

1

3,421,923

**PROCESS FOR FLAME-PROOFING OF
CELLULOSE-CONTAINING TEXTILES**

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7 Claims

ABSTRACT OF THE DISCLOSURE

A process for the flame-proofing of cellulose-containing textile materials is provided, wherein the textile material first is impregnated with an aminoplast, wet-fixed and dried and then impregnated in an aqueous bath containing tetrakis-(hydroxymethyl)-phosphonium chloride. The textile material is dried and after-treated with ammonia. The process yields textile materials with an unaltered hand, a wash-fast flame-proofing finish, and excellent tensile and tear strengths.

The present invention concerns the treatment of cellulose-containing textiles with a tetrakis-(hydroxymethyl)-phosphonium salt, preferably with tetrakis-(hydroxymethyl)-phosphonium chloride, which is abbreviated in what follows as THPC, or with tris-(hydroxymethyl)-phosphine oxide.

The use of THPC for the flame-proofing of cellulose textiles is known. Eight development stages can be distinguished. To begin with, it was recommended to impregnate aminated cellulose with THPC as such or in admixture with melamine or methylolmelamine and then to carry out the fixation by heat treatment, cf. U.S. Patent 2,668,096, patented Feb. 2, 1954, to Wilson A. Reeves and John D. Guthrie, New Orleans, U.S.A. Further development was represented by the proposal to use polymerisable precondensates of THPC with urea, melamine or formaldehyde condensation products of amides such as urea or melamine. The process was now recommended also for mercerized cotton or for viscose, cf. British Patents 740,269 to Albright & Wilson Limited, Oldbury, Warwickshire, England, published Nov. 9, 1955; and 761,985 to Albright & Wilson Limited, Oldbury, Warwickshire, England, published Nov. 21, 1956. As the thermo-fixation of THPC or of THPC precondensates was not satisfactory, a third stage in the development was proposed, namely the treatment of the impregnation agents with gaseous ammonia or with aqueous ammonia. This treatment brought about a certain degree of improvement but the fixation was still too slow, cf. U.S. Patent 2,772,188 and British Patent 882,993 to Albright & Wilson Limited, Oldbury, Warwickshire, England, published Nov. 22, 1961. As a result an attempt was made to expedite the ammonia fixation by the addition of sodium hydroxide or sulfite. A further proposal was to treat the cellulose textiles with aqueous emulsions of an aminoplast-THPC-precondensate and dispersions of hardened THPC-precondensates. The sixth development stage concerns the proposal to treat the cellulose textiles first of all with an aminoplast with dry hardening and then with a THPC-precondensate. The treatment with the aminoplast consists in impregnation with an aqueous solution

2

followed by hardening of the aminoplast, preferably by heat treatment. The fixation of the subsequently applied THPC-precondensate was brought about by thermo-fixation, cf. British Patent 884,785 to Bradford Dyers' Association Limited, Bradford 1, Yorkshire, England, and Albright & Wilson Limited, Oldbury, Birmingham, Warwickshire, England, published Dec. 20, 1961. Further progress was brought about by the seventh development stage which recommended the fixation of the THPC-precondensates applied to the fibres, not with ammonia gas or ammonium hydroxide but with ammonia gas and ammonium hydroxide cf. U.S. Patent 2,983,623, patented May 9, 1961 to Harold Coates, Wombourne, England, and British Patent 906,314 to Albright & Wilson Limited, Oldbury, Warwickshire, England, published Sept. 19, 1962. The last proposal returns to the treatment of cellulose textiles with THPC alone which is applied in a bath at a pH of 3 to 9.5. The THPC is fixed on the fabric by heat treatment after which an after-treatment with gaseous ammonia or with ammonium hydroxide is carried out, cf. British Patent 938,990.

All the processes mentioned so far have certain disadvantages. Of these it is worth mentioning in particular the occurrence of a stiffening effect, an insufficient wash-fastness and therefore loss of the flameresisting effect as well as especially a considerable reduction in the tensile strength and tear strength of the treated textiles. A disadvantage occurs in the use of precondensates because these are largely unstable condensation products. For example not more than 16 parts urea may be added to 63 parts THPC otherwise polymerisation occurs, cf. British Patent 906,314 to Albright & Wilson Limited, Oldbury, Warwickshire, England, published Sept. 19, 1962.

It has now been found that cellulose-containing textiles can be flame-proofed without the above mentioned various disadvantages occurring. The process consists in that a cellulose fabric treated with an aminoplast, in which the hardening of the aminoplast is brought about by a special process, is padded with an aqueous solution of THPC, dried and then after-treated with gaseous and/or aqueous ammonia. The essential features of the process are that the aminoplast is not hardened by drying and/or heating but wet in the presence of the impregnation liquid, that THPC as such is used that the latter is not thermo-fixed. It is particularly surprising that no wash-fast fixation of the THPC is obtained by thermofixation of the aminoplast for 5 minutes at 155° C. and subsequent THPC treatment, but that wash-fast fixation occurs with a fabric on which the aminoplast has been hardened in the presence of the impregnation liquid.

The object of the present invention is thus a process for the flameproofing of cellulose-containing textiles wherein the textile material is impregnated in a first stage with a water soluble hardenable aminoplast, the hardening of the aminoplast is carried out in the presence of impregnation liquid on the textile material, dried if desired, and the textile material impregnated in a second stage in an aqueous bath which contains a tetrakis-(hydroxymethyl)-phosphonium halide or tris-(hydroxymethyl)-phosphine oxide, dried and after-treated with gaseous and/or aqueous ammonia.

The superiority of the process according to the present invention with regard to wash-fast flame-proofing, unaltered hand of the material and excellent tensile strength and tear strength is shown in comparison to the previous processes in the following Tables I and II.

TABLE I

	B.P. 761,985, Example 22	B.P. 882,993, Example 2	B.P. 882,993, Example 4	B.P. 884,785, Example 1	B.P. 884,785, Example 9	B.P. 906,314, Example 1	Example 1 of the application
THPC amount (g./l.)	250	150	330	230	260	410	300
Squeeze-off effect per cent.	80	85	80	85	76	78	700
Calculated P-content on the fabric (percent)	2.8	1.6	3.4	2.5	2.5	4.6	2.7
Weight increase (percent)	15	1	10	24	14	20	15
Hand of fabric	Very stiff	Unaltered	Unaltered	Very stiff	Very stiff	Fuller stiffer	Unaltered
Flame resistance as such:							
Burning time (sec.)	0		0	0		0	0
Glow time (sec.)	0		0	0		0	0
Char length (cm.)	5		8	6		5	7
1 x SNV*4:							
Burning time (sec.)	0	Totally burnt	0	Totally burnt	Totally burnt	0	0
Glow time (sec.)	0		0	do	do	0	0
Char length (cm.)	7	do	8	do	do	7	7.5
3 x SNV*4:							
Burning time (sec.)	0	do	0	do	do	0	0
Glow time (sec.)	0	do	0	do	do	0	0
Char length (cm.)	5	do	4	do	do	5	5
5 x SNV*4:							
Burning time (sec.)	0	do	0	do	do	3	0
Glow time (sec.)	0	do	0	do	do	0	0
Length (cm.)	10	do	8	do	do	8.5	10
Process	Mixture of THPC+Aminoplast thermofixing.	Mixture of THPC+Aminoplast with NH ₄ OH fixing.	THPC-urea precondensate with NH ₄ OH fixing.	(1) Aminoplast (urea) thermofixing. (2) THPC+aminoplast thermofixing.	(1) Aminoplast (melamine) dry fixing. (2) THPC+aminoplast thermofixing.	THPC-urea condensate with NH ₄ OH fixing.	(1) Aminoplast wet fixing (2) THPC as such with NH ₄ OH fixing.
Assessment	Very good flame resistance, but stiff hand.	No flame resistance, no fixing.	Very good flame proofing, good hand, unstable precondensate.	Initial flame-proofness, no permanence.	No flame resistance.	Very good flame resistance but stiff hand.	Very good flame resistance, good hand.

*Standard of the "Schweizerischer Normenverband".
B.P.=British Patent.

The mechanical testing of the treated fabric gave the following results:

Material.—(a) Cotton fabric; (b) Cellulose fabric.

Tests.—(I) Tensile strength in accordance with SNV (= Standard of the "Schweizerischer Normenverband") 98461; (II) Tear strength in accordance with Elmendorf.

TABLE II

	Breaking load (kg.)/2.5 cm.		Tear strength, kg./cm./cm.	
	Warp	Weft	Warp	Weft
(1) Cotton fabric untreated	38.6	36.2	1.82	1.59
(2) Cellulose fabric untreated	21.9	16.6	1.56	1.64
(3) B.P. 761,985 Ex. 22	24.2	17.0	0.42	0.59
(4) B.P. 882,993 Ex. 2	36.0	31.0	1.80	1.54
(5) B.P. 882,993 Ex. 4	35.7	27.5	1.50	1.30
(6) B.P. 884,785 Ex. 1	14.7	7.2	0.22	0.19
(7) B.P. 884,785 Ex. 9	30.4	22.3	0.90	0.77
(8) B.P. 906,314 Ex. 1	35.3	29.5	1.50	1.40
(9) Process according to Ex. 1	34.9	32.0	1.50	1.11

B.P.=British Patent.

The testing of the flame resistance in accordance with Table I is carried out by the vertical method of DIN (= "Deutsche Industrie Norm") 53906 as such and by 5xSNV (= "Schweizerischer Normenverband")—4. The arrangement of the test is as follows:

An ordinary Bunsen burner is used, the length of the luminous flame of which is adjusted to 4 cm.

The fabric 7 x 15 cm., taken in the warp and weft direction, is hung in the flame so that it dips 2 cm. into it.

After a certain test time, which depended on the weight of the fabric, the flame is removed. The flaming time (sec.) and the glow time (sec.) as well as the char length are measured.

Test time:

	Sec.
Weight of fabric up to 100 g./m. ²	4
Weight of fabric from 100–200 g./m. ²	6
Weight of fabric from 200–300 g./m. ²	8
Weight of fabric from 300–500 g./m. ²	10
Weight of fabric from 500–750 g./m. ²	12
Weight of fabric from 750–1000 g./m. ²	14

In assessing the flame resistance, an after-flame time of 1–2 seconds represents a very good degree of protection. The fabric must not after-glow.

The amount of the aminoplast to be applied to the fibres amounts to 2 to 10, preferably 4 to 6%, based upon the weight of the fabric. The concentration of THPC amounts to 150 to 400, preferably 200 to 350 g. per liter. For neutralisation of the THPC 50 to 70, preferably 55 to 65 g. triethanolamine per liter is added to the bath. After impregnation in the THPC bath the fabric is dried, preferably at the temperatures of 60 to 70° C. The fixing of the THPC is carried out for instance by padding in a bath containing 50 to 500, preferably 100 to 300 g. 25% ammonia per litre. The application of gaseous ammonia proved to be especially favorable in this case. The add-on with the aminoplast bath and the THPC bath varies according to the type of fabric. It amounts as a rule to 50 to 150%, for cotton 70 to 80% and for cellulose 90 to 120%. After treatment with ammonia the fabric is advantageously left in the air for 1 to 15 minutes and then treated in a boiling bath which contains sodium carbonate if desired; also a wetting agent and hydrogen peroxide.

As already mentioned, in contrast to the usual hardening of the aminoplast, which is called dry hardening or thermo-fixing, the hardening used in the present process, which occurs in the presence of water, is called wet fixing. The wet fixing is carried out in such a way that the fabric, after impregnation in a bath which contains the water soluble aminoplast as well as a suitable reaction accelerator, is treated, without preliminary drying, at normal or raised temperature. It is advantageous to carry out the fixing at raised temperature and as principal source of heat, direct steam, if desired under pressure, is used.

The fixing of the aminoplast fabric can be completely achieved without previous drying of the impregnated fabric or with partial drying before or during the fixing process, provided that the drying proceeds uniformly without disturbing migration of the hardening products. The simplest process consists in storing for a lengthy time the fabric which has been impregnated with a solution or emulsion after squeezing out or centrifuging, i.e., after mechanical removal of the excess bath liquid without drying steps and with avoidance of premature drying out. The time during which the material should be stored varies between a few minutes and several days. It is dependent on the one hand on the aminoplasts and reaction

accelerators employed and on the other hand on the storage temperature. The storage can be carried out at normal or raised temperature, e.g., at 80° C. It has proved advantageous to store the impregnated fibre in a closed vessel, since by this means premature drying out is avoided. After fixing of the resin the fabric is dried. As stated above a partial drying, in accordance with the process of the invention, can also be carried out before or during the fixing of the resin. In this case care should be taken that no excessive drying of individual parts of the treated textile material occurs and no migration of the unfixed resin during the drying, as otherwise the success of the treatment can be unfavorably affected. Uniform drying can, for example, be achieved by storing the impregnated fabric in a drying chamber through which a stream of air, with a controlled relative humidity, is passed. The fabric can then only give up so much moisture until it reaches the degree of humidity of the air passing over it.

How far this drying can go, cannot in general be stated because various factors such as the storage and activity of the hardening catalysts must be taken into account.

In accordance with a particularly advantageous method of carrying out the invention the wet fixing can be brought about simply and quickly if instead of hot air containing more or less water vapor, steam is used as the source of heat. By the use of saturated water vapor no danger of local drying-out can arise. By working at raised temperatures, e.g., at 110 to 120° C. under pressure, the fixing time can be considerably reduced so that the whole process, including time for heating up, can be concluded in 1 to 2 hours or even considerably less.

Care must be taken that, in heating up the wet fabric, water formed from the vapor is removed without it causing the impregnating solution to flow. This can best be achieved by through removal of the excess impregnating solution by pressing centrifuging or sucking off.

The present process can be employed with all cellulose-containing fabrics made from fibers such as cotton, regenerated cellulose, jute, manila hemp, sisal and ramie. It is especially useful for the treatment of cotton fabrics for clothing materials such as well as for tents or awning materials. In general the process of the invention is advantageous in cases where cellulose-containing materials are exposed to the danger of fire and where, besides good flamer resistance, optimum mechanical strength after repeated washing is required. A particular advantage of the process of the invention is that the textile material also acquires good resistance to rotting.

By the term water soluble, hardenable aminoplasts which can be used for the present process there are to be understood primarily hardenable aminotriazine resins that are soluble in water or are of limited solubility in water and which may be etherified; they are obtained by known methods by condensation of formaldehyde with melamine, acetoguanamine, benzoguanamine or formoguanamine. Mixtures of such condensation products are also suitable. Particularly good results are obtained with water-soluble condensation products of 2 to 3 mols of formaldehyde with 1 mol of melamine.

By condensation products of limited water-solubility are to be understood as usually those colloidal intermediate products which are first produced on further condensation beyond the crystalline methylol stage. They are characterized in that they are precipitated from their concentrated aqueous solutions by the addition of water (cf. Kolloid-Zeitschrift, vol. LVII, October-December 1931, p. 233, left-hand column).

The completely water-soluble condensation products are employed in the form of aqueous solutions, while those of limited solubility are used either in the form of solutions of the condensation products made soluble with the help of acids or in the form of emulsions. As hardening accelerators, which can be added either to the solutions or to the emulsions, the usual hardening catalysts, e.g. acids, such as hydrochloric acid, sulfuric acid or

formic acid, are used; alternatively, salts of strong acids with weak bases e.g. ammonium salts of strong inorganic or organic acids, such as ammonium chloride, ammonium sulfate, ammonium nitrate, ammonium oxalate and ammonium lactate, can be employed. When using solutions of aminoplasts to which acids have been added care must be taken that the solutions are freshly prepared as owing to certain changes to the solutions on standing their suitability for the purposes of the present invention are adversely affected.

It is advantageous to use as catalyst an oxidising agent, dispersible in water, which in aqueous phase possesses neither strong alkali-binding properties nor strong acid-binding properties and which, after application of the impregnating liquid to the fabric, has an accelerating effect on the hardening of the aminoplast owing to the formation of oxidation products.

As an oxidizing agent possessing sufficient oxidizing power to oxidize formaldehyde to formic acid at elevated temperature or during long storage of the treated fabric, hydrogen peroxide is suitable as are addition products of hydrogen peroxide to certain inorganic or organic compound, such as for example "perborate" $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$ or the addition compound of hydrogen peroxide and urea. Another suitable oxidizing agent is chlorine dioxide or its stable addition products especially the addition product of ClO_2 to pyridine.

The salts of peroxymonosulfuric acid, H_2SO_5 , and the peroxydisulfuric acid, $\text{H}_2\text{S}_2\text{O}_8$, e.g. its alkali salts, especially $\text{H}_2\text{S}_2\text{O}_8$, are also suitable for use as oxidizing agents.

The impregnation can be carried out by the usual processes and by means of the usual equipment. Flame-proofing can also be combined with hydrophobation, e.g. with hydrophobing agents known per se.

EXAMPLE 1

A cotton fabric is padded in a bath which contains:

(I)

Water soluble condensation product of 1 mol melamine and 2 to 3 mols of formaldehyde -----g./l. 75
 H_2O_2 (35%) -----ml./l. 10

The weight increases amounts to 70%. The fabric is rolled up in polyethylene sheet, wet-fixed 24 hours at 40° C. and then dried at 60 to 70° C.

(II)

The padding is carried out in a bath containing:

THPC (80%) -----G./l. 300
 Triethanolamine ----- 60

(liquid uptake 70%) and the fabric then dried in a box at 60 to 70° C. It is then padded again in a bath containing:

NH_4OH (25%) -----ML./l. 250

and left 1 to 2 minutes in the air.

The subsequent washing is carried out in a bath containing:

Anhydrous sodium carbonate -----g./l. 2
 H_2O_2 (35%) -----ml./l. 1

The treatment lasts 5 to 10 minutes at 80 to 95° C. and the fabric is then rinsed and dried.

Percent
 Calculated phosphorous content on the fibre ----- 2.7
 Weight increase ----- 15

EXAMPLE 2

A cotton fabric is padded in a bath which contains:

(I)

Water-soluble condensation product of 1 mol melamine and 2 to 3 mols of formaldehyde -----g./l. 150
 H_2O_2 (35%) -----ml./l. 10

The liquid uptake amounts to 75%. The fabric is rolled up in a polyethylene sheet, stored for 5 days at 25 to 30° C. and then dried at 60 to 70° C.

(II)

The fabric so finished is padded in a bath containing:

	G./l.
THPC (80%)	300
Triethanolamine	60

and then dried at 60 to 70° C.

(III)

It is then fixed in a dry jigger equipped with a hood by gaseous ammonia during 4 passages.

(IV)

To eliminate the THPC-odor, the subsequent washing is carried out in a bath containing:

Anhydrous sodium carbonate	g./l.	2
H ₂ O ₂ (35%)	ml./l.	10

The treatment lasts 10 minutes at boiling temperature and the fabric is then rinsed and dried.

EXAMPLE 3

By an additional treatment with a hydrophobing agent, the cotton-fabric is given a hydrophobic dressing in addition to the mold-resisting, rot-proofing, and flame-proofing finishes.

(I, II)

The cotton-fabric treated according to Example 2, (I) is padded at 60 to 80° C. in a bath containing:

- 300 g./l. THPC (80%) neutralized with
- 30 ml./l. sodium hydroxide (40%) to a pH of about 6,
- 150 g./l. of an emulsion containing—
 - 22½% block-paraffin with a melting point of 60° C.
 - 22½% of a condensation product obtained from 2 mols of stearic acid, 1 mol of hexamethylolmelaminepentamethyl-ether
 - 3% of emulsifier obtained by reacting 1 mole of a high molecular alkylamine with 30 mols of ethylene oxide and quaternized with dimethylsulfate
 - 1% of polyvinyl alcohol
 - ½% of triethanolamine
 - 50½% of water
 - 20 g./l. of a catalyst consisting of—
 - 24% of aluminium-triglycolate
 - 8% of glycolic acid
 - 68% of water

(III)

Fixation by gaseous ammonium during 4 passages follows in a dry jigger equipped with a hood.

(IV)

The fabric is kept at 155° C. for 5 minutes to fix the hydrophobic finish.

(V)

In the same manner as in Example 2(IV) the fabric is washed, rinsed and dried.

Test-results

Flame-resistance of the fabrics treated according to Examples 1 to 3:

Untreated	Totally burnt.
With flame-proofing finish	Very good.
With flame-proofing finish and washed 5 times SNV—4	Very good.

Water-repellency of the fabric treated according to Example 3: The fabric is sprinkled with water and shows the following water-content in percent:

Untreated	70
With flame-proofing finish	4
With flame-proofing finish and washed 5 times SNV—4	9.5

What is claimed is:

1. Process for the flame-proofing of cellulose-containing textile material, which comprises in a first stage impregnating the material with a water-soluble hardenable aminoplast and hardening the aminoplast in the presence of the impregnating liquid present on the textile material, and in a second stage impregnating the material in an aqueous bath containing tetrakis-(hydroxymethyl)-phosphonium chloride, drying it and after-treating it with ammonia.

2. Process for the flame-proofing of cellulose-containing textile material, which comprises in a first stage impregnating the material with a water soluble, hardenable aminoplast and hardening the aminoplast in the presence of the impregnating liquid present on the textile material, and in a second stage impregnating the material in an aqueous bath containing tetrakis-(hydroxymethyl)-phosphonium chloride, drying it and after-treating it with gaseous ammonia.

3. Process for the flame-proofing of cellulose-containing material, which comprises in a first stage impregnating the material with a water soluble, condensation product of melamine and formaldehyde and hardening the melamine-formaldehyde condensation product in the presence of the impregnating liquid present on the textile material, and in a second stage impregnating the material in an aqueous bath containing tetrakis-(hydroxymethyl)-phosphonium chloride, drying it and after-treating it with gaseous ammonia.

4. Process for the flame-proofing of cellulose-containing textile material, which comprises in a first stage impregnating the material with a water soluble, condensation product of 1 mol of melamine and 3 mols of formaldehyde and hardening the melamine-formaldehyde condensation product in the presence of the impregnating liquid present on the textile material, and in a second stage impregnating the material in an aqueous bath containing tetrakis-(hydroxymethyl)-phosphonium chloride, drying it and after-treating it with gaseous ammonia.

5. Process for the flame-proofing of cellulose-containing textile material, which comprises in a first stage impregnating the material with a water soluble, condensation product of 1 mol of melamine and 3 mols of formaldehyde and hardening the melamine-formaldehyde condensation product in the presence of the impregnating liquid present on the textile material, and drying the material and in a second stage impregnating the material in an aqueous bath containing tetrakis-(hydroxymethyl)-phosphonium chloride, drying it and after-treating it with gaseous ammonia.

6. Process for the flame-proofing of cellulose-containing textile material, which comprises in a first stage impregnating the material with a water soluble condensation product of 1 mol of melamine and 3 mols of formaldehyde and hardening the melamine-formaldehyde condensation product in the presence of the impregnating liquid present on the textile material, and hydrogen peroxide and drying the material, and in a second stage impregnating the material in an aqueous bath containing tetrakis-(hydroxymethyl)-phosphonium chloride, drying it and after-treating it with gaseous ammonia.

7. Process for the flame-proofing of cellulose-containing textile material, which comprises in a first stage impregnating the material with a water soluble condensation product of 1 mol of melamine and 3 mols of formaldehyde, hardening the melamine-formaldehyde condensation product in the presence of the impregnating liquid present on the textile material and hydrogen peroxide

storing the material in the moist state and drying it, and in a second stage impregnating the material in an aqueous bath containing tetrakis-(hydroxymethyl)-phosphonium chloride, drying it and after-treating it with gaseous ammonia.

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5

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