pick up of 30 to 130%, e.g. 60 to 100% (based on the original weight of the fabric). The fabric after impregnation usually has an organophosphorus pick-up of less than 40% e.g. 10 to 40% such as 10 to 30% (e.g. 15 to 30% and especially 15 to 25% as THP⁺ ion), based on the original weight of the fabric.

The impregnated fabric is then dried e.g. to a moisture content of 0 to 20%, e.g. 5 to 15%, such as about 10%, the percentage being calculated from the increase in weight of the 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 to 120°C for 10 minutes to 1 minute.

The dried fabric then enters the apparatus of the present invention where it is cured with ammonia. Preferably, the fabric passes through the lower compartment fabric entry point, then through the lower compartment and finally enters the chamber via the chamber entry point. The fabric is then passed over the orifices and ammonia is forced through it.

Subsequently the fabric travels through the ammonia/water vapour atmosphere in the chamber, prior to leaving via the fabric chamber exit point, and (if present) through the lower compartment and lower compartment fabric exit point.

When the operation is started, the chamber is filled with ammonia which displaces the air through the fabric entry and exit points and also through additional vents in the base of the chamber which may be provided for this purpose, until the ammonia concentration is at least 40% by volume (as determined by means of the sampler and analyzer). The initial ammonia concentration is preferably set at a high level (70% to 90%), in order to provide a reservoir of ammonia which is used to compensate for the higher ammonia usage during the initial warm-up period.

The fabric is then passed through the chamber using an ammonia feed-rate calculated to provide sufficient ammonia to ensure maximum chemical reaction plus a small margin to allow for the loss of unreacted ammonia. The molar relationship between the ammonia input and the phosphorus in the THP composition on the fabric is at least

1.2:1 and preferably between 1.7:1 and 2.2:1 (when the THP composition is a condensate of THP salt and nitrogen-containing compound such as urea) or at least 1.7:1 and preferably between 2.2:1 and 2.7:1 (when the THP composition is a THP salt per se or a partially neutralized derivative thereof).

During the initial stage of curing the ammonia usage slightly exceeds the ammonia feed rate and the cured fabric takes out from the chamber an excess of unreacted ammonia. The ammonia concentration in the chamber falls during this initial stage, but, provided that the exposure time and the concentration remain sufficiently high, this does not reduce the ammonia uptake by the fabric. Heat and steam are produced in the reaction and the temperature within the chamber rises. The ammonia uptake by the fabric drops as the temperature rises and the chamber eventually reaches a steady-state condition.

Under steady-state conditions the ammonia concentration and the chamber temperature will remain substantially constant and the ammonia usage will balance the ammonia feed-rate. The selected ammonia feed rate determines the ammonia usage, which is independent of the ammonia concentration.

The cure chamber usually contains 1 to 20m (e.g. 10 to 20m) of fabric, moving at a speed of 5 to 100m/min (e.g. 30 to 100m/min and especially 50 to 80m/min). The cure chamber contains sufficient fabric to give an exposure time of at least 4 seconds and preferably 10 seconds at the required fabric speed. The volume of the cure chamber should be at least 1.5 times the maximum volume of ammonia to be fed per minute. The fresh ammonia gas is preferably undiluted, but may be diluted with up to 30% by volume of steam or air. The ammonia gas issuing from the duct into the chamber may be at 10 to 120°C but is preferably at a temperature below 100°C, eg 10 to 30°C.

After the cured fabric has left the cure apparatus, the fabric is preferably treated with an oxidising agent in order to convert at least some of the trivalent phosphorus in the THP composition to pentavalent phosphorus in the cured resin, followed preferably by neutralization with an aqueous solution of a base and washing with water. The oxidizing agent is preferably a peroxy compound, such as aqueous hydrogen peroxide solution. Alternatively, the oxidation may be performed with a gas containing molecular oxygen, (preferably air) and particularly by the gas being drawn or blown through the fabric. Thus, the fabric can be passed over a vacuum slot or perforate tube through which the oxidising gas is blown or sucked.

A preferred embodiment of an apparatus according to the present invention will be illustrated, merely by way of example, in the following description and with reference to the accompanying drawing. In the drawing, there is shown schematically a vertical section through the apparatus.

The apparatus has an upper chamber 1 and a lower compartment 2. Inside chamber 1 is a gassing tube 3 having perforations (not shown) and rollers, exemplified at 4. Chamber 1 has a sloping roof 5, at the apex of which is an exhaust pipe 6 leading from the chamber 1 via a condenser (not shown) and an exhaust fan 7, through a gas return line 8 which leads back into the chamber. The chamber 1 has a dished floor 9 with an annular or circumferential gully 10 against the wall 11 of the chamber 1. On either side of floor 9 are fabric entry 12 and fabric exit 13 slots, substantially sealed with rubber flaps 14. Ammonia sampling point 15 is located in the upper part of chamber 1.

In the wall 11 of the lower compartment 2 there are provided a fabric entry slot 16 and a fabric exit slot 17, and near to exit slot 16 a gas exit slot 18, leading to an exhaust fan 19. Compartment 2 also contains rollers 4.

Chamber 1 also preferably has one or more resealable panels (not shown) which can be removed to allow access to the gassing tube and rollers. Alternatively, the chamber may be made in two parts, one of which may be removed to allow access.

In use impregnated fabric enters the apparatus via slot 16, compartment 2, entry slot 12 and thence into chamber 1. The fabric passes over gassing tube 3 through whose perforations ammonia issues through the fabric. The fabric then passes over the rollers 4 through the atmosphere of ammonia and steam and thence out of chamber 1 via exit slot 13 compartment 2 and exit slot 17. Ammonia steam is if desired sucked by a fan 7 out of chamber 1 via exhaust pipe 6 and if desired water is condensed by a condenser (not shown) before the gas is returned by line 8 and is emitted into chamber 1; any condensate leaves via a condensate line (not shown).

Steam condenses on walls 11 and is collected in gully 10, from which it is periodically drained (by means not shown). Any excess of ammonia, together with entrained air and residual water vapour, leaves chamber 1 via the fabric entry and exit slots 12 and 13 and, with any entrained air and ammonia from the exiting fabric, are sucked out of compartment 2 via slot 18.

The process of the present invention is illustrated by way of the following Examples:

Example 1

A precondensate of **tetrakis** (hydroxymethyl) phosphonium chloride (THPC) and urea was prepared, having a molar ratio of urea to THPC of 0.5:1.0. The precondensate was diluted with water to give a solution containing the equivalent of 25% THP⁺ ion. A bleached white cotton drill, weighing 280 g/m², was padded through this solution to give approximately 80% wet pick-up. The fabric was dried for 1 minute at 100°C. It was then cured in a scaled-down version of the apparatus holding 1.2 metres of fabric 0.45 metres wide, using an ammonia input rate of 1.7:1 ammonia

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to phosphorus and an exposure time of 14.4sec. The ammonia concentration in the apparatus was adjusted to different levels before curing commenced. The cured fabric was jig-washed in a cold solution of 55g/l hydrogen peroxide, then in 2g/l sodium carbonate solution at 60°C, and finally in cold water before drying.

Samples were taken after curing and after final drying and analysed for phosphorus and nitrogen content. The results are given in TABLE 1 (below).

TABLE 1

% Ammonia concentration	N/P increase on cure	% P efficiency
40	1.66	91.7
50	1.64	92.3
55	1.64	91.4
65	1.69	92.3
75	1.67	91.7

Example 2

5 metre lengths of drill fabric were treated as described in Example 1 but using instead a bath containing the equivalent of 22.5% THP⁺ ion, an exposure time of 24secs., and an initial ammonia concentration of 80%. The ammonia input rate was either 1.7 to 1 or 2.2 to 1 ammonia to phosphorus. With an input ratio of 1.7:1, the ammonia concentration fell to 69%, but with an input of ratio of 2.2:1: the ammonia concentration remained constant at 80%. Samples were taken from both ends of each fabric and the results are given in TABLE 2 (below).

TABLE 2

Ammonia/P ratio	Ammonia conc.	N/P increase on cure	%P efficiency
1.7 start	80	1.85	93.6
1.7 end	69	1.84	89.9
2.2 start	80	1.85	91.9
2.2 end	80	1.83	93

Example 3

A precondensate as described in Example 1 was diluted to 27.7% THP⁺ ion content. 1000 metres of dyed cotton drill weighing 266/gm² and 1.52 metres wide was padded through this solution to give a wet pick-up of 70.3%. The fabric was dried on a four-bay stenter to about 12% moisture content. It was then cured in the cure apparatus (holding 13 metres of fabric). Initially the ammonia concentration was 76%, the speed was set at 32 metres/min and the ammonia flow-rate at 2.2 NH₃/P. During this stage the temperature rose to 60°C and the ammonia concentration fell to 67% before rising to 69%.

The processing speed was then increased to 39 metres/min and the relative ammonia flowrate reduced to 1.8 NH₃/P. The temperature continued to rise to 77°C and the ammonia concentration first fell to 68% and then rose to 83%.

The fabric was then washed with hydrogen peroxide, soda ash and water in a continuous wash range and dried.

13 samples were taken at regular intervals throughout the run. All the samples met the requirements of BS 6249 Class B both before and after 50 washes at 93°C as specified in DIN 53920 clause 4.1. The mean phosphorus content of the treated samples was 2.92% with a coefficient of variation of only 5.3%.

Example 4

1000 metres of drill fabric was treated as described in Example 1, but with a bath containing 27.0% THP⁺ ion and a wet pick-up of 74.2%. Curing commenced with an ammonia concentration of 68% and with a speed of 40 metres/min and an ammonia flowrate of 1.8 NH₃/P. The temperature rose to 73°C and the ammonia concentration fell to 36% before rising back to 53%.

17 samples were taken from throughout the run. All the samples met the requirements of BS 6249 Class B both before and after 50 washes at 93°C as specified in DIN 53920 clause 4.1. The mean phosphorus content of the treated samples was 2.67% with a coefficient of variation of only 3.3%.

Example 5

500 metres of white cotton sheeting weighing 178g/m² and 1.52 metres wide were treated as described in Example 4 but with a wet pick-up of 92.9%. Curing was carried out immediately after the process of Example 4, so that the starting conditions were ammonia concentration 53%, temperature 73°C, speed 40 metres/min and ammonia flowrate 2.16 NH₃/P. The temperature remained steady at 73 to 74°C but the ammonia concentration rose to 82%.

10 samples were taken from throughout this run. All the samples met the requirements of BS 6249 Class B both before and after 50 washes at 93°C as specified in DIN 53920 clause 4.1. The mean phosphorus content of the treated samples was 2.83% with a coefficient of variation of only 2.5%.

Example 6

1000 metres of drill fabric were treated as described in Example 4 but with cooling of the recirculated gases. The bath contained 26.2% THP⁺ ion and the wet pick-up was 84%. The initial ammonia concentration was 82%, the curing speed was 48 metres/min and the ammonia flowrate was 1.7 NH₃/P. The temperature rose to 67°C and the ammonia concentration fell to 52% before rising to 55%.

8 samples were taken from throughout this run. All the samples met the requirements of BS 6249 Class B both before and after 50 washes at 93°C as specified in DIN 53920 clause 4.1. The mean phosphorus content of the treated samples was 2.85% with a coefficient of variation of only 4.7%.

Example 7

3500 metres of narrow width cotton sheeting weighing 178 g/m² and 0.96 metres wide was treated as described in Example 6 but with a bath containing 30.2% THP⁺ ion and a wet pick-up of 68%. The initial ammonia concentration was 78%, the curing speed was 52 metres/min and the ammonia flowrate was 2.1 NH₃/P. The temperature rose to 58°C and the ammonia concentration fell to 37% before rising to 43%.

11 samples were taken from throughout this run. All the samples met the requirements of BS 6249 Class B both before and after 50 washes at 74°C as specified in BS 5651:1989 clause 6.5.3. Washed samples were also recorded as not ignited when tested by BS 7175 Section 3: Ignitability of individual Bedcovers, when using ignition sources 0, 1 and 5. The mean phosphorus content of the treated samples was 2.79% with a coefficient of variation 9.2%.

Example 8

9000 metres of narrow width cotton sheeting was treated as described in Example 7, but with a bath containing 21.7% THP⁺ ion and a wet pick-up of 81%.

Curing was carried out in three batches with a curing speed of 53 metres/min and an ammonia flowrate of 2.1 NH₃/P. For all three batches the temperature rose to an equilibrium value of 58 to 60°C and the ammonia concentration fell to within the range 45 to 50%.

13 samples were taken from throughout this run. All the samples met the requirements of BS 6249 Class B both before and after 3 washes at 74°C as specified in BS 5651:1989 clause 6.5.3. The mean phosphorus content of the treated samples was 2.54% with a coefficient of variation of only 3.8%.

Claims

1. Process for the flame-retardant treatment of a cellulosic fabric, said process comprising the following stages:

(i) impregnating the fabric with an aqueous solution of a **tetrakis** (hydroxyorgano) phosphonium (THP) composition, said aqueous solution containing from 5% to 50% (especially 15% to 25%) by weight of THP⁺ion and at least partly drying the impregnated fabric;

(ii) treating the impregnated fabric with a gas including ammonia in an apparatus including a chamber, the initial concentration of ammonia in said gas being from 70% to 90% and the ratio of ammonia in the gas to the THP composition being at least 1.2 to 1;

(iii) removing the treated fabric from the apparatus, together with at least some of the gas including ammonia, **characterised in that** said gas is recycled back into the apparatus during the course of the process.

2. Process according to Claim 1 **characterised in that** the fabric consists essentially of cellulosic fibres, e.g. natural cotton, ramie, flax or regenerated fibres.
- 5 3. Process according to Claim 1 or 2, **characterised in that** the fabric comprises cellulosic fibres and other fibres co-blendable or co-weavable therewith, e.g. polyester fibres (such as copolymers of alkylene diamines and alkylene dicarboxylic acids), polyamide fibres, polyactam fibres or aramid fibres.
- 10 4. Process according to Claim 3, **characterised in that** the fabric comprising up to 30% by weight of cellulosic fibres and corresponding up to 70% by weight of polyester fibres.
- 15 5. Process according to any one of Claims 1 to 4, **characterised in that** the fabric is a woven fabric or a fabric comprising core spun yarns.
- 20 6. Process according to any one of Claims 1 to 5, **characterised in that** the **tetrakis** (hydroxyorgano) phosphonium (THP) composition contains a hydroxyorgano group of the general formula $\text{HOC}(\text{R}^1\text{R}^2)-$, wherein R^1 and R^2 (which may be the same or different) are each selected from hydrogen and alkyl groups having from 1 to 4 carbon atoms (e.g. methyl or ethyl).
- 25 7. Process according to Claim 6, **characterised in that** the THP composition is a THP salt (such as a chloride or a sulphate), a partially-neutralized derivative of a THP salt, a mixture of a THP salt and a nitrogen-containing compound (such as urea, melamine or a methylolated melamine) or a precondensate of a THP salt and a nitrogen-containing compound.
- 30 8. Process according to any one of Claims 1 to 7, **characterised in that** the ratio of ammonia to the THP composition is in the range 1.7 to 2.2:1 ($\text{NH}_3:\text{P}$) when the THP composition is the mixture or precondensate of Claim 7, and in the range 2.2 to 2.7:1 ($\text{NH}_3:\text{P}$) when the THP composition is the THP salt of Claim 7.
- 35 9. Process according to any one of Claims 1 to 8, **characterised in that** after removal from the apparatus, the fabric is treated with an oxidising agent, such as an aqueous solution of hydrogen peroxide or a gas comprising molecular oxygen.
- 40 10. Process according to Claim 9, **characterised in that** after oxidation, the fabric is neutralised with an aqueous solution of a base, such as sodium carbonate.
- 45 11. Process according to Claim 10, **characterised in that** after neutralisation, the fabric is washed with water and dried.
- 50 12. Apparatus for carrying out the process of any one of Claims 1 to 11, comprising a chamber (1), entry (12) and exit (13) points, sealed relative to the chamber in a substantially gas-tight manner, for the fabric respectively into and out of the chamber (1), at least one duct (3) located within the chamber (1) and having at least one orifice which (or the totality of which) extends over the width of said fabric, means to close any portion of said orifice not covered by said fabric, means to cause the fabric to travel in contact with the duct (3) and over the orifice, **characterised by** recycling means (6; 7; 8) to remove at least some of said gas from said chamber (1) and to return said gas thereto, sampling means (15) for analysing the ammonia content of the gas, means for measuring the rate of ammonia fed into the chamber (1), and means for measuring the temperature within the chamber (1).
- 55 13. Apparatus according to Claim 12 **characterised in that** means are provided to maintain the angle of contact between the fabric and the orifice at less than 60 degrees.

50 **Patentansprüche**

1. Verfahren zur flammhemmenden Ausrüstung eines zellulosestoffes, wobei dieses Verfahren nachstehende Verfahrensschritte aufweist:
- 55 (I) der Stoff wird mit einer wässrigen Lösung einer Tetrakis-(hydroxyorgano)-phosphonium-Zusammensetzung (THP-Zusammensetzung) imprägniert, wobei diese wässrige Lösung 5 bis 50 Gew.-%, insbesondere 15 bis 25 Gew.-% THP⁺-Ion enthält; der imprägnierte Stoff wird wenigstens teilweise getrocknet;

(II) der imprägnierte Stoff wird mit einem Ammoniak enthaltenden Gas in einer Vorrichtung behandelt, die eine Kammer aufweist; hierbei wird die Anfangskonzentration an Ammoniak in diesem Gas zwischen 70 und 90 % gehalten, und das Verhältnis von Ammoniak in dem Gas zu der THP-Zusammensetzung wird bei wenigstens 1,2 : 1 (1,2 Teile Ammoniak auf 1 Teil Phosphor in der THP-Zusammensetzung) gehalten;

(III) der behandelte Stoff wird aus der Vorrichtung entnommen, zusammen mit wenigstens einem Teil des Ammoniak enthaltenden Gases;

dadurch gekennzeichnet, daß

dieses entnommene Gas im weiteren Verlauf des Verfahrens wieder in die Vorrichtung zurückgeführt (recycled) wird.

2. Verfahren nach Anspruch 1,

dadurch gekennzeichnet, daß

der Stoff im wesentlichen aus Zellulosefasern besteht, beispielsweise aus natürlicher Baumwolle, aus Ramie, aus Flachs oder aus regenerierten Fasern.

3. Verfahren nach Anspruch 1 oder 2,

dadurch gekennzeichnet, daß

der Stoff enthält Zellulosefasern und andere damit mischbare Fasern oder damit gemeinsam webbare Fasern, wie beispielsweise Polyesterfasern (hier etwa Copolymere aus Alkylen-diaminen und Alkylen-dicarbonsäuren), Polyamidfasern, Polylactamfasern oder Aramidfasern.

4. Verfahren nach Anspruch 3,

dadurch gekennzeichnet, daß

der Stoff enthält bis zu 30 Gew.-% Zellulosefasern und bis zu 70 Gew.-% Polyesterfasern.

5. Verfahren nach einem der Ansprüche 1 bis 4,

dadurch gekennzeichnet, daß

der Stoff ein Gewebe ist oder ein Stoff ist, der aus Kern-gesponnenen Garnen besteht.

6. Verfahren nach einem der Ansprüche 1 bis 5,

dadurch gekennzeichnet, daß

die Tetrakis-(hydroxyorgano)-Phosphonium-Zusammensetzung (THP-Zusammensetzung) enthält eine Hydroxyorgano-Gruppe der allgemeinen Formel $\text{HOC}(\text{R}^1\text{R}^2)-$, wobei die Reste R^1 und R^2 , die gleich oder unterschiedlich sein können, jeweils stehen für Wasserstoff oder für eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen (wie beispielsweise die Methylgruppe oder die Ethylgruppe).

7. Verfahren nach Anspruch 6,

dadurch gekennzeichnet, daß

die TRP-Zusammensetzung ein THP-Salz ist (wie etwa das Chlorid oder das Sulfat), oder ein teilweise neutralisiertes Derivat eines TRP-Salzes ist, oder ein Gemisch aus einem THP-Salz und einer Stickstoff-haltigen Verbindung ist (wie etwa Harnstoff, Melamin oder ein methyliertes Melamin) oder ein Präkondensat aus einem THP-Salz und einer Stickstoff-haltigen Verbindung ist.

8. Verfahren nach einem der Ansprüche 1 bis 7,

dadurch gekennzeichnet, daß

das Verhältnis von Ammoniak zu der THP-Zusammensetzung im Bereich von 1,7 bis 2,2 : 1 ($\text{NH}_3:\text{P}$) gehalten wird, wenn die THP-Zusammensetzung eine Mischung oder ein Präkondensat nach Anspruch 7 ist; und das Verhältnis von Ammoniak zu der THP-Zusammensetzung im Bereich von 2,2 bis 2,7 : 1 ($\text{NH}_3:\text{P}$) gehalten wird, wenn die TXP-Zusammensetzung ein THP-Salz nach Anspruch 7 ist.

9. Verfahren nach einem der Ansprüche 1 bis 8,

dadurch gekennzeichnet, daß

der Stoff nach Austritt aus der Vorrichtung mit einem Oxidationsmittel behandelt wird, etwa mit einer wässrigen Wasserstoffperoxid-Lösung oder mit einem Gas, das molekularen Sauerstoff enthält.

10. Verfahren nach Anspruch 9,

dadurch gekennzeichnet, daß

der Stoff nach der Oxidationsbehandlung mit einer wässrigen Lösung einer Base neutralisiert wird, etwa mit einer wässrigen Lösung von Natriumcarbonat.

- 5 11. Verfahren nach Anspruch 10,
dadurch gekennzeichnet, daß
der Stoff nach der Neutralisationsbehandlung mit Wasser gewaschen und daraufhin getrocknet wird.
- 10 12. Vorrichtung zur Durchführung des Verfahrens nach einem der Ansprüche 1 bis 11,
wobei diese Vorrichtung aufweist:
- eine Kammer (1) mit einem Stoffbahn-Einlaß (12) und mit einem Stoffbahn-Auslaß (13), die gegenüber der Kammer im wesentlichen gasdicht abgedichtet sind, um eine Stoffbahn in die Kammer (1) einzuführen und aus der Kammer (1) herauszuführen;
 - wenigstens eine Rohrleitung (3), die innerhalb der Kammer (1) angeordnet ist und die mit wenigstens einer Auslaßöffnung bzw. Perforierung versehen ist, die sich (oder deren Gesamtheit sich) über die Stoffbahnbreite erstrecken; wobei Einrichtungen vorgesehen sind, um solche Abschnitte der Auslaßöffnung(en) zu verschließen, die nicht von der Stoffbahn bedeckt sind;
 - Einrichtungen, um die Stoffbahn zwangsweise in Kontakt mit der Rohrleitung (3) und über die Auslaßöffnung(en) durch die Kammer (1) zu führen;
- dadurch gekennzeichnet, daß
zusätzlich vorhanden sind:
- Rückführeinrichtungen (Recyclingeinrichtungen) (6; 7; 8), um wenigstens einen Teil des Gases aus der Kammer (1) herauszuführen und dieses herausgeführte Gas anschließend wieder in die Kammer (1) zurückzuführen;
 - eine Probenentnahmeeinrichtung (15) oder eine Meßeinrichtung (15), um den Ammoniakgehalt des Gases innerhalb der Kammer (1) zu analysieren;
 - eine Meßeinrichtung, um die Ammoniakzufuhr in die Kammer (1) zu messen; und
 - eine Einrichtung, um die Temperatur innerhalb der Kammer (1) zu messen.
13. Vorrichtung nach Anspruch 12,
dadurch gekennzeichnet, daß
Einrichtungen vorgesehen sind, um den Kontaktwinkel zwischen der Stoffbahn und der Auslaßöffnung oder den Auslaßöffnungen kleiner als 60 Grad zu halten.

Revendications

1. Procédé pour le traitement ignifuge d'un tissu cellulosique, ledit procédé comprenant les étapes ci-après consistant à:
- (i) imprégner le tissu avec une solution aqueuse d'une composition de tétrakis (hydroxyorgano) phosphonium (THP), ladite solution aqueuse contenant de 5% à 50% (en particulier de 15% à 25%) en poids d'ions THP⁺, et sécher au moins partiellement le tissu imprégné;
 - (ii) traiter le tissu imprégné avec un gaz englobant de l'ammoniac dans un appareil englobant une chambre, la concentration initiale d'ammoniac dans ledit gaz étant de 70% à 90% et le rapport de l'ammoniac dans le gaz à la composition THP étant d'au moins 1,2 à 1;
 - (iii) retirer de l'appareil le tissu traité conjointement avec au moins une certaine quantité du gaz englobant l'ammoniac, caractérisé en ce que ledit gaz est recyclé dans l'appareil au cours du procédé.
2. Procédé selon la revendication 1, caractérisé en ce que le tissu est constitué essentiellement de fibres celluloseuses, par exemple du coton naturel, de la ramie, du lin ou des fibres régénérées.

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3. Procédé selon la revendication 1 ou 2, caractérisé en ce que le tissu comprend des fibres cellulosiques et d'autres fibres qui peuvent être mélangées ou tissées conjointement avec les premières, par exemple des fibres de polyester (telles que des copolymères d'alkylènediamines et d'acides alkylènedicarboxyliques), des fibres de polyamide, des fibres de polylactame ou des fibres d'aramide.
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4. Procédé selon la revendication 3, caractérisé en ce que le tissu comprend à concurrence de 30% en poids de fibres cellulosiques et à concurrence de 70% en poids de fibres de polyester.
- 10
5. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que le tissu est un tissu tissé ou un tissu comprenant des filés à fils d'âme.
- 15
6. Procédé selon l'une quelconque des revendications 1 à 5, caractérisé en ce que la composition de tétrakis(hydroxyorgano)phosphonium (THP) contient un groupe hydroxyorgano répondant à la formule générale $\text{HOC}(\text{R}^1\text{R}^2)$ - où R^1 et R^2 (qui peuvent être identiques ou différents) sont respectivement choisis parmi un atome d'hydrogène et des groupes alkyle contenant de 1 à 4 atomes de carbone (par exemple un groupe méthyle ou un groupe éthyle).
- 20
7. Procédé selon la revendication 6, caractérisé en ce que la composition THP est un sel de THP (tel qu'un chlorure ou un sulfate), un dérivé partiellement neutralisé d'un sel de THP, un mélange d'un sel de THP et d'un composé azoté (tel que l'urée, la mélamine ou la méthylolmélamine) ou encore un précondensat d'un sel de THP et d'un composé azoté.
- 25
8. Procédé selon l'une quelconque des revendications 1 à 7, caractérisé en ce que le rapport de l'ammoniac à la composition THP se situe dans le domaine de 1,7 à 2,2:1 ($\text{NH}_3:\text{P}$) lorsque la composition THP est le mélange ou le précondensat selon la revendication 7, et dans le domaine de 2,2 à 2,7:1 ($\text{NH}_3:\text{P}$) lorsque la composition THP est le sel de THP selon la revendication 7.
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9. Procédé selon l'une quelconque des revendications 1 à 8, caractérisé en ce que, après l'avoir retiré de l'appareil, on traite le tissu avec un agent oxydant tel qu'une solution aqueuse de peroxyde d'hydrogène ou un gaz comprenant de l'oxygène moléculaire.
- 35
10. Procédé selon la revendication 9, caractérisé en ce que, après l'oxydation, on neutralise le tissu avec une solution aqueuse d'une base telle que le carbonate de sodium.
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11. Procédé selon la revendication 10, caractérisé en ce que, après neutralisation, on lave le tissu avec de l'eau et on le sèche.
- 45
12. Appareil pour la mise en oeuvre du procédé selon l'une quelconque des revendications 1 à 11, comprenant une chambre (1), des endroits d'entrée (12) et de sortie (13) étanchés par rapport à la chambre d'une manière essentiellement étanche aux gaz, pour l'entrée, respectivement la sortie du tissu dans et hors de la chambre (1), au moins un conduit (3) situé à l'intérieur de la chambre (1) et comportant au moins un orifice qui (ou dont la totalité) s'étend sur toute la largeur dudit tissu, un moyen pour fermer n'importe quelle portion dudit orifice non recouvert par ledit tissu, un moyen pour permettre le défilement du tissu en contact avec le conduit (3) et par-dessus l'orifice, caractérisé par un moyen de recyclage (6; 7; 8) pour évacuer au moins une certaine quantité dudit gaz de ladite chambre (1) et pour y renvoyer ledit gaz, un moyen de prélèvement d'échantillon (15) pour analyser la teneur du gaz en ammoniac, un moyen pour mesurer le débit d'alimentation d'ammoniac dans la chambre (1) et un moyen pour mesurer la température régnant dans la chambre (1).
- 50
13. Appareil selon la revendication 12, caractérisé en ce qu'on prévoit un moyen pour maintenir un angle de contact formé entre le tissu et l'orifice inférieur à 60 degrés.
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