(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
5 April 2001 (05.04.2001)

PCT

(10) International Publication Number
WO 01/23663 A1

(51) International Patent Classification[7]: D06M 15/263, 13/192, 13/288, 13/292, 13/295, 15/667, 13/207

(21) International Application Number: PCT/US00/26133

(22) International Filing Date:
22 September 2000 (22.09.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/406,529 27 September 1999 (27.09.1999) US

(71) Applicants: UNIVERSITY OF GEORGIA RESEARCH FOUNDATION, INC. [US/US]; 621 Boyd Graduate Studies Research Center, Athens, GA 30602-7411 (US). AKZO NOBEL N.V. [NL/NL]; Velperweg 76, P.O. Box 9300, NL-6800 SB Arnhem (NL).

(72) Inventors: STOWELL, Jeffrey, K.; 230 Mulberry Road, Ramsey, NJ 07446 (US). WEIL, Edward, D.; 200 East 57th Street, Apt. 5L, New York, NY 10022 (US). COBLE, William, L.; 1105 Aycock Avenue, Burlington, NC 27215 (US). YANG, Charles, Q.; 189 Elderberry Circle, Athens, GA 30605 (US).

(74) Agent: FENNELLY, Richard, P.; Akzo Nobel Inc., Intellectual Property Dept., 7 Livingstone Avenue, Dobbs Ferry, NY 10522-3408 (US).

(81) Designated States *(national)*: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IN, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/23663 A1

(54) Title: FORMALDEHYDE-FREE FLAME RETARDANT TREATMENT FOR CELLULOSE-CONTAINING MATERIALS

(57) Abstract: An aqueous finishing composition for cellulose-containing materials, comprising a hydroxyalkyl-functional organophosphorus flame retardant (which contains a substantially non-volatile component at the curing temperature) and a non-formaldehyde cross-linking agent (such as a polycarboxylic acid cross-linking agent), and the materials treated with such a composition. Optional ingredients for the aqueous finishing composition include a cross-linking catalyst and/or an inexpensive saturated alpha-hydroxy polycarboxylic acid such as citric acid (partial replacement of a more expensive preferred polycarboxylic acid will reduce finishing costs).

FORMALDEHYDE-FREE FLAME RETARDANT TREATMENT FOR CELLULOSE-CONTAINING MATERIALS

Background of the Invention

The present invention relates to a formaldehyde-free flame retardant treatment for cellulose-containing materials, such as cotton or cotton blends (e.g., cotton/polyester and cotton/nylon), which is durable to both laundering and dry cleaning operations.

There are currently several different types of chemical finishes that can be applied to cellulose-containing materials to impart flame retardant (FR) properties. Of these systems, only a few create finished fabrics that can be laundered and dry-cleaned without losing their FR qualities. These treatments are generally referred to as durable FR finishes. Of these finishes, the most pertinent to the current invention are PROBAN and the PYROVATEX brand materials. The PROBAN technology, from Albright & Wilson, is based on the use of tetrakis-(hydroxymethyl)phosphonium chloride ("THPC")-based products and an ammoniation chamber. It is described in detail in the following U.S. Pat. Nos. 4,078,101; 4,145,463; 4,311,855 and 4,494,951, all to Albright and Wilson. The PYROVATEX CP methodology, originally developed by Ciba-Geigy, utilizes dimethyl (N-hydroxymethylcarbamoyl-ethyl)phosphonate or a similar methylol-functional phosphorus-containing analogue as the flame retardant agent. Given the market share that PROBAN and PYROVATEX products control in the industry, it is often difficult to understand the widespread tolerance of the negative aspects associated with the use of these products and the various chemistries they employ.

There have been several versions of the THPC cross-linking chemistry used over the years. For example, the precondensate-NH_3 process (e.g., PROBAN) technology is the most recent of these versions. Although this may be the most durable treatment on the market, this technology involves the use of an ammoniation chamber and strict application conditions to obtain consistent results without significant strength loss to the fabric. In addition to difficult application conditions, the startup costs for implementing this finishing technique and the regulatory issues associated with ammonia gas make it less than attractive, especially for new arrivals to the market.

In many ways, the PYROVATEX technology suffers from much the same sort of downfalls as the PROBAN technology. Whether it is the original PYROVATEX CP methodology, based on the use of dimethyl (N-hydroxymethylcarbamoyl-ethyl)phosphonate, or other methods using different N-methylol-functional phosphorus-containing analogs, all of the products contain and emit the toxic component formaldehyde (a known carcinogen). In addition to the molecule forming the basis of the PYROVATEX-type approach, a formaldehyde-containing cross-linking resin, such as a N-methylolurea (for example, 1,3-dimethylol-4,5-dihydroxyethyleneurea - "DMDHEU"), N-methylolamide, or N-methylolmelamine, is also required to ensure adequate durability of the chemical finish. These resins are also independently used as durable-press cross-linking agents in the textile industry. The combination of a N-methylol phosphorus-containing analog and a N-methylol cross-linking resin, or the use of either reagent separately, often leads to the release of

significant amounts of formaldehyde both during fabric application and throughout the lifetime of the garment. As a result, formaldehyde emission levels are limited and closely regulated throughout the industry. The only reason formaldehyde emissions are still tolerated is due to the lack of an acceptable formaldehyde-free replacement technology.

Given the negative impact of formaldehyde on human health, it has been a primary focus of the cotton apparel and textile finishing industries to create equivalent non-formaldehyde technologies. Accounting for their widespread use, most of the current research effort has been spent on the creation and design of new formaldehyde-free cross-linking agents for cellulose-containing materials. These reagents could be used in many different applications, ranging from use in durable-press finishes to general fixation additives for products such as the PYROVATEX-type FR additives. In the past several years, research efforts have led to the discovery of several new low formaldehyde based systems. These finishes are generally based on the structural modification of DMDHEU, either via substitution or elimination of the pendant methylol functionality. Nevertheless, these new finishing agents have never gained widespread acceptance due to their inadequate performance as cross-linking agents. In general, removal or modification of the most reactive aspect of the DMDHEU molecule has only resulted in the generation of less reactive and less desirable finishing agents.

In addition to modifying DMDHEU, other technologies have also begun to develop. One of the more promising non-formaldehyde systems is based on the use of

polycarboxylic acids. These molecules create a cross-linked cellulosic material via the in-situ generation of five-membered cyclic anhydrides and their subsequent reaction with hydroxyl moieties contained within the treated textile. This technology was developed at the United States Department of Agriculture in New Orleans under the direction of Clark Welch and was based on the use of 1,2,3,4-butanetetra-carboxylic acid (BTCA). Representative patents describing this approach are: U.S. Patent Nos. 4,820,307; 4,936,865; 4,975,209; and 5,221,285.

Since the invention of the BTCA technology, additional investigators have begun to work with polycarboxylic acids to improve their commercial attractiveness. Some of the recent work has focused on the use of polymaleic acid and in some cases citric acid or combinations containing citric acid. Polymaleic acid (PMA) is an inexpensive, commercially available material commonly used as a water treatment chemical. Some aspects of this work are described in PCT International Patent Publication No. WO 98/30387. In addition to PMA, there is a wide range of alternative non-formaldehyde cross-linking resins that can be used in creating durable non-formaldehyde FR treatments for cellulose-containing materials. Many of these resins are currently available and used in the water treatment business for scale-inhibition, some of which even contain small amounts of phosphorus. The utilization of these formaldehyde-free, phosphorus-containing resins may even offer additional advantages over the phosphorus-free cross-linking resins such as PMA. Incorporation of phosphorus species into the cross-linking resin itself may eliminate the need for

an external cross-linking catalyst and/or the added phosphorus may result in improved FR properties of the treated cellulose-containing materials. Examples of these resins can be seen in the following U.S. Pat. Nos. 4,046,707; 4,105,551; 4,621,127; 5,376,731; 5,386,038; 5,496,476; 5,705,475; and 5,866,664.

Summary of the Present Invention

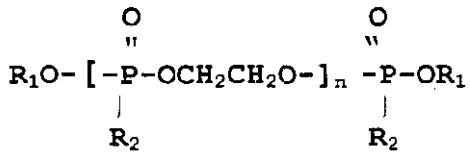
The present invention relates to an aqueous finishing composition for cellulose-containing materials and the materials treated with such a composition. The aqueous finishing composition, in its broadest embodiment, comprises a hydroxyalkyl-functional organophosphorus flame retardant and a non-formaldehyde cross-linking agent, optionally with a cross-linking catalyst also being included therein.

Description of the Preferred Embodiments

The aqueous finishing composition, which is intended to be used to treat cellulose-containing materials in accordance with the present invention contains two essential components: (1) a hydroxyalkyl-functional organophosphorus flame retardant (excluding N-methylol, ethers thereof, and potentially formaldehyde releasing reagents); and (2) a non-formaldehyde cross-linking agent.

Monomeric, oligomeric (which generally contain from about two to ten repeat units) and polymeric (which generally contain over about ten repeat units) hydroxyalkyl-functional organophosphorus flame retardant additives are intended for use herein.

A reactive oligomeric phosphorus-containing flame retardant of the type that is described in U.S. Patent No. 3,695,925 to E.D. Weil and 4,199,534, 4,268,633, and 4,335,178 to R.B. Fearing is an example of one of the hydroxyalkyl-functional organophosphorus flame retardants that can be used in accordance with the present invention. A preferred embodiment has the following structure:



where R_1 is independently selected from methyl and hydroxyethyl, R_2 is independently selected from methyl, methoxy, and hydroxyethoxy, and n is equal to or greater than 1. This embodiment is made by a multistep process from dimethyl methylphosphonate, phosphorus pentoxide, ethylene glycol, and ethylene oxide and is available under the registered trademark FYROL® 51 from Akzo Nobel Chemicals Inc. The endgroups are principally hydroxyl groups.

Another class of materials for use herein includes water soluble oligomeric alkenylphosphonate materials, examples of which are described in U.S. Patent Nos. 3,855,359 and 4,017,257, both to E.D. Weil. The presence of alkenyl substituents in these materials provide an additional mechanism for permanence utilizing free radical curing conditions (described in the patents above). A preferred species of this type was available under the trademark FYROL® 76 from Akzo Nobel Chemicals Inc. and is produced by reacting bis(2-chloroethyl)

vinylphosphonate and dimethyl methylphosphonate with the substantial elimination of methyl chloride.

Another type of hydroxyalkyl-functional organophosphorus flame retardant that can be employed are oligomeric phosphoric acid esters that carry hydroxyalkoxy groups as described in U.S. Patent Nos. 2,909,559, 3,099,676, 3,228,998, 3,309,427, 3,472,919, 3,767,732, 3,850,859, 4,244,893, 4,382,042, 4,458,035, 4,697,030, 4,820,854, 4,886,895, 5,117,033, and 5,608,100.

The flame retardant is generally present at from about 1% to about 60%, preferably from about 10% to about 40%, by weight of the aqueous finshing composition.

The non-formaldehyde cross-linking agent, which is the second essential component of the aqueous finishing composition of the present invention, is generally present at from about 1% to about 40%, by weight, of the total weight of that composition, preferably from about 5% to about 20%.

Polycarboxylic acid cross-linking agents form one type of cross-linking agent for use herein. The polycarboxylic acids effective as cellulose cross-linking agents in regard to this invention include aliphatic, alicyclic and aromatic acids either olefinically saturated or unsaturated with at least three and preferably more carboxyl groups per molecule or with two carboxyl groups per molecule if a carbon-carbon double bond is present alpha, beta to one or both carboxyl groups. An additional requirement is that to be reactive in esterifying cellulose hydroxyl groups, a given carboxyl group in an aliphatic or alicyclic polycarboxylic acid should be separated from a second

carboxyl group by no less than two carbon atoms and no more than three carbon atoms. In an aromatic acid, a carboxyl group must be ortho to a second carboxyl group if the first carboxyl is to be effective in esterifying cellulosic hydroxyl groups. It appears from these requirements that for a carboxyl group to be reactive, it should be able to form a cyclic 5-or 6-membered anhydride ring with a neighboring carboxyl group in the polycarboxylic acid molecule. Where two carboxyl groups are separated by a carbon-carbon double bond or are both connected to the same ring, the two carboxyl groups should be in the cis configuration relative to each other if they are to interact in this manner. The aliphatic or alicyclic polycarboxylic acid may also contain an oxygen or sulfur atom in the chain or ring to which the carboxyl groups are attached.

In aliphatic acids containing three or more carboxyl groups per molecule, a hydroxyl group attached to a carbon atom alpha to a carboxyl group does not interfere with the esterification and cross-linking of cellulose by the acid. However, the presence of the hydroxyl group may cause a noticeable yellowing of the material during the heat cure. Such an alpha-hydroxy acid is suitable for durable press finishing of suitably dyed cotton fabric, since the color of the dye conceals the discoloration that may be caused by the presence of the hydroxyl group. Fabric discoloration is similarly observed with an unsaturated acid having an olefinic double bond that is not only alpha, beta to one carboxyl group but also beta, gamma to a second carboxyl group.

The discoloration produced in a white cellulose-containing material by cross-linking it with an alpha-

hydroxy acid such as citric acid can be removed by impregnating the discolored material with an aqueous solution containing from 0.5% to 5% by weight of a decolorizing agent selected from the group consisting of magnesium monoperoxyphthalate, sodium perborate, sodium tetraborate, boric acid, sodium borohydride, sodium hypochlorite, and hydrogen chloride. The material is immersed in the solution of decolorizing agent and soaked for 5 to 120 minutes at ambient temperature or if necessary in such a solution warmed to a temperature not exceeding 60°C. The material is subsequently rinsed with water to remove excess chemicals and solubilized colored products, and then is dried.

A particularly preferred polycarboxylic acid cross-linking agent for use herein is 1,2,3,4-butanetetra-carboxylic acid.

Another preferred polycarboxylic acid cross-linking agent for use herein is polymaleic acid.

Another embodiment for this component is a hydrolyzed terpolymer of maleic anhydride with vinyl acetate and ethyl acrylate. The molar ratio of maleic anhydride to the combined moles of vinyl acetate and ethyl acrylate is preferably from about 2.5:1 to about 5:1 and the molar amount of vinyl acetate to ethyl acrylate is preferably from about 1:4 to about 4:1, most preferably from about 1:2 to about 2:1. The molecular weight of the terpolymer has an upper limit of about 4,000. A product of this type is available under the trademark BELCLENE 283 from FMC Corporation.

Examples of other specific polycarboxylic acids which fall within the scope of this invention are the following: maleic acid; citraconic acid also called

methylmaleic acid; citric acid also known as 2-hydroxy-1,2,3-propanetri-carboxylic acid; itaconic acid also called methylenesuccinic acid; tricarballylic acid also known as 1,2,3,-propanetri-carboxylic acid; trans-aconitic acid also known as trans-1-propene-1,2,3-tricarboxylic acid; 1,2,3,4-butanetetra-carboxylic acid; all-cis-1,2,3,4-cyclopentanetetracarboxylic acid; mellitic acid also known as benzenehexacarboxylic acid; oxydisuccinic acid also known as 2,2'-oxybis-(butanedioic acid); thiodisuccinic acid; the phosphorus-containing polycarboxylic acid resins described in U.S. Pat. Nos. 4,046,707; 4,105,551; 4,621,127; 5,376,731; 5,386,038; 5,496,476; 5,705,475; 5,866,664; and the like.

In the event that adequate cross-linking is not accomplished using the previously mentioned systems, it may be necessary to add a suitable cross-linking catalyst to enhance the reaction between the cellulose-containing material which is to be treated, the hydroxyalkyl-functional organophosphorus flame retardant, and the non-formaldehyde cross-linking agent. This catalyst can be present at up to about 30 wt% of the total weight of the aqueous finishing composition, preferably up to about 10%. Examples of suitable catalyst types to select, as set forth in PCT International Patent Publication No. WO 98/30387 and U.S. Patent Nos. 4,820,307, 4,936,865, 4,975,209, and 5,221,285 include one or more of the alkali metal salts of the known hypophosphite, phosphite, pyrophosphate, dihydrogen phosphate, phosphate, and hydrogen phosphate species, and such acids as one or more of the polyphosphoric, hypophosphorous, phosphorous, and alkyl phosphinic acids. Alternative basic cross-linking catalysts such as $NaHCO_3$ and Na_2CO_3 can also be used.

In some cases, in order to raise the pH of the treating solution to improve compatibility of the bath or additives and/or for improved strength retention, a portion of the polycarboxylic acid may be used in salt form, especially as a water soluble salt. Suitable for this purpose are alkali metal salts of the acid. Alternatively, or in combination with use of the polycarboxylic acid in salt form, the pH of the treating solution may be raised, or the solution partially neutralized, by the addition of a base, preferably a water soluble base, such as an alkali metal hydroxide, ammonium hydroxide, or an amine. The pH may be elevated for such purpose to about 2.3 to about 5, preferably about 2.5 to 4.

The present invention is further illustrated by the Examples that follow.

EXPERIMENTAL BACKGROUND

Flame Retardant ("FR") Additives Used

Sample Compound #1: Modified FYROL® 51 Flame Retardant (low OH#)

Sample Compound #2: PEEOP (low OH#)

Sample Compound #3: Modified PEEOP (high OH#)

Sample Compound #4: FYROL® 51 Flame Retardant (high OH#)

Sample Compound #5: FYROL® 6 Flame Retardant

Sample Compound #6: FYROL® 76 Flame Retardant

In the listing given above, "PEEOP" is a poly(ethyl ethyleneoxy) phosphate of the type described in U.S. Serial No. 08/677,283, having a molecular weight of around 915 (number average)/1505 (weight average), and a typical hydroxyl number of under about 5 mg KOH/g (low hydroxyl number version) and about 150 mg KOH/g (high hydroxyl number version). The modified FYROL® 51 flame retardant has a hydroxyl number of under about 5 mg KOH/g and the high hydroxyl version of the FYROL® 51 brand product has a hydroxyl number of about 125 mg KOH/g. The FYROL® 6 flame retardant has a hydroxyl number of about 440 mg KOH/g whereas the FYROL® 76 flame retardant has a hydroxyl number of about 100 mg KOH/g.

Polycarboxylic Acid Resins and Other Chemicals Used

Belclene 283: a 35% aqueous solution of the hydrolysis product of a terpolymer (TMPA) of maleic anhydride, vinyl acetate, and ethyl acrylate.

Belclene 200: a 35% aqueous solution of polymaleic acid (PMA).

BTCA: 1,2,3,4-butanetetracarboxylic acid (solid).

NaH_2PO_2 (hydrate): used as a cross-linking catalyst.

Equipment Used

Pad Applicator (laboratory size): an instrument used to apply a solution to fabric at a specified level (% wet-pickup).

Curing Oven (laboratory size): an oven that is used to dry and subsequently cure chemically treated fabrics at high temperatures.

Washing Machine (household size): used for laundering (with Tide® detergent) fabrics before and after chemical treatment and curing.

Fabric Used

Medium weight (about 1mm thick), white, prewashed, 100% cotton fabric (12 X 16 inch samples).

Experimental Details

Preliminary Work:

The cotton fabric was laundered to ensure its cleanliness, and then cut into about 12 X 16 inch samples for subsequent use. Using water and fabric samples, the pad applicator was set to a wet-pickup of about 75% (additional weight of the liquid divided by the original weight of the dry cloth). A 75% wet-pickup of water translated to about 80% wet-pickup for the chemical solutions.

General Procedure:

The application solutions with and without FR were prepared. Each solution contained a FR (except blanks), polycarboxylic acid, NaH_2PO_2, and water. Given a wet-

pickup of 80%, the solution concentrations were adjusted to give the desired add-on weights of each chemical.

After preparation, each application solution was used within a period of five hours.

Each solution was then applied to a fabric sample. The fabric was immersed in the solution, fed through the pad applicator, immersed in the solution again, and fed through the pad applicator again to ensure adequate homogeneity throughout the fabric sample.

After application, each fabric sample was placed on a metal frame and inserted into the oven at 80°C to dry (three to five minutes).

After drying, each sample was placed in the oven again at 180°C to cure the chemical treatment (one and one half to two minutes).

Each cured sample was then removed from the metal rack and its physical properties recorded. Any observations made while drying and curing the fabric were also recorded.

Informal Ignition Tests:

Each fabric sample was held in a horizontal position and ignited with a propane lighter. The flammability properties of each fabric sample were recorded.

EXPERIMENTAL DATA

1st Trial Application:

	BELCLENE 283 Resin			BTCA		
	Sample Comp. #2	Sample Comp. #4	Sample Comp. #5	Sample Comp. #2	Sample Comp. #4	Sample Comp. #5
Dry Add-On Weight	10% FR#2 4% TMPA 2% NaH_2PO_2	10% FR#4 4% TMPA 2% NaH_2PO_2	10% FR#5 4% TMPA 2% NaH_2PO_2	10% FR#2 4% BTCA 2% NaH_2PO_2	10% FR#4 4% BTCA 2% NaH_2PO_2	10% FR#5 4% BTCA 2% NaH_2PO_2
Application Solution Recipe	26.6g FR#2 30.4g BELCLENE 283 5.4g NaH_2PO_2 137.6g H_2O	26.6g FR#4 30.4g BELCLENE 283 5.4g NaH_2PO_2 137.6g H_2O	26.6g FR#5 30.4g BELCLENE 283 5.4g NaH_2PO_2 137.6g H_2O	26.6g FR#2 10.7g BTCA 5.4g NaH_2PO_2 157.3g H_2O	26.6g FR#4 10.7g BTCA 5.4g NaH_2PO_2 157.3g H_2O	26.6g FR#5 10.7g BTCA 5.4g NaH_2PO_2 157.3g H_2O
Drying Conditions	3 min. @ 80°C	3 min. @ 80°C	3 min. @ 80°C	3 min. @ 80°C	3 min. @ 80°C	3 min. @ 80°C
Curing Conditions	1.5 min. @ 180°C	1.5 min. @ 180°C	1.5 min. @ 180°C	1.5 min. @ 180°C	1.5 min. @ 180°C	1.5 min. @ 180°C
Burn (before washing)	Bad - fabric burned	Bad - fabric burned	Bad - fabric burned	Bad - fabric burned	Bad - fabric burned	Bad - fabric burned

2nd Trial Application:

Blank Samples (without FR)			
	BELCLENE 283 (TMPA)	BTCA	BELCLENE 200 (PMA)
Dry Add-On Weight	8% TMPA 4% NaH_2PO_2	8% TMPA 4% NaH_2PO_2	8% TMPA 4% NaH_2PO_2
Application Solution Recipe	57.1g BELCLENE 283 10.0g NaH_2PO_2 132.9g H_2O	57.1g BELCLENE 283 10.0g NaH_2PO_2 132.9g H_2O	57.1g BELCLENE 283 10.0g NaH_2PO_2 132.9g H_2O
Drying Conditions	5 min. @ 80°C	5 min. @ 80°C	5 min. @ 80°C
Curing Conditions	2 min. @ 180°C	2 min. @ 180°C	2 min. @ 180°C
Burn Test (before wash)	Bad - fabric burned	Bad - fabric burned	Bad - fabric burned
Fabric Color	Slight off-white tint	White	Yellow tint
Fabric Hand	Very hard	Hard	Very hard
Other Observations	No smoke	No smoke	No smoke

BELCLENE 283 Resin (TMPA)						
	Sample Comp. #1	Sample Comp. #2	Sample Comp. #3	Sample Comp. #4	Sample Comp. #5	Sample Comp. #6
Dry Add-On Weight	20% FR#1 8% TMPA 4% NaH_2PO_2	20% FR#2 8% TMPA 4% NaH_2PO_2	20% FR#3 8% TMPA 4% NaH_2PO_2	20% FR#4 8% TMPA 4% NaH_2PO_2	20% FR#5 8% TMPA 4% NaH_2PO_2	20% FR#6 8% TMPA 4% NaH_2PO_2
Application Solution Recipe	50.0g FR#1 57.1g BELCLENE 283 10.0g NaH_2PO_2 82.9g H_2O	50.0g FR#2 57.1g BELCLENE 283 10.0g NaH_2PO_2 82.9g H_2O	50.0g FR#3 57.1g BELCLENE 283 10.0g NaH_2PO_2 82.9g H_2O	50.0g FR#4 57.1g BELCLENE 283 10.0g NaH_2PO_2 82.9g H_2O	50.0g FR#5 57.1g BELCLENE 283 10.0g NaH_2PO_2 82.9g H_2O	50.0g FR#6 57.1g BELCLENE 283 10.0g NaH_2PO_2 82.9g H_2O
Drying Conditions	5 min. @ 80°C	5 min. @ 80°C	5 min. @ 80°C	5 min. @ 80°C	5 min. @ 80°C	5 min. @ 80°C
Curing Conditions	2 min. @ 180°C	2 min. @ 180°C	2 min. @ 180°C	2 min. @ 180°C	2 min. @ 180°C	2 min. @ 180°C
Burn Test (before wash)	Good	Good	Good	Good	Bad - fabric burned	Good
Burn Test (after 1 water wash)	Acceptable	Bad - fabric burned	Good	Good	Bad - fabric burned	Good
Burn Test (after 5 launderings)	-	-	Acceptable	Good	-	Acceptable
Fabric Color	Pink color	Dark pink color	Pink color	Dark pink color	Pink color	Light pink tint
Fabric Hand	Hard	Soft	Very hard	Very hard	Very hard	Very hard
Other Observations	Smoked during cure	Solubility problem-FR	No smoke	No smoke	Smoked during cure	No smoke

	BTCA					
	Sample Comp. #1	Sample Comp. #2	Sample Comp. #3	Sample Comp. #4	Sample Comp. #5	Sample Comp. #6
Dry Add-On Weight	20% FR#1 5% BTCA 2.5% NaH_2PO_2	20% FR#2 5% BTCA 2.5% NaH_2PO_2	20% FR#3 5% BTCA 2.5% NaH_2PO_2	20% FR#4 5% BTCA 2.5% NaH_2PO_2	20% FR#5 5% BTCA 2.5% NaH_2PO_2	20% FR#6 5% BTCA 2.5% NaH_2PO_2
Application Solution Recipe	50.0g FR#1 12.5g BTCA 6.3g NaH_2PO_2 131.2g H_2O	50.0g FR#2 12.5g BTCA 6.3g NaH_2PO_2 131.2g H_2O	50.0g FR#3 12.5g BTCA 6.3g NaH_2PO_2 131.2g H_2O	50.0g FR#4 12.5g BTCA 6.3g NaH_2PO_2 131.2g H_2O	50.0g FR#5 12.5g BTCA 6.3g NaH_2PO_2 131.2g H_2O	50.0g FR#6 12.5g BTCA 6.3g NaH_2PO_2 131.2g H_2O
Drying Conditions	5 min. @ 80°C	5 min. @ 80°C	5 min. @ 80°C	5 min. @ 80°C	5 min. @ 80°C	5 min. @ 80°C
Curing Conditions	2 min. @ 180°C	2 min. @ 180°C	2 min. @ 180°C	2 min. @ 180°C	2 min. @ 180°C	2 min. @ 180°C
Burn Test (before wash)	Good	Good	Good	Good	Bad - fabric burned	Good
Burn Test (after 1 water wash)	Acceptable	Bad - fabric burned	Good	Good	Bad - fabric burned	Good
Burn Test (after 5 launderings)	-	-	Good	Good	-	Good
Fabric Color	White	White	White	White	Slight yellow tint	White
Fabric Hand	Semi-soft	Soft	Hard	Very hard	Hard	Very hard
Other Observations	Smoked during cure	Solubility problem-FR	No smoke	No smoke	Smoked during cure	No smoke

	BELCLENE 200 (PMA)			
	Sample Comp. #1	Sample Comp. #3	Sample Comp. #4	Sample Comp. #6
Dry Add-On Weight	20% FR#1 8% PMA 4% NaH_2PO_2	20% FR#3 8% PMA 4% NaH_2PO_2	20% FR#4 8% PMA 4% NaH_2PO_2	20% FR#6 8% PMA 4% NaH_2PO_2
Application Solution Recipe	50.0g FR#1 57.1g BELCLENE 200 10.0g NaH_2PO_2 82.9g H_2O	50.0g FR#3 57.1g BELCLENE 200 10.0g NaH_2PO_2 82.9g H_2O	50.0g FR#4 57.1g BELCLENE 200 10.0g NaH_2PO_2 82.9g H_2O	50.0g FR#6 57.1g BELCLENE 200 10.0g NaH_2PO_2 82.9g H_2O
Drying Conditions	5 min. @ 80°C	5 min. @ 80°C	5 min. @ 80°C	5 min. @ 80°C
Curing Conditions	2 min. @ 180°C	2 min. @ 180°C	2 min. @ 180°C	2 min. @ 180°C
Burn Test (before wash)	Good	Good	Good	Good
Burn Test (after 1 water wash)	Acceptable	Good	Good	Good
Burn Test (after 5 launderings)	-	-	Good	-
Fabric Color	Yellow tint	Yellow tint	Yellow tint	Yellow tint
Fabric Hand	Hard	Very hard	Hard	Very hard
Other Observations	Smoked during cure	No smoke	No smoke	No smoke

3rd Trial Application:

	Sample Compound #5		
	BELCLENE 283 (TMPA)	BTCA	BELCLENE 200 (PMA)
Dry Add-On Weight	40% FR#5 8% TMPA 4% NaH_2PO_2	40% FR#5 5% BTCA 2.5% NaH_2PO_2	40% FR#5 8% PMA 4% NaH_2PO_2
Application Solution Recipe	100.0g FR#5 57.1g BELCLENE 283 10.0g NaH_2PO_2 32.9g H_2O	100.0g FR#5 12.5g BTCA 6.3g NaH_2PO_2 81.2g H_2O	100.0g FR#5 57.1g BELCLENE 200 10.0g NaH_2PO_2 32.9g H_2O
Drying Conditions	5 min. @ 80°C	5 min. @ 80°C	5 min. @ 80°C
Curing Conditions	2 min. @ 180°C	2 min. @ 180°C	2 min. @ 180°C
Burn Test (after 1 water wash)	Bad - fabric burned	Bad - fabric burned	Bad - fabric burned
Fabric Color	Yellow tint	Yellow tint	Yellow tint
Fabric Hand	Soft	Soft	Soft
Other Observations	Smoked during cure	Smoked during cure	Smoked during cure

Analysis of Selected Fabric Samples

Sample Compound #3 (20% add-on) with TMPA and BTCA (samples - before washing, after one water wash, and after five launderings).

Sample Compound #4 (20% add-on) with TMPA, BTCA, and PMA (samples - before washing, after one water wash, and after five launderings).

Sample Compound #6 (20% add-on) with TMPA and BTCA (samples - before washing, after one water wash, and after five launderings).

Sample Compound #5 (40% add-on) with TMPA, BTCA, and PMA (samples - after one water wash).

Percent Phosphorus Determinations on Selected Fabric Samples

Sample Identification (dry add-on weights)	Before Washing (%P)	After 1 Water Wash (%P)	After 5 launderings (%P)
20% FR#3, 5.0% BTCA, 2.5% NaH_2PO_2	2.8	1.9	1.6
20% FR#3, 8.0% TMPA, 4.0% NaH_2PO_2	3.6	2.1	2.1
20% FR#4, 5.0% BTCA, 2.5% NaH_2PO_2	3.4	2.0	2.1
20% FR#4, 8.0% TMPA, 4.0% NaH_2PO_2	4.2	2.7	2.5
20% FR#4, 8.0% PMA, 4.0% NaH_2PO_2	3.9	2.2	2.3
20% FR#6, 5.0% BTCA, 2.5% NaH_2PO_2	3.9	2.6	2.3
20% FR#6, 8.0% TMPA, 4.0% NaH_2PO_2	4.5	1.5	1.5
40% FR#5, 5.0% BTCA, 2.5% NaH_2PO_2	-	0.35	-
40% FR#5, 8.0% TMPA, 4.0% NaH_2PO_2	-	0.37	-
40% FR#5, 8.0% PMA, 4.0% NaH_2PO_2	-	0.34	-

Percent Sodium Determinations on Selected Fabric Samples

Sample Identification (dry add-on weights)	After 5 launderings (%Na)
20% FR#3, 5.0% BTCA, 2.5% NaH_2PO_2	72 ppm*
20% FR#3, 8.0% TMPA, 4.0% NaH_2PO_2	58 ppm*
20% FR#4, 5.0% BTCA, 2.5% NaH_2PO_2	55 ppm*
20% FR#4, 8.0% TMPA, 4.0% NaH_2PO_2	95 ppm*
20% FR#4, 8.0% PMA, 4.0% NaH_2PO_2	92 ppm*
20% FR#6, 5.0% BTCA, 2.5% NaH_2PO_2	51 ppm*
20% FR#6, 8.0% TMPA, 4.0% NaH_2PO_2	76 ppm*

*Numbers are blank corrected (sodium level in blank was ~75 ppm)

As can be seen from the results above, several of the FR/resin application mixtures resulted in FR durability even after five launderings (the maximum number of washings that were used) with detergent. Given the above reported successful runs and the other tested embodiments that did not give the desired results either due to a lack of fire retardant reactivity (insufficient hydroxyl functionality) or to the volatility of the flame retardant additive, one trend became very clear. The presence of OH functionality in the flame retardant additive is needed to achieve the most satisfactory FR durability. Application mixtures containing Sample Compounds #3, #4, and #6 (OH-functional) resulted in the most durable FR treatments recorded.

Based on OH functionality, it seemed very likely that Sample Compound #5 would turn out to be the most durable FR

additive evaluated. However, this was not the case during the experiments that were performed. The most likely explanation for this is that the FR additive vaporized during the oven curing stage. This was not surprising since the TGA and DSC analytical results for Compound #5 showed a significant weight loss (TGA & DSC) around 160°C, about twenty degrees below the set curing temperature (180°C). Volatilization would also explain the large amount of smoke and vapor observed during the curing step of treated fabric. Given these results, the volatility of the selected FR additive(s) also needs to be considered when practicing the invention. Potential FR additives should have a substantially non-volatile, reactive component at the curing temperature to ensure cross-linking takes place before volatilization of the FR additive. The curing temperature is defined as the temperature at which the cross-linking reaction takes place.

In addition to the types of FR additives used, several observations were also made regarding the type of cross-linking resin used. Out of the various characteristics noted during the trials, the color and hand of the fabric samples were the most important. In general, the BTCA resin gave the softest hand and whitest color, both very desirable qualities. PMA and TMPA however gave less preferred results. As a general rule, the hand imparted by both resins was much stiffer than with BTCA, a property likely caused by the higher resin levels used. Either by reducing the add-on of these resins or by using softeners, the hand of the fabrics should improve. Another negative aspect of PMA and TMPA was the color they imparted on the fabric. The

PMA-treated fabric developed a slight yellow tint. A quality that may be reduced by lowering the curing temperature and/or the addition of a whitening agent, two techniques commonly used in the industry to remedy this type of problem. In addition to PMA, TMPA also colored the fabric. However, the pink color produced by this resin was much more intense and noticeable.

During these initial trials, all but one of the fabric samples using Sample Compounds #3, #4, and #6 retained 56-68% of the applied phosphorus after one water wash. In addition, the phosphorus that did adhere to the fabric through the first wash seemed to remain there throughout all five launderings.

In addition to percent phosphorus determinations, it was also decided to confirm the level of sodium in the laundered samples. A high level of sodium would reflect badly on the long-term durability of the FR treatments tested. It is a well known fact that the hydrolysis and subsequent ion exchange of sodium into a phosphorus FR treatment from detergent significantly affects the FR performance of the treatment over time (i.e., sodium salts of phosphorus esters make poor FRs). Other than hydrolysis and removal of phosphorus from a fabric, the ion exchange of sodium into a FR treatment is one of the leading causes of FR performance loss after laundering. As the data above shows, all of the laundered samples contained very low levels of sodium, a good indication that the bonded phosphorus is stable to laundering and should retain good FR properties well after five washings.

The foregoing Example should not be construed in a limiting fashion since they are only intended to set forth certain preferred embodiments of the present invention. The scope of protection sought is set forth in the Claims that follow.

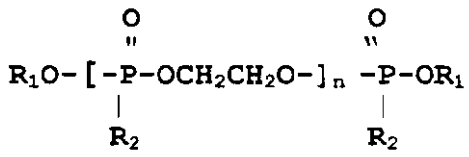
We Claim:

1. An aqueous finishing composition for application to materials comprising cellulose, comprising a hydroxyalkyl-functional organophosphorus flame retardant and a non-formaldehyde cross-linking agent.

2. A composition as claimed in Claim 1 wherein the hydroxyalkyl-functional organophosphorus flame retardant has a substantially non-volatile, reactive component at the curing temperature.

3. A composition as claimed in Claim 2 wherein the organophosphorus flame retardant is selected from the group consisting of oligomeric phosphate, polymeric phosphate, oligomeric phosphonate, or mixed phosphate/phosphonate ester flame retardant compositions.

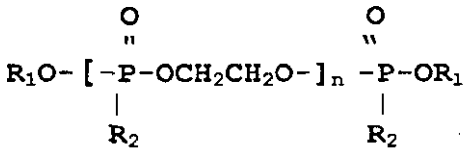
4. A composition as claimed in Claim 3 wherein the organophosphorus flame retardant has the following structure:



where R_1 is independently selected from alkyl and hydroxyalkyl, R_2 is independently selected from alkyl,

alkenyl, alkoxy, and hydroxyalkoxy, and n is equal to or greater than 1.

5. A composition as claimed in Claim 4 wherein the organophosphorus flame retardant has the following structure:



where R_1 is independently selected from methyl and hydroxyethyl, R_2 is independently selected from methyl, methoxy, and hydroxyethoxy, and n is equal to or greater than 1.

6. A composition as claimed in Claim 1 wherein the non-formaldehyde cross-linking agent is selected from the group consisting of a polycarboxylic acid, a polycarboxylic acid salt, and mixtures thereof having one or more dicarboxylic groups on adjacent carbon atoms, optionally containing phosphorus.

7. A composition as claimed in Claim 6 wherein the polycarboxylic acid cross-linking agent is 1,2,3,4-butanetetracarboxylic acid.

8. A composition as claimed in Claim 6 wherein the polycarboxylic acid cross-linking agent is polymaleic acid.

9. A composition as claimed in Claim 1 that further comprises up to about 10%, by weight of the composition, of a cross-linking catalyst.

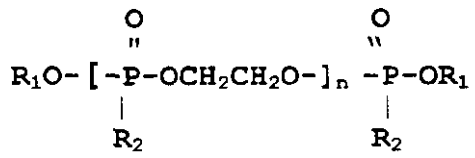
10. A composition as claimed in Claim 1 that further comprises at least one saturated alpha-hydroxypolycarboxylic acid, and/or salt thereof, having at least two carboxyl groups bonded to adjacent carbons.

11. An aqueous finishing composition for application to a material comprising cellulose that comprises from about 1% to about 60%, by weight of the composition, of a non-volatile, hydroxyalkyl-functional organophosphorus flame retardant and from about 1% to about 40%, by weight of the composition, of a non-formaldehyde cross-linking agent.

12. A composition as claimed in Claim 11 wherein the hydroxyalkyl-functional organophosphorus flame retardant has a substantially non-volatile, reactive component at the curing temperature.

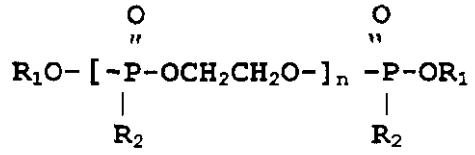
13. A composition as claimed in Claim 12 wherein the organophosphorus flame retardant is a hydroxyalkyl-functional oligomeric and/or polymeric phosphate, phosphonate, or mixed phosphate/phosphonate ester flame retardant product.

14. A composition as claimed in Claim 13 wherein the organophosphorus flame retardant has the following structure:



where R_1 is independently selected from alkyl and hydroxyalkyl, R_2 is independently selected from alkyl, alkenyl, alkoxy, and hydroxyalkoxy, and n is equal to or greater than 1.

15. A composition as claimed in Claim 14 wherein the organophosphorus flame retardant has the following structure:



where R_1 is independently selected from methyl and hydroxyethyl, R_2 is independently selected from methyl, methoxy, and hydroxyethoxy, and n is equal to or greater than 1.

16. A composition as claimed in Claim 11 wherein the non-formaldehyde cross-linking agent is selected from the group consisting of a polycarboxylic acid, a polycarboxylic

acid salt, and mixtures thereof having one or more dicarboxylic groups on adjacent carbon atoms, optionally containing phosphorus.

17. A composition as claimed in Claim 16 wherein the polycarboxylic acid cross-linking agent is 1,2,3,4-butanetetracarboxylic acid.

18. A composition as claimed in Claim 16 wherein the polycarboxylic acid cross-linking agent is polymaleic acid.

19. A composition as claimed in Claim 11 that further comprises up to about 30%, by weight of the composition, of a cross-linking catalyst.

20. A material comprising cellulose that has been treated with the aqueous finishing composition of Claim 1.

21. A material comprising cellulose that has been treated with the aqueous finishing composition of Claim 2.

22. A material comprising cellulose that has been treated with the aqueous finishing composition of Claim 3.

23. A material comprising cellulose that has been treated with the aqueous finishing composition of Claim 4.

24. A material comprising cellulose that has been treated with the aqueous finishing composition of Claim 5.

25. A material comprising cellulose that has been treated with the aqueous finishing composition of Claim 6.

26. A material comprising cellulose that has been treated with the aqueous finishing composition of Claim 7.

27. A material comprising cellulose that has been treated with the aqueous finishing composition of Claim 8.

28. A material comprising cellulose that has been treated with the aqueous finishing composition of Claim 9.

29. A material comprising cellulose that has been treated with the aqueous finishing composition of Claim 10.

30. A material comprising cellulose that has been treated with the aqueous finishing composition of Claim 11.

31. A material comprising cellulose that has been treated with the aqueous finishing composition of Claim 12.

32. A material comprising cellulose that has been treated with the aqueous finishing composition of Claim 13.

33. A material comprising cellulose that has been treated with the aqueous finishing composition of Claim 14.

34. A material comprising cellulose that has been treated with the aqueous finishing composition of Claim 15.

35. A material comprising cellulose that has been treated with the aqueous finishing composition of Claim 16.

36. A material comprising cellulose that has been treated with the aqueous finishing composition of Claim 17.

37. A material comprising cellulose that has been treated with the aqueous finishing composition of Claim 18.

38. A material comprising cellulose that has been treated with the aqueous finishing composition of Claim 19.

INTERNATIONAL SEARCH REPORT

Inter ɔnal Application No
PCT/US 00/26133

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D06M15/263 D06M13/192 D06M13/288 D06M13/292 D06M13/295
D06M15/667 D06M13/207

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 00 29662 A (COTTON INC) 25 May 2000 (2000-05-25) page 27, line 16 -page 32, line 17	1-3, 11-13, 20-22, 30-32
A	US 5 320 785 A (DERMEIK SALMAN) 14 June 1994 (1994-06-14) the whole document	1-38
A	US 5 695 528 A (SAITO AKIRA ET AL) 9 December 1997 (1997-12-09) the whole document	1-38
A	US 3 975 154 A (BRUNO JOSEPH S ET AL) 17 August 1976 (1976-08-17) the whole document	1-38

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 December 2000	05/01/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Blas, V

2

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inter onal Application No
PCT/US 00/26133

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 273 549 A (DIDIER WILHELM ET AL) 28 December 1993 (1993-12-28) the whole document	1-38
A	WELCH C M: "FORMALDEHYDE-FREE DURABLE-PRESS FINISHES" REVIEW OF PROGRESS IN COLORATION & RELATED TOPICS,GB,SOCIETY OF DYERS AND COLOURISTS. BRADFORD, vol. 22, 1992, pages 32-41, XP000305372 ISSN: 0557-9325 the whole document	1-38
A	US 4 220 610 A (DURSCH WALTER ET AL) 2 September 1980 (1980-09-02) the whole document	1-38

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter onal Application No
PCT/US 00/26133

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0029662 A	25-05-2000	AU 1712600 A	05-06-2000
US 5320785 A	14-06-1994	AU 641265 B	16-09-1993
		AU 8162691 A	06-02-1992
		BR 9103340 A	05-05-1992
		DE 4122929 A	06-02-1992
		EP 0469387 A	05-02-1992
		JP 4233993 A	21-08-1992
		PT 98527 A	30-06-1992
		ZA 9106094 A	27-05-1992
US 5695528 A	09-12-1997	JP 7145561 A	06-06-1995
US 3975154 A	17-08-1976	NONE	
US 5273549 A	28-12-1993	FR 2668506 A	30-04-1992
		AT 124099 T	15-07-1995
		CA 2054341 A	01-05-1992
		DE 69110617 D	27-07-1995
		DE 69110617 T	04-01-1996
		DK 484196 T	21-08-1995
		EP 0484196 A	06-05-1992
		ES 2073706 T	16-08-1995
		JP 6100575 A	12-04-1994
		KR 201800 B	15-06-1999
US 4220610 A	02-09-1980	DE 2806049 A	16-08-1979
		EP 0003599 A	22-08-1979
		JP 54117426 A	12-09-1979

[19]中华人民共和国国家知识产权局

[51]Int. Cl[7]
D06M 15/263
D06M 13/192 D06M 13/288
D06M 13/292 D06M 13/295
D06M 15/667 D06M 13/207

[12]发明专利申请公开说明书

[21]申请号 00813423.5

[43]公开日 2002年10月23日

[11]公开号 CN 1376225A

[22]申请日 2000.9.22 [21]申请号 00813423.5
[30]优先权
[32]1999.9.27 [33]US [31]09/406,529
[86]国际申请 PCT/US00/26133 2000.9.22
[87]国际公布 WO01/23663 英 2001.4.5
[85]进入国家阶段日期 2002.3.27
[71]申请人 佐治亚州大学研究基金会
地址 美国佐治亚州
共同申请人 阿克佐诺贝尔公司
[72]发明人 J·K·斯托维尔 E·D·维尔
W·L·科布尔
C·Q·杨

[74]专利代理机构 中国国际贸易促进委员会专利商标事务所
代理人 王 杰

权利要求书 4 页 说明书 17 页 附图页数 0 页

[54]发明名称 用于含纤维素材料的无甲醛阻燃处理

[57]摘要

用于含纤维素的材料的含水整理组合物，包括羟烷基官能化有机磷阻燃剂（它含有在固化温度下的基本无挥发组分）和无甲醛交联剂（如多羧酸交联剂），以及用这种组合物处理的材料。用于含水整理组合物的任选成分包括交联剂和/或低廉的饱和α－羟基多羧酸如柠檬酸（更昂贵的优选多羧酸的部分替代）。

ISSN1008-4274

知识产权出版社出版

02.03.27

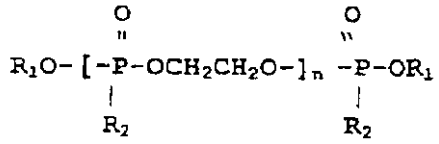
权 利 要 求 书

1、应用于包含纤维素的材料的含水整理组合物，包括羟烷基官能化有机磷阻燃剂和无甲醛交联剂。

2、如权利要求 1 中所要求的组合物，其中羟烷基官能化有机磷阻燃剂具有在固化温度下基本无挥发、反应活性的组分。

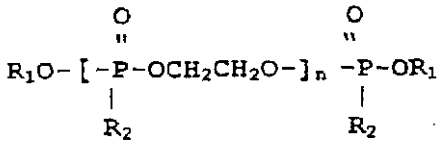
3、如权利要求 2 中所要求的组合物，其中有机磷阻燃剂选自低聚磷酸酯，聚合磷酸酯，低聚膦酸酯，或混合磷酸酯/膦酸酯阻燃剂组合物。

4、如权利要求 3 中所要求的组合物，其中有机磷阻燃剂具有下式结构:



其中 R_1 独立选自甲基和羟烷基，R_2 独立选自烷基、烯基、烷氧基和羟基烷氧基，和 n 等于或大于 1.

5、如权利要求 4 中所要求的组合物，其中有机磷阻燃剂具有下式结构:



其中 R_1 独立选自甲基和羟乙基，R_2 独立选自甲基，甲氧基和羟基乙氧基，和 n 等于或大于 1.

6、如权利要求 1 中所要求的组合物，其中无甲醛交联剂选自在相邻碳原子上具有一个或多个二羧酸基，任选含有磷的多羧酸、多羧酸

盐，和它们的混合物。

7、如权利要求 6 中所要求的组合物，其中多羧酸交联剂是 1,2,3,4-丁烷四甲酸。

8、如权利要求 6 中所要求的组合物，其中多羧酸交联剂是聚马来酸。

9、如权利要求 1 中所要求的组合物，进一步包括占组合物的至多大约 10wt%的交联催化剂。

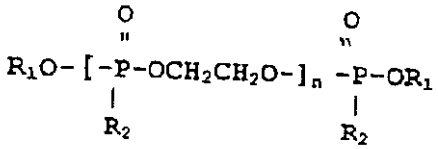
10、如权利要求 1 中所要求的组合物，进一步包括至少一种饱和 α-羟基多羧酸，和/或它的盐，其具有连接于相邻碳的至少两个羧基。

11、应用于包括纤维素的材料的含水整理组合物，包括占组合物的大约 1 - 大约 60wt%的无挥发、羟烷基官能化有机磷阻燃剂，和占组合物的大约 1 - 大约 40wt%的无甲醛交联剂。

12、如权利要求 11 中所要求的组合物，其中羟烷基官能化有机磷阻燃剂具有在固化温度下基本无挥发的、反应活性的组分。

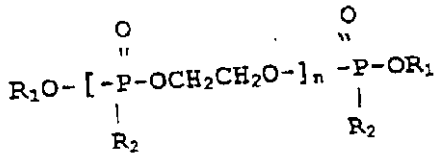
13、如权利要求 12 中所要求的组合物，其中有机磷阻燃剂是羟乙基官能化低聚和/或聚合磷酸酯，膦酸酯，或混合磷酸酯/膦酸酯阻燃剂产物。

14、如权利要求 13 中所要求的组合物，其中有机磷阻燃剂具有下式结构：



其中 R_1 独立选自烷基和羟烷基，R_2 独立选自烷基、烯基、烷氧基和羟基烷氧基，和 n 等于或大于 1。

15、如权利要求 14 中所要求的组合物，其中有机磷阻燃剂具有下式结构：



其中 R_1 独立选自甲基和羟乙基，R_2 独立选自甲基，甲氧基和羟基乙氧基，和 n 等于或大于 1.

16、如权利要求 11 中所要求的组合物，其中无甲醛交联剂选自在相邻碳原子上具有一个或多个二羧酸，任选含有磷的多羧酸，多羧酸盐，和它们的混合物。

17、如权利要求 16 中所要求的组合物，其中多羧酸交联剂是 1,2,3,4-丁烷四甲酸。

18、如权利要求 16 中所要求的组合物，其中多羧酸交联剂是聚马来酸。

19、如权利要求 11 中所要求的组合物，进一步包括占组合物的至多大约 30wt%的交联催化剂.

20、已经用权利要求 1 的含水整理组合物处理的包括纤维素的材料.

21、已经用权利要求 2 的含水整理组合物处理的包括纤维素的材料.

22、已经用权利要求 3 的含水整理组合物处理的包括纤维素的材料.

23、已经用权利要求 4 的含水整理组合物处理的包括纤维素的材料.

24、已经用权利要求 5 的含水整理组合物处理的包括纤维素的材料.

25、已经用权利要求 6 的含水整理组合物处理的包括纤维素的材料.

26、已经用权利要求 7 的含水整理组合物处理的包括纤维素的材料。

27、已经用权利要求 8 的含水整理组合物处理的包括纤维素的材料。

28、已经用权利要求 9 的含水整理组合物处理的包括纤维素的材料。

29、已经用权利要求 10 的含水整理组合物处理的包括纤维素的材料。

30、已经用权利要求 11 的含水整理组合物处理的包括纤维素的材料。

31、已经用权利要求 12 的含水整理组合物处理的包括纤维素的材料。

32、已经用权利要求 13 的含水整理组合物处理的包括纤维素的材料。

33、已经用权利要求 14 的含水整理组合物处理的包括纤维素的材料。

34、已经用权利要求 15 的含水整理组合物处理的包括纤维素的材料。

35、已经用权利要求 16 的含水整理组合物处理的包括纤维素的材料。

36、已经用权利要求 17 的含水整理组合物处理的包括纤维素的材料。

37、已经用权利要求 18 的含水整理组合物处理的包括纤维素的材料。

38、已经用权利要求 19 的含水整理组合物处理的包括纤维素的材料。

说　明　书

用于含纤维素材料的无甲醛阻燃处理

本发明的背景

本发明涉及用于含纤维素的材料，如棉花或棉花混纺物（棉花/聚酯和棉花/尼龙）的无甲醛阻燃处理，它能够耐受浆洗和干洗操作。

目前，有几种不同类型的化学整理剂能够应用于含纤维素的材料以赋予阻燃（FR）性。在这些体系当中，只有几种获得了能够进行浆洗和干洗而不损失它们的FR质量的整理织物。这些处理一般称之为耐久FR整理。在这些整理剂当中，跟本发明最相关的是PROBAN和PYROVATEX商标材料。来自Albright & Wilson的PROBAN技术以使用氯化四-(羟甲基)鏻（"THPC"）型产物和氨化室为基础。它在以下U.S.专利Nos.4,078,101; 4,145,463; 4,311,855和4,494,951中均有详细描述，所有这些专利都属于Albright and Wislson。PYROVATEX CP工艺，最初由Ciba-Geigy开发，利用(N-羟甲基氨基甲酰基-乙基)膦酸二甲酯或类似的羟甲基官能化含磷类似物作为阻燃剂。由于市场受到了在工业中的PROBAN和PYROVATEX产品控制，依次常常难以令人理解的是，人们会普遍忍受与使用这些产品和它们所应用的各种化学过程相关的负面影响。

在近年来，对所使用的THPC交联化学过程提出了几种变型。例如，预缩合-NH_3方法（例如PROBAN）技术是这些变型的最近一种。虽然它可能是市场上最耐久的处理，但该技术包括使用氨化室和严格的操作条件，以获得织物没有显著强度损失的一致结果。除了困难的操作条件以外，实施该整理工艺的启动成本和与氨气相关的法规问题使得它不那么吸引人，尤其对于市场的新的到来者。

在许多方面，PYROVATEX技术遭到了与PROBAN技术几乎同样的衰落。无论它是以使用(N-羟甲基氨基甲酰基-乙基)膦酸二甲酯为基础的最初PYROVATEX CP工艺，或者是使用不同N-羟甲基官能化含磷类似

物的其它方法，所有这些产物含有和排放毒性组分甲醛（已知的致癌物质）。除了构成 PYROVATEX 型方法的基础的该分子以外，还需要含甲醛的交联树脂，如 N-羟甲基脲（例如，1,3-二羟甲基-4,5-二羟亚乙基脲－ "DMDHEU"），N-羟甲基酰胺，或 N-羟甲基蜜胺以确保化学整理的充足的耐久性。这些树脂也独立用作纺织品工业中的耐久压烫交联剂。N-羟甲基含磷类似物和 N-羟甲基交联树脂的结合，或者单独使用这两种试剂的任一种经常导致在织物应用过程中和衣服的整个使用期间释放大量的甲醛。因此，全工业中限制和仔细规定甲醛释放水平。甲醛释放仍然被忍受的唯一理由是由于缺乏可接受的无甲醛替代技术。

由于甲醛对人健康的负面影响，棉服和纺织品整理工业主要集中在创造等效的无甲醛技术。因为它们广泛的用途，目前的大多数研究努力花费在用于含纤维素材料的新型无甲醛交联剂的制造和设计上。这些试剂能够用于许多不同的应用，包括在耐久压烫整理中的使用到用于产物的通用固定添加剂如 PYROVATEX 型 FR 添加剂。在过去几年里，研究努力已经导致了几种新的低甲醛型体系的发现。这些整理剂一般以 DMDHEU 的结构改性，即通过侧挂羟甲基官能团的取代或消除为基础。虽然如此，这些新整理剂从未曾获得广泛的赞同，由于它们作为交联剂性能不充分。一般，对 DMDHEU 分子的最高活性部分的去除或改性仅仅导致了无活性的产生和得到不需要的整理剂。

除了改性 DMDHEU 以外，其它技术也开始被开发。更有希望的无甲醛体系之一以多羧酸的使用为基础。这些分子通过五元环酐的原位形成和它们随后与在处理纺织品内含有的羟基结构部分的反应产生了交联纤维素材料。该技术在 Clark Welch 的指导下在新奥尔良的 the United States Department of Agriculture 开发，以使用 1,2,3,4-丁烷四羧酸（BTCA）为基础。描述该方法的代表性专利是：U.S.专利 Nos.4,820,307; 4,936,865; 4,975,209; 和 5,221,285.

因为 BTCA 技术的发明，其它研究者已经开始用多羧酸处理来改进它们的商业吸引力。一些最近的工作已经集中在使用聚马来酸和在一

些情况下使用柠檬酸，或含柠檬酸的混合物。聚马来酸（PMA）是廉价、可商购的材料，通常用作水处理化学品。该工作的一些方面描述在 PCT 国际专利公开 No. WO 98/30387 中。除了 PMA 以外，有各种各样的供选择的无甲醛交联树脂能够用来获得用于含纤维素材料的耐久无甲醛 FR 处理。这些树脂中的许多目前可以购得并用于抑制结垢的水处理行业中，它们中的一些甚至含有少量的磷。这些无甲醛含磷树脂的使用甚至可以提供与无磷交联树脂如 PMA 相比的附加优点。将磷物质引入到交联树脂本身可以使得不需要外部交联催化剂和/或加入的磷可以获得处理含纤维素材料的改进 FR 性能。这些树脂的实例能够在以下 U.S. 专利 Nos. 4,046,707; 4,105,551; 4,621,127; 5,376,731; 5,386,038; 5,496,476; 5,705,475; 和 5,866,664 中看到。

本发明的概述

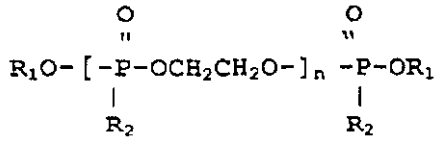
本发明涉及用于含纤维素材料的含水整理组合物和用这种组合物处理的材料。含水整理组合物在它最宽的实施方案中包括了羟烷基官能化有机磷阻燃剂和无甲醛交联剂，任选还有包括在其中的交联催化剂。

优选实施方案的描述

根据本发明的目的用于处理含纤维素材料的含水整理组合物含有两种必需组分：（1）羟烷基官能有机磷阻燃剂（排除 N-羟甲基，及其醚，和潜在的甲醛释放剂）；和(2) 无甲醛交联剂。

单体、低聚（一般含有大约 2－10 个重复单元）和聚合（一般含有超过大约 10 个重复单元）羟烷基官能化有机磷阻燃添加剂希望在这里使用。

描述在 U.S. 专利 No. 3,695,925(E.D. Weil) 和 4,199,534，4,268,633，和 4,335,178(R.B. Fearing) 中的那类反应性低聚含磷阻燃剂是能够根据本发明使用的羟烷基官能化有机磷阻燃剂的实例之一。优选的实施方案具有下式结构：



其中 R_1 独立选自甲基和羟乙基，R_2 独立选自甲基，甲氧基和羟基乙氧基，和 n 等于或大于 1。该实施方案通过多步法从甲基膦酸二甲酯、五氧化磷、乙二醇和环氧乙烷来制备，并可以注册商标 FYROL® 51 从 Akzo Nobel Chemicals Inc. 获得。端基主要是羟基。

用于这里使用的另一类物质包括水溶性低聚烯基膦酸酯物质，它们的实例描述在 U.S. 专利 Nos. 3,855,359 和 4,017,257 中，二者都属于 E.D. Weil。在这些物质中烯基取代基的存在提供了利用自由基永久固化条件的其它机理（描述在以上专利中）。这类优选物质可以商标 FYROL®76 从 Akzo Nobel Chemicals Inc. 获得，并通过使双(2-氯乙基)乙烯基膦酸酯和甲基膦酸二甲酯反应，以及基本清除氯甲烷来生产。

能够使用的另一类羟烷基官能化有机磷阻燃剂是如描述在 U.S. 专利 Nos. 2,909,559, 3,099,676, 3,228,998, 3,309,427, 3,472,919, 3,767,732, 3,850,859, 4,244,893, 4,382,042, 4,458,035, 4,697,030, 4,820,854, 4,886,895, 5,117,033, 和 5,608,100 中的携带羟基烷氧基的低聚磷酸酯。

阻燃剂一般以含水整理组合物的大约 1 - 大约 60wt%，优选大约 10 - 大约 40wt% 存在。

无甲醛交联剂，即本发明含水整理组合物的第二必要组分，一般以组合物总重量的大约 1 - 大约 40wt%，优选大约 5 - 大约 20wt%存在。

多羧酸交联剂形成了可以在这里使用的一类交联剂。有效作为根据本发明的纤维素交联剂的多羧酸包括烯属饱和或不饱和脂族、脂环族和芳族酸，具有至少三个和优选三个以上羧基/分子或具有两个羧基/分子，如果碳-碳双键存在于一个或两个羧基的α,β位。其它要求是:

它在酯化纤维素羟基中是反应活性的，在脂族或脂环族多羧酸中的既定羧基应该被不少于两个的碳原子和不多于三个的碳原子与第二羧基分开。在芳族酸中，如果第一羧基在酯化纤维素羟基中是有效的，羧基必须是第二个羧基的邻位。从这些要求可以发现，羧基必需是反应性的，它应该能够与多羧酸分子中的相邻羧基形成环状 5-或 6-元酸酐环。在两个羧基被碳-碳双键分开或二者连接于同一环上，两个羧基应该彼此成顺式结构，倘若它们要以这种方式相互作用的话。脂族或脂环族多羧酸还可以在羧基所连接的链或环中含有氧或硫原子。

在含有三或多个羧基/分子的脂族酸中，连接于羧基的α位碳原子上的羟基不受纤维素被酸酯化和交联的干扰。然而，羟基的存在可以引起材料在热固化过程中的显著发黄。这种α羟基酸适合用于适宜染色的棉布的耐久压烫整理，因为染料的颜色掩盖了可由羟基存在引起的变色。用不仅在一个羧基的α、β位上具有烯属双键，而且在第二个羧基的β、γ位上具有烯属双键的不饱和酸同样发现了织物的变色。

通过用α-羟基酸如柠檬酸交联而在白色含纤维素材料中产生的变色能够通过用含有 0.5－5wt%的选自一过氧邻苯二甲酸镁，过硼酸钠，四硼酸钠，硼酸，硼氢化钠，次氯酸钠，和氯化氢中的脱色剂的水溶液浸渍变色材料来消除。将该材料浸渍在脱色剂的溶液中并在室温下，或者必要的话，在升温至不超过 60℃温度的这种溶液中浸泡 5－120 分钟。材料随后用水冲洗以除去过量的化学品和溶解着色产物，然后干燥。

用于这里使用的特别优选的多羧酸交联剂是 1,2,3,4-丁烷四甲酸。

用于这里使用的其它优选的多羧酸交联剂是聚马来酸。

用于该组分的其它方案是马来酸酐与乙酸乙烯酯和丙烯酸乙酯的水解三元共聚物。马来酸酐与乙酸乙酯和丙烯酸乙酯的总摩尔数的摩尔比优选是大约 2.5:1－大约 5:1 并且乙酸乙烯酯与丙烯酸乙酯的摩尔量优选是大约 1:4－大约 4:1，最优选大约 1:2－大约 2:1。三元共聚物的分子量具有大约 4,000 的上限。这类产物可以商标 BELCLENE

283 从 FMC Corporation 购得。

在本发明范围内的其它具体的多羧酸的实例是以下物质：马来酸；柠康酸，也称为甲基马来酸；柠檬酸，也称为 2-羟基-1,2,3-丙烷三羧酸；衣康酸，也称为亚甲基丁二酸；丙三羧酸，也称为 1,2,3-丙烷三羧酸；反式乌头酸，也称为反式-1-丙烯-1,2,3-三羧酸；1,2,3,4-丁烷四羧酸；全顺式-1,2,3,4-环戊烷四羧酸；苯六甲酸，也称为苯六羧酸；氧联丁二酸，也称为 2,2'-氧双-(丁二酸)；硫二丁二酸；描述在 U.S.专利 Nos.4,046,707；4,105,551；4,621,127；5,376,731；5,386,038；5,496,476；5,705,475；5,866,664 中的含磷多羧酸树脂；以及其它等等。

如果使用前面提及的体系没有获得充分的交联，也许有必要添加适合的交联催化剂以增强所要处理的含纤维素材料、羟烷基官能化有机磷阻燃剂，和无甲醛交联剂之间的反应，该催化剂能够以含水整理组合物总重量的至多大约 30wt%，优选至多大约 10wt%存在。如在 PCT 国际专利公开 No. WO98/303387 和 U.S.专利 Nos.4,820,307，4,936,865，4,975,209 和 5,221,285 中所述，所选择的适合催化剂类型的实例包括已知的次磷酸盐、亚磷酸盐、焦磷酸盐、磷酸二氢盐、磷酸盐和磷酸一氢盐类的一种或多种碱金属盐，以及诸如聚磷酸、次磷酸、亚磷酸和烷基次膦酸的一种或多种的这类酸。还能够使用供选择的碱性交联催化剂如 $NaHCO_3$ 和 Na_2CO_3。

在一些情况下，为了升高处理溶液的 pH 以改进浴或添加剂的相容性和/或用于改进强度保持率，一部分多羧酸可以盐的形式使用，尤其作为水溶性盐。适合于该目的的是酸的碱金属盐。另外，或者与盐形式的多羧酸的使用相结合，可以升高处理溶液的 pH，或者溶液通过添加碱，优选水溶性碱，如碱金属氢氧化物，氢氧化铵或胺来部分中和。为此，pH 可以升高至大约 2.3 - 大约 5，优选大约 2.5 - 4。

本发明进一步通过以下的实施例来说明。

实验背景资料

所使用的阻燃（“FR”）添加剂

#1 样品化合物: 改性 FYROL® 51 阻燃剂（低 OH#）

#2 样品化合物: PEEOP（低 OH#）

#3 样品化合物: 改性 PEEOP（高 OH#）

#4 样品化合物: FYROL® 51 阻燃剂（高 OH#）

#5 样品化合物: FYROL® 6 阻燃剂

#6 样品化合物: FYROL®76 阻燃剂

在以上给出的列举中，"PEEOP"是在 U.S.序列 No. 08/677,283 中所述的那类聚（乙基亚乙基氧基）磷酸酯，具有大约 915（数均）/1505（重均）的分子量，和在大约 5mg KOH/g 之下（低羟基值型）和大约 150mg KOH/g（高羟基值型）的典型羟基值。改性 FYROL®51 阻燃剂具有在大约 5mg KOH/g 之下的羟基值，以及 FYROL®51 牌的产品的高羟基型具有大约 125mg KOH/g 的羟基值。FYROL®6 阻燃剂具有大约 440mg KOH/g 的羟基值，而 FYROL®76 阻燃剂具有大约 100mg KOH/g 的羟基值。

所使用的多羧酸树脂和其它化学品

Belclene 283: 马来酸酐、乙酸乙烯酯和丙烯酸乙酯的三元共聚物（TMPA）的水解产物的 35％水溶液。

Belclene 200: 聚马来酸（PMA）的 35％水溶液。

BTCA: 1,2,3,4-丁烷四甲酸（固体）。

NaH_2PO_2（水合物）: 用作交联催化剂。

所用设备

浸轧涂敷装置（实验室规格）: 用于以规定水平将溶液涂布于织物上的仪器（％纤维吸液率）。

固化烘箱（实验室规格）: 用于在高温下干燥和随后固化化学处理的织物的烘箱。

洗衣机（家用规格）: 用于在化学处理和固化之前和之后机洗织物（用 Tide®洗衣粉）。

所用织物

中厚（大约 1mm 厚），白色，预洗涤，100％棉织物（12 ×16 英寸

样品）.

实验细节

初步工作:

浆洗该棉织物以确保它的清洁，然后切割成大约 12 ×16 英寸样品用于以后使用。使用水和织物样品，设置浸轧涂敷装置至大约 75% 的纤维吸液率（液体的附加重量除以干布的初始重量）。将水的 75% 纤维吸液率换算成化学品溶液的大约 80% 纤维吸液率.

一般操作程序:

制备有和没有 FR 的涂布溶液。各溶液含有 FR（空白除外），多羧酸，NaH_2PO_2，和水。已知纤维吸液率为 80%，调节溶液浓度以获得各化学品的所需加合重量.

在制备后，在 5 小时内使用各涂布溶液.

然后将各溶液涂布于织物样品。将织物浸渍在溶液中，从浸轧涂敷装置中过一下，再次浸渍在溶液中，以及再次从浸轧涂敷装置中过一下以确保整个织物样品具有充分的均匀性.

在涂布后，各织物样品放置在金属框架上和送入 80℃的烘箱以进行干燥（3－5 分钟）.

在干燥后，将各样品再次放入 180℃的烘箱中以固化该化学处理（1.5－2 分钟）.

然后从金属架上取出各固化样品，并记录它的物理性能。还记录在干燥和固化织物同时所做的任何观测.

非正式点燃试验:

将各织物样品保持在水平位置和用丙烷打火机点燃。记录各织物样品的可燃性.

实验数据

第一次试验涂布:

	BELELENE 283 树脂			BTCA		
	样品化合物#2	样品化合物#4	样品化合物#5	样品化合物#2	样品化合物#4	样品化合物#5
干燥添加重量	10% FR#2 4% TMPA 2% NaH_2PO_2	10% FR#4 4% TMPA 2% NaH_2PO_2	10% FR#5 4% TMPA 2% NaH_2PO_2	10% FR#2 4% BTCA 2% NaH_2PO_2	10% FR#4 4% BTCA 2% NaH_2PO_2	10% FR#5 4% BTCA 2% NaH_2PO_2
涂布溶液配方	26.6g FR#2 30.4gBELCLENE283 5.4g NaH_2PO_2 137.6g H_2O	26.6g FR#4 30.4gBELCLENE283 5.4g NaH_2PO_2 137.6g H_2O	26.6g FR#5 30.4gBELCLENE283 5.4g NaH_2PO_2 137.6g H_2O	26.6g FR#2 10.7g BTCA 5.4g NaH_2PO_2 157.3g H_2O	26.6g FR#4 10.7g BTCA 5.4g NaH_2PO_2 157.3g H_2O	26.6g FR#5 10.7g BTCA 5.4g NaH_2PO_2 157.3g H_2O
干燥条件	3分钟 @ 80℃	3分钟@ 80℃	3分钟 @ 80℃	3分钟 @ 80℃	3分钟 @ 80℃	3分钟 @ 80℃
固化条件	1.5分钟@ 180℃	1.5分钟 @ 180℃	1.5分钟 @ 180℃	1.5分钟 @ 180℃	1.5分钟 @ 180℃	1.5分钟 @ 180℃
燃烧（在洗涤前）	不良－织物燃烧	不良－织物燃烧	不良－织物燃烧	不良－织物燃烧	不良－织物燃烧	不良－织物燃烧

第二次试验涂布:

空白样品（没有FR）			
	BELCENE 283 （TMPA）	BTCA	BELCLENE 200 （PMA）
干燥添加重量	8% TMPA 4% NaH_2PO_2	8% TMPA 4% NaH_2PO_2	8% TMPA 4% NaH_2PO_2
涂布溶液配方	57.1g BELCLENE 283 10.0g NaH_2PO_2 132.9g H_2O	57.1g BELCLENE 283 10.0g NaH_2PO_2 132.9g H_2O	57.1g BELCLENE 283 10.0g NaH_2PO_2 132.9g H_2O
干燥条件	5分钟 @ 80℃	5分钟 @ 80℃	5分钟 @ 80℃
固化条件	2分钟 @ 180℃	2分钟 @ 180℃	2分钟 @ 180℃
燃烧试验（在洗涤前）	不良－织物燃烧	不良－织物燃烧	不良－织物燃烧
织物颜色	轻微米色	白色	黄色
织物手感	非常硬	硬	非常硬
其它发现	无烟	无烟	无烟

	BELELENE 283 树脂（TMPA）					
	样品化合物#1	样品化合物 #2	样品化合物#3	样品化合物#4	样品化合物#5	样品化合物#6
干燥添加重量	20% FR#1 8% TMPA 4% NaH_2PO_2	20% FR#2 8% TMPA 4% NaH_2PO_2	20% FR#3 8% TMPA 4% NaH_2PO_2	20% FR#4 8% BTCA 4% NaH_2PO_2	80% FR#5 8% BTCA 4% NaH_2PO_2	20% FR#6 8% BTCA 4% NaH_2PO_2
涂布溶液配方	50.0g FR#1 57.1gBELCLENE283 10.0g NaH_2PO_2 82.9g H_2O	50.0g FR#2 57.1gBELCLENE283 10.0g NaH_2PO_2 82.9g H_2O	50.0g FR#3 57.1gBELCLENE283 10.0g NaH_2PO_2 82.9g H_2O	50.0g FR#4 57.1gBELCLENE283 10.0g NaH_2PO_2 82.9g H_2O	50.0g FR#5 57.1gBELCLENE283 10.0g NaH_2PO_2 82.9g H_2O	50.0g FR#6 57.1gBELCLENE283 10.0g NaH_2PO_2 82.9g H_2O
干燥条件	5分钟 @80℃	5分钟 @80℃	5分钟 @80℃	5分钟 @80℃	5分钟 @80℃	5分钟 @80℃
固化条件	2分钟@180℃	2分钟@180℃	2分钟@180℃	2分钟@180℃	2分钟@180℃	2分钟@180℃
燃烧试验（在洗涤之前）	良好	良好	良好	良好	不良－织物燃烧	良好
燃烧试验（在1次水洗后）	可以接受	不良－织物燃烧	良好	良好	不良－织物燃烧	良好
燃烧试验（在5次洗涤后）	－	－	可接受	良好	－	可接受
织物颜色	粉红色	暗粉红色	粉红色	暗粉红色	粉红色	浅粉红色
织物手感	硬	柔软	非常硬	非常硬	非常硬	非常硬
其它发现	在固化过程中冒烟	溶解性问题－FR	无烟	无烟	在固化过程中冒烟	无烟

	样品化合物#1	样品化合物 #2	样品化合物#3	样品化合物#4	样品化合物#5	样品化合物#6
干燥添加重量	20% FR#1 5% BTCA 2.5% NaH_2PO_2	20% FR#2 5% BTCA 2.5% NaH_2PO_2	20% FR#3 5% BTCA 2.5% NaH_2PO_2	20% FR#4 5% BTCA 2.5% NaH_2PO_2	20% FR#5 5% BTCA 2.5% NaH_2PO_2	20% FR#6 5% BTCA 2.5% NaH_2PO_2
涂布溶液配方	50.0g FR#1 12.5g BTCA 6.3g NaH_2PO_2 131.2g H_2O	50.0g FR#2 12.5g BTCA 6.3g NaH_2PO_2 131.2g H_2O	50.0g FR#3 12.5g BTCA 6.3g NaH_2PO_2 131.2g H_2O	50.0g FR#4 12.5g BTCA 6.3g NaH_2PO_2 131.2g H_2O	50.0g FR#5 12.5g BTCA 6.3g NaH_2PO_2 131.2g H_2O	50.0g FR#6 12.5g BTCA 6.3g NaH_2PO_2 131.2g H_2O
干燥条件	5分钟 @80℃	5分钟 @80℃	5分钟 @80℃	5分钟 @80℃	5分钟 @80℃	5分钟 @80℃
固化条件	2分钟@180℃	2分钟@180℃	2分钟@180℃	2分钟@180℃	2分钟@180℃	2分钟@180℃
燃烧试验（在洗涤之前）	良好	良好	良好	良好	不良－织物燃烧	良好
燃烧试验（在1次水洗后）	可以接受	不良－织物燃烧	良好	良好	不良－织物燃烧	良好
燃烧试验（在5次洗涤后）	－	－	良好	良好	－	良好
织物颜色	白色	白色	白色	白色	浅黄色	白色
织物手感	半柔软	柔软	硬	非常硬	硬	非常硬
其它发现	在固化过程中冒烟	溶解性问题－FR	无烟	无烟	在固化过程中冒烟	无烟

	BELCLENE 200（PMA）			
	样品化合物#1	样品化合物 #3	样品化合物#4	样品化合物#6
干燥添加重量	20% FR#1 8% PMA 4% NaH_2PO_2	20% FR#3 8% PMA 4% NaH_2PO_2	20% FR#4 8% PMA 4% NaH_2PO_2	20% FR#6 8% PMA 4% NaH_2PO_2
涂布溶液配方	50.0g FR#1 57.1gBELCLENE 200 10.0g NaH_2PO_2 82.9g H_2O	50.0g FR#3 57.1gBELCLENE 200 10.0g NaH_2PO_2 82.9g H_2O	50.0g FR#4 57.1gBELCLENE 200 10.0g NaH_2PO_2 82.9g H_2O	50.0g FR#4 57.1gBELCLENE 200 10.0g NaH_2PO_2 82.9g H_2O
干燥条件	5 分钟 @ 80℃	5 分钟 @ 80℃	5 分钟 @ 80℃	5 分钟 @ 80℃
固化条件	2 分钟 @ 180℃	2 分钟 @ 180℃	2 分钟 @ 180℃	2 分钟 @ 180℃
燃烧试验（在洗涤之前）	良好	良好	良好	良好
燃烧试验（在 1 次水洗后）	可以接受	良好	良好	良好
燃烧试验（在 5 次洗涤后）	-	-	良好	-
织物颜色	黄色	黄色	黄色	黄色
织物手感	硬	非常硬	硬	非常硬
其它发现	在固化过程中冒烟	无烟	无烟	无烟

第三次试验涂布:

	#5 样品化合物		
	BELCLENE 283(TMPA)	BTCA	BELCLENE 200 (PMA)
干燥添加重量	40% FR#5 8% TMPA 4% NaH_2PO_2	40% FR#5 5% BTCA 2.5% NaH_2PO_2	40% FR#5 8% PMA 4% NaH_2PO_2
涂布溶液配方	100.0g FR#5 57.1g BELCLENE 283 10.0g NaH_2PO_2 32.9g H_2O	100.0g FR#5 12.5g BTCA 6.3g NaH_2PO_2 81.2g H_2O	100.0g FR#5 57.1g BELCLENE 200 10.0g NaH_2PO_2 32.9g H_2O
干燥条件	5 分钟 @ 80℃	5 分钟 @ 80℃	5 分钟 @ 80℃
固化条件	2 分钟@ 180℃	2 分钟@ 180℃	2 分钟 @ 180℃
燃烧试验（在 1 次水洗后）	不良－织物燃烧	不良－织物燃烧	不良－织物燃烧
织物颜色	黄色	黄色	黄色
织物手感	柔软	柔软	柔软
其它发现	在固化过程中冒烟	在固化过程中冒烟	在固化过程中冒烟

所选织物样品的分析

#3 样品化合物（20％用量）与 TMPA 和 BTCA（样品－在洗涤前，在 1 次水洗后，和在 5 次浆洗后）。

#4 样品化合物（20％用量）与 TMPA，BTCA，和 PMA（样品－在洗涤前，在 1 次水洗后，和在 5 次浆洗后）。

#6 样品化合物（20％用量）与 TMPA 和 BTCA（样品－在洗涤前，在 1 次水洗后，和在 5 次浆洗后）。

#5 样品化合物（40％用量）与 TMPA，BTCA，和 PMA（样品－在 1 次水洗后）。

对选择织物样品的百分数磷测定

样品标识（干燥添加重量）	在洗涤前(%P)	在 1 次水洗后(%P)	在 5 次浆洗后(%P)
20% FR#3, 5.0%BTCA, 2.5% NaH_2PO_2	2.8	1.9	1.6
20% FR#3, 8.0%TMPA, 4.0 % NaH_2PO_2	3.6	2.1	2.1
20% FR#4, 5.0%BTCA, 2.5% NaH_2PO_2	3.4	2.0	2.1
20% FR#4, 8.0%TMPA, 4.0 % NaH_2PO_2	4.2	2.7	2.5
20% FR#4, 8.0%PMA, 4.0 % NaH_2PO_2	3.9	2.2	2.3
20% FR#6, 5.0%BTCA, 2.5% NaH_2PO_2	3.9	2.6	2.3
20% FR#6, 8.0%TMPA, 4.0 % NaH_2PO_2	4.5	1.5	1.5
40% FR#5, 5.0%BTCA, 2.5% NaH_2PO_2	-	0.35	-
40% FR#5, 8.0%TMPA, 4.0 % NaH_2PO_2	-	0.37	-
40% FR#5, 8.0%PMA, 4.0 % NaH_2PO_2	-	0.34	-

对选择织物样品的百分数钠测定

样品标识（干燥添加重量）	在5次浆洗后(%Na)
20% FR#3, 5.0%BTCA, 2.5% NaH_2PO_2	72ppm*
20% FR#3, 8.0%TMPA, 4.0 % NaH_2PO_2	58ppm*
20% FR#4, 5.0%BTCA, 2.5% NaH_2PO_2	55ppm*
20% FR#4, 8.0%TMPA, 4.0 % NaH_2PO_2	95ppm*
20% FR#4, 8.0%PMA, 4.0 % NaH_2PO_2	92ppm*
20% FR#6, 5.0%BTCA, 2.5% NaH_2PO_2	51ppm*
20% FR#6, 8.0%TMPA, 4.0 % NaH_2PO_2	76ppm*

*数字用空白修正（空白样品的钠水平是~75ppm）

从以上结果可以看出，几种FR/树脂涂布混合物获得了FR耐久性，即使在用洗涤剂5次浆洗后（所使用的洗涤的最大数字）。对于以上报道的成功试验和其它没有获得所需结果的实施方案，后者是由于缺乏阻燃反应活性（羟基官能度不足）或由于阻燃添加剂的挥发性，一种趋势变得非常明显。需要OH官能团在阻燃添加剂中存在以获得最令人满意的FR耐久性。含有#3，#4和#6样品化合物的涂布混合物（OH官能化）获得了所记录的最耐久的FR处理。

根据OH官能团，似乎很可能的是，#5样品化合物将被证明是所评价的最耐久的FR添加剂。然而，这不是在所进行的实验过程中的实际情况。对此最可能的解释是FR添加剂在烘箱固化阶段中蒸发。这不是令人惊奇的，因为#5化合物的TGA和DSC分析结果显示了在大约160℃下，即在设定固化温度（180℃）以下大约20℃，重量显著损失(TGA & DSC)。蒸发也解释了在处理织物的固化步骤过程中所观察到的大量烟雾和蒸汽。在已知这些结果的情况下，当实施本发明时，还需要考虑选择FR添加剂的挥发性。有潜力的FR添加剂应该具有在固化温度下基本无挥发的、反应活性的组分，以确保在FR添加剂的挥发之前发生交联。固化温度被定义为交联反应发生的温度。

除了所使用的FR添加剂的类型以外，对所使用的交联树脂的类型也进行了观察。除了在试验过程中记录的各种特性以外，织物的颜色和手感是最重要的。一般，BTCA树脂获得了最柔软的手感和最白的颜

色，二者是非常理想的质量。PMA 和 TMPA 然而获得了不太优选的结果。一般来说，由两种树脂赋予的手感比用 BTCA 要僵硬得多，这很可能是由所使用的高树脂水平引起的性质。通过减少这些树脂的用量或通过使用软化剂，可以改进织物的手感。PMA 和 TMPA 的另一负面作用是它们在织物上赋予的颜色。PMA 处理的织物产生了浅黄色。通过降低固化温度和/或添加增白剂这两种通常用于工业中以矫正这类问题的工艺可能会降低质量。除了 PMA 以外，TMPA 也对织物着色。然而，由该树脂产生的粉红色是更强烈和显著的。

在这些初步试验中，除了使用样品化合物#3、#4 和#6 的一个以外的所有织物样品在一次水洗后保持了 56－68％的应用磷。另外，经第一次洗涤后附着于织物的磷似乎在经过所有 5 次浆洗后都保留在其中。

除了百分数磷测定以外，还决定来证实钠在浆洗样品中的水平。高水平的钠将不良地影响所测试的 FR 处理的长期耐久性。众所周知的事实是，水解和随后的钠离子交换至来自洗涤剂的磷 FR 处理剂中将随时间推移显著影响处理的 FR 性能（即，磷酯的钠盐使得 FR 低劣）。除了水解和磷从织物中除去以外，钠离子交换至 FR 处理剂中是在浆洗后 FR 性能损失的首要原因之一。如以上数据所显示的那样，所有的浆洗样品都含有非常低水平的钠，这意味着该结合磷对浆洗稳定并应该在 5 次洗涤后保持良好的 FR 性能。

前述实施例应该不以限制的方式来解释，因为它们仅用于阐述本发明的某些优选实施方案。请求保护范围在所附权利要求书中阐明。