United States Patent Office

3,690,941

Patented Sept. 12, 1972

3,690,941

PROCESS FOR PROVIDING CELLULOSE FIBRE MATERIAL WITH A FLAME-PROOF FINISH FAST TO WASHING

Martin Reuter, Kronberg, Taunus, Claus Beermann, Neu-Isenburg, and Fritz Linke, Konigstein, Taunus, Germany, assignors to Farbkerke Hoechst Aktiengesellschaft vormals Meister Lucius & Bruning, Frankfurt am Main, Germany

No Drawing. Continuation-in-part of application Ser. No. 43,192, June 3, 1970. This application Dec. 8, 1970, Ser. No. 96,286

Claims priority, application Germany, Aug. 29, 1970, P 20 42 949.6

Int. Cl. C09k 3/28; D06m 13/28

U.S. Cl. 117—136 9 Claims

ABSTRACT OF THE DISCLOSURE

Cellulose fiber materials are rendered flame proof and fast to washing by (a) impregnation with aqueous bath containing phosphoric acid esters with N-methylol groups and, optionally, aminoplast precondensates and/or aminoplast condensation catalysts, and (b) a subsequent heat treatment.

This application is a continuation-in-part application of our copending application Ser. No. 43,192, filed June 3, 1970.

A number of processes are known for providing cellulose fibre materials, especially textiles, with a flame-proof finish fast to washing by using condensation products of organophosphoric compounds. Processes are mostly used in which condensates of methylol-phosphoric compounds, especially of quaternization products of the tris-hydroxymethylphosphine, for example of tetrahydroxy-methylphosphonium-hydroxide and its salts, are produced on the textiles, partly with addition of aminoplast forming agents, partly cross-linking with gaseous ammonia. These compounds, however, have some drawbacks: they are obtained only in a risky and dangerous manner from hydrogen phosphide, the access to which is very difficult, further, they have an unfavorable influence on the shades of several textile dyeings.

In other known processes, condensation products of phosphoryl or phosphonyl-ethylene-imides of the

$$R_1P(O)—(NC_2H_4)_2$$

type are produced on the textiles, in which R_1 stands for an aliphatic radical or signifies the radical $—NC_2H_4$ of the very toxic ethylene-imine. The drawbacks of these phosphoric compounds are: they can be prepared only by very lengthy synthesis and they have only a limited stability under normal temperatures.

Further, there have been used condensates from phosphoric acid or phosphonic acids and urea in order to produce a flameproof finish fast to washing on cellulose textiles, which, however, damage the ultimate tensile strength of the textiles. These finishes also behave towards anion active detergents as ion exchangers which, as a result of a washing process, considerably reduces the flame-proofness. High textile tear strength losses of the textiles result when finishes with phosphorus nitrilamido-methyl esters are used.

There has further been suggested to react cellulose with N-hydroxy-methyl-iodoacetamide and to convert the iodoacetamido-methylcellulose compound of the general formula

$$Cell—OCH_2—NHCOCH_2I$$

by further reaction according to the Arbuzov reaction ex-

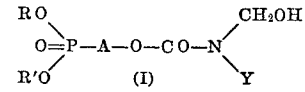
cess trialkylphosphites and thus converting these to the corresponding phosphonic esters of the general formula

$$Cell—OCH_2NHCOCH_2P(O)(OR)_2$$

This process requires a special equipment for the recovery of the phosphites and it cannot be carried out on the finishing machines usual in industrial practice. Moreover, all of these processes are odoriferous, the odor elimination of which can be ensured only by expensive apparatuses.

The present invention relates to a process for providing cellulose fibre material with a flame-proof finish fast to washing by means of condensates of organophosphoric compounds, in which the aforementioned drawbacks are eliminated.

The object of the invention is a process for providing cellulose fibre material with a flame-proof finish fast to washing, wherein the fibrous material is treated with an aqueous impregnation bath which contains a phosphonic acid ester having N-methylol groups of the Formula I



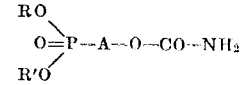
(I)

in which R and R′ represent lower alkyl having preferably from 1 to 4 carbon atoms, A is straight-chain or branched alkylene of 1 to 5 carbon atoms and Y stands for hydrogen or the radical $—CH_2OH$, and, preferably, aminoplast precondensates and/or aminoplast condensation catalysts, and subsequently is subjected to a heat-treatment. In this process, tear strength losses and feel deterioration of the cellulosic fibre as well as alteration of the shades are eliminated, and good flame-proof effects fast to washing are obtained. Also, an odoriferous emission does not occur.

As compounds corresponding to Formula I those are preferred in which A stands for methylene, 1,1-ethylene or 1,1-propylene, i.e. compounds in which A represents a bridge-member of the formula

in which A′ stands for hydrogen, methyl or ethyl.

As starting products for the preparation of the compounds of Formula I used in the process of the invention there may be used for example urethano-alkyl-phosphonic esters of the Formula II



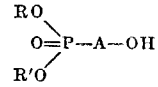
(II)

in which R, R′ and A have the meanings given above. The compounds of the Formula II may be obtained by reaction of the corresponding halo-alkyl urethanes of the formula

$$Hal—(CH_2)_n—O—CO—NH_2$$

in which n is an integer of 1 to 4 and Hal is halogen, especially chlorine, with di- or trialkylphosphites.

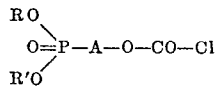
The compounds of Formula II are, furthermore, obtained by reacting the known hydroxyalkyl phosphonic ac id-esters (cf. Houben-Weyl, Methoden der organischen Chemie, 4th Edition, vol. 12/1, page 478) of the formula



(III)

in which R, R′ and A are as defined above, in known

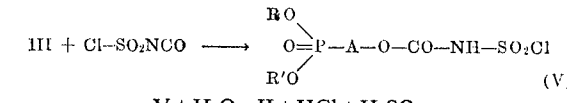
manner, with phosgene and reacting the so-obtained chlorocarbonic acid esters of the formula



(IV)

in which R, R' and A are as defined above, with ammonia.

The urethano-alkyl-phosphonic esters of Formula II may also be obtained by reaction of the hydroxyalkyl-phosphonic acid esters of Formula III with chlorosulfonyl isocyanate according to the following formula equations:



(V)

$$V + H_2O \rightarrow II + HCl + H_2SO_4$$

In Formula V, R, R' and A are as defined above.

Thereafter, these urethano-alkyl-phosphonic esters of the Formula II are converted according to known methods into the N-monomethylol or N-dimethylol compounds of Formula I to be used in the process of the invention by reaction with 1 to 2 mols of aqueous formaldehyde or with paraformaldehyde at temperatures of from about 10° to 70° C., preferably in the alkaline pH range, for example at pH 8 to 9. Preferred examples of such phosphonic acid esters containing N-methylol groups used in the process of the invention are: N-mono-methylol-urethano-ethyl-phosphonic acid diethyl ester

$$(C_2H_5O)_2P(O)CH_2OCONHCH_2OH$$

N-monomethylol - urethano - ethyl - phosphonic acid dimethyl ester $(CH_3O)_2P(O)CH_2OCONHCH_2$ or the corresponding N-dimethylol compounds.

In the process of the invention, the cellulose fibre materials are preferably treated with aqueous solutions or dispersions which contain per litre about 50 to 400 g. of the phosphonic acid esters of Formula I. Further, about 20 to 200 g./l. of known aminoplast precondensates, for example N-methylol-urea, N'N - dimethylol-cycloethylene-urea, trimethylolmelamine, penta-methylolmelamine trimethyl ether or other such substances are preferably added, as well as known acid forming condensation catalysts, for example ammonium chloride or magnesium chloride.

The cellulose fibre material impregnated in known manner on a foulard is subsequently squeezed off; the resulting increase in weight (squeezing effect) being preferably of from 60 to 100%. Then, the goods are dried in known-manner and subjected to a further heat-treatment. The drying is advantageously carried out at about 80° to 120° C., preferably up to a residual moisture content of about 4 to 8 percent by weight. The subsequently heat-treatment is carried out at a temperature in excess of 110° C. and up to about 200° C., preferably for about 1 to 10 minutes at 130° C. and up to about 180° C. Finally, the fibrous material may be subjected to an alkaline washing, for example with a 0.2%-aqueous sodium carbonate solution.

Further known textile auxiliaries, such as plasticizers, crease-proofing or hydrophobizing agents, may be added to the impregnation solutions to be used in the process of the invention.

The following examples illustrate the invention:

EXAMPLE 1

A cotton-moleskin fabric (200 g./m.²) was impregnated on a foulard at about 25° C. with an aqueous solution which contained per litre 250 g. of N-methylol-urethanomethyl-phosphonic acid diethyl ester of the formula

$$(C_2H_5O)_2P(O)CH_2OCONHCH_2OH$$

further 50 g. of pentamethylolmelamine trimethyl ether and 4 g. of ammonium chloride. The N-methylol-urethanomethyl-phosphonic acid diethyl ester was prepared from hydroxymethyl-phosphonic acid diethyl ester and phosgene and by the action of ammonia on the so-obtained chlorocarbonic acid ester of the formula

$$(C_2H_5O)_2P(O)CH_2O—C(O)Cl$$

followed by known methylolization with formaldehyde. During the impregnation a squeezing effect of 80% was maintained.

The fabric was predried at 100° C. so that it contained a residual moisture of about 8% by weight, and subsequently heated for 4 minutes at 170° C. for condensation purposes. The fabric so finished had a pleasant full feel (hand), showed no damage in its tear strength and showed in the vertical flame-proof test according to DIN 53 906 (German Industrial Standards, equivalent to the "Framed Vertical Strip CCC–T–19 1 b Method 5902," cf. M. J. Koroskys, American Dyestuff Reporter, Mar. 24, 1969, page 15 et seq., especially page 19, col. 3) a burning length of 18.0 cm. These properties were maintained also after a washing of 15 minutes at 95° C. with a 0.2%-aqueous sodium carbonate solution.

EXAMPLE 2

When working as described in Example 1 but using 330 g. of (N,N-dimethylol)-urethanomethyl phosphonic acid diethyl ester of the formula

$$(C_2H_5O)_2P(O)CH_2OCON(CH_2OH)_2$$

Instead of the 250 g. of the monomethyl compound and adding to the impregnation bath 50 g. of 1,3-dimethylol-4,5-dihydroxyimidazolidinone - 2 and 8 g. of magnesium chloride the so-obtained fabric showed after the condensation at 170° C. a burning length of 11.0 cm. only. The other properties of the fabric remained essentially unchanged. After washing the fabric for 15 minutes at 95° C. with a 0.2% aqueous sodium carbonate solution the burning length was 10.5 cm. After a washing for 3 hours in a bath containing 5 g./l. of soap and 3 g./l. of sodium carbonate in an open beaker at the boil the burning length was, likewise, 10.5 cm.

EXAMPLE 3

A cotton moleskin fabric (200 g./m.²) was padded at 25° C. on a foulard with an aqueous solution containing 250 g./l. of (N,N-dimethylol) - 1 - urethanoethyl-phosphonic acid dimethyl ester of the formula

$$(CH_3O)_2P(O)CH(CH_3)OCON(CH_2OH)_2$$

50 g./l. of pentamethylolmelamine trimethyl ether and 4 g./l. of ammonium chloride. The impregnated fabric was squeezed between rollers until the increase in weight, referred to dry fabric, was 80%.

The padded fabric was dried at 100° C. until the moisture content was about 8% and, subsequently, heated to effect condensation for 4 minutes to 170° C. The so-obtained fabric showed a pleasant soft handle and was not impaired in respect to tear strength. The burning length according to DIN 53 906 was 8.0 cm. These properties were maintained after a washing for 15 minutes at 95° C. with an 0.2% aqueous sodium carbonate solution.

The (N,N-dimethylol)-1-urethanoethyl dimethyl phosphonate mentioned above was prepared as follows: 1 mol of 1-hydroxyethyl-1-phosphonic acid dimethyl ester of the formula

$$(CH_3O)_2P(O)CH(CH_3)—O—H$$

(known from Houben-Weyl, Methoden der organischen Chemie, 4th Edition, vol. 12/1, page 478) was added dropwise at 0° C. to 2 moles of phosgene. After distilling off the hydrogen chloride and the surplus phosgene at 10 to 20° C. the oily chloro-carbonic acid ester of the formula

$$(CH_3O)_2P(O)CH(CH_3)—O—CO—Cl$$

was obtained in 95% yield.

Analysis.—Calculated 16.9% Cl. Found 16.4% Cl. The chlorocarbonic acid ester was addded dropwise to the five-fold amount by volume of chloroform, in which 2 mols of ammonia was bubbled in. The ammonium chloride formed as by-product was removed by filtration with suction and washed with chloroform for several times. From the combined chloroform filtrates the chloroform was distilled off in vacuo at about 40° C. There remained the urethane of the formula

$$(CH_3O)_2P(O)CH(CH_3)—O—CO—NH_2$$

in 80% yield as a crystalline solid, melting point 98° C., after recrystallization from hot acetone 108° C.

Analysis.—$C_5H_{12}NO_5P$ (197): Calculated 30.5% C, 6.0% H, 7.0% N, 15.7% P, 31.5% CH_3O. Found: 30.3% C, 6.1% H, 7.5% N, 15.6% P, 31.4% CH_3O.

0.55 mol of the so-obtained urethane was dissolved in 1.1 mol of 37% formaline at 50° C. while stirring and this temperature maintained for a further hour. The initial pH value of 4 was raised to 8.4 by means of 13 cc. of 2 N NaOH and maintained at this value.

There was found by means of alkaline iodine solution 17.3% of HCHO (theoretically: 17.0%), with hydroxylamine, however, only 4.3% of free HCHO was found. These values indicate that a mixture of at least 50 mol-percent the dimethylol compound and of at most 50 mol-percent of the monomethylol compound was present.

EXAMPLE 4

When impregnating a cotton moleskin fabric as described in Example 3, but adding, furthermore, to the impregnation bath 40 g./l. of 1,3-dimethylol-4,5-dihydroxy-imidazolidinone-2 and 8 g./l. of magnesium chloride a flame-proof fabric was obtained the burning length of which was 8 cm., which was maintained after a washing at the boil with a bath containing 5 g./l. of soap and 3 g./l. of sodium carbonate for 3 hours.

EXAMPLE 5

When impregnating a cotton moleskin fabric as described in Example 3, but using instead of the (N,N-dimethylol)-1-urethanoethyl phosphonic acid dimethyl ester the same amount of (N,N-dimethylol)-1-urethanopropyl phosphonic acid diethyl ester of the formula

$$(C_2H_5O)_2P(O)—CH(C_2H_5)—OCO—N(CH_2OH)_2$$

substantially the same results were obtained as given in Example 3.

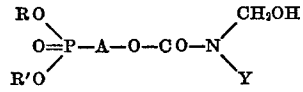
The (N,N-dimethylol) - 1 - urethanopropyl-phosphonic acid dimethylester was obtained as folows: 1 - hydroxypropyl - 1 - phosphonic acid diethyl ester (known from Houben-Weyl, 4th Ed., vol. 12/1, p. 478) was reacted as described in Example 3 with phosgene, and, subsequently with ammonia to yield the urethane of the formula

$$(C_2H_5O)_2P(O)CH(C_2H_5)—OCO—NH_2$$

(melting point 80° C.) and reacting said urethane finally with 2 mols of formaline.

We claim:

1. In a process for flame proofing fibrous materials of cellulose, the improvement of which comprises impregnating said material in an aqueous bath comprising a phosphonic acid ester of the formula



in which R and R′ are lower alkyl, A is straight-chain or branched alkylene of 1 to 5 carbon atoms each and Y is hydrogen or CH_2OH, and heating said impregnated material at a temperature from 80° C. to 200° C.

2. The process as claimed in claim 1, wherein the impregnated goods are predried at about 80 to 120° C., and finally subjected to a heating at a temperature up to 200° C.

3. The process as claimed in claim 1, wherein heating is at a temperature above about 110° C. and below 200° C.

4. The process as claimed in claim 1, wherein the heating is at a temperature from 130° C. to 180° C.

5. The process as claimed in claim 1, wherein the impregnating aqueous bath consists essentially of about 50 to 400 g. per liter of the phosphonic acid ester.

6. The process as claimed in claim 1, wherein the impregnating bath additionally contains an aminoplast precondensate.

7. The process as claimed in claim 1, wherein the impregnation bath additionally contains about 20 to 200 g. per liter of an aminoplast precondensate.

8. The process as claimed in claim 1, wherein the impregnated goods are squeezed to yield an increase in weight of about 60 to 100%, referred to dry goods.

9. The process as claimed in claim 1, wherein the heating lasts from 1 to 10 minutes at a temperature from 130° C. to 180° C.

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WILLIAM D. MARTIN, Primary Examiner

H. J. GWINNELL, Assistant Examiner

U.S. Cl. X.R.

117—139.5 CQ, 143 R; 252—8.1

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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Inventor(s) Martin Reuter et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Heading:

"Application Germany" should read --applications Germany, June 14, 1969, P 19 30 308.3 and--.

Signed and sealed this 13th day of February 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334.

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