Fibrous material such as cotton cloth is rendered flame retardant by treating the material with cyanamide and at least one halomethyl phosphonic acid represented by the structural formula:

\[
\begin{align*}
\text{H} & \quad \text{O} & \quad \text{OH} \\
\text{R}^1 & \quad \text{C} & \quad \text{P} \\
\text{R}^2 & \quad \text{O} & \quad \text{R}^1
\end{align*}
\]

wherein \( R^1 \) represents a monovalent radical such as chloro or bromo and \( R^2 \) represents a monovalent radical such as hydrogen or methyl. Durability of the flame retardancy to repeated hard water washing may be improved through a subsequent treatment with N-methylol compounds such as methylolated melamine precondensate. A particularly high degree of flame retardancy is imparted to mercerized cotton cloth.

6 Claims, No Drawings
1. Field of the Invention

This invention relates to flame retardant fiber-containing material and to processes for producing the same.

2. State of the Art

Natural fiber-containing textile materials such as cotton cloth have been employed since ancient times. However, the combustibility of these textile materials have inhibited their wider use in certain instances. A great number of flame retardants have been proposed for use with cellulose textile materials, but these flame retardants suffer from one or more disadvantages.

A major disadvantage of many prior flame retardants is their lack of wash fastness or durability, by which is meant that while they initially render the cellulose textile material flame retardant, such flame retardancy disappears after one or more household launderings, especially in hard water. This phenomenon is described by O'Brien in "Cyanamide-Based Durable Flame- Retardant Finish for Cotton." Textile Research Journal, March 1968, pp. 256-266. This article describes imparting flame retardancy to cellulose textile materials with flame retardants of cyanamide and phosphoric acid. However, the flame retardants disclosed therein by O'Brien are not resistant to hard water washing. Similarly, East German Pat. Nos. 15,357 and 18,253, and Schilchner et al in Faserforsch u. Textiltech., 14, (9), 375-86 (1963) describe specific attempts to impart flame resistance to textile material with certain flame retardants, including combinations of urea or dicyandiamide with chloromethyl phosphonic acid, or urea with hydroxymethyl phosphonic acid, which combinations may also not be resistant or durable to repeated cycles of hard water washings, or which may unduly degrade the physical strengths of fabrics.

Other disadvantages include the relatively large quantities (high add-on) which may be necessary in order to impart flame retardance, and the undesirable alteration of other properties of the cellulose textile material such as color, hand, and susceptibility to dyeing.

3. SUMMARY OF THE INVENTION

Accordingly, a primary object of the present invention is to render fiber-containing material flame retardant while preventing or substantially alleviating one or more of the above-discussed disadvantages of prior processes.

Another object is to provide an improved process for imparting flame retardancy to cellulose textile materials which flame retardancy is durable and resistant to multiple household launderings in general and especially in hard water.
where R\(^1\) represents a monovalent chlorine or bromine radical and R\(^2\) represents a monovalent radical such as hydrogen or lower alkyl. The alkyl radicals or portions of the radicals may contain, for example, from 1 to 4 carbon atoms.

Non-limiting examples of phosphonic acids having the abovedescribed structural formula and which may be used according to the process of the present invention include chloromethyl phosphonic acid, chloromethyl phosphonic acid monomethy l ester, bromomethyl phosphonic acid and bromomethyl phosphonic acid monomethyl ester. Mixtures of two or more phosphonic acids may be used if desired.

The manner in which the phosphonic acids and cyanamide are prepared or derived is at present well known and does not form a part of the present invention.

The cellulosic and wool fiber-containing materials which may be treated according to the present invention are generally any of those which have been previously employed to conjunction with known flame retardants. The fibercontaining or textile material can have a wide variety of physical forms and can be fibers, filaments, yarns, threads, and particularly woolen and nonwoolen cloth. The cellulosic fiber material can be cotton, flax, linen, hemp, or regenerated cellulose such as rayon (e.g., viscous rayon). Mercerized cotton may give particularly advantageous results. (Mercerized cotton is well known per se; mercerization typically comprises passing cotton through a 25 to 30 percent solution of sodium hydroxide under tension, and then washing the cotton with water while under tension. Mercerization using liquid ammonia is also known). These fiber-containing or textile materials can be mixtures of two or more different fibers, e.g., a mixture of cellulosic fibers with other fibrous materials such as nylon (e.g., nylon 6, 6), polyester (e.g., polyethylene terephthalate), acrylics (e.g., polyacrylonitrile), polyolefins (e.g., polypropylene), polylviny1 chloride, poly(vinylidene chloride), and polyvinyl alcohol fibers. The preferred cellulosic textile materials are those containing 50 weight percent or more of cotton and especially pure, i.e., essentially 100 weight percent, cotton cloth.

According to a broad aspect of the present invention, fire or flame retardancy can be imparted to fibrous material by simply contacting or impregnating the material with the phosphonic acid and cyanamide under widely varying conditions of temperature and pH. However, durable, i.e., wash resistant, flame retardancy is imparted only to fixing, i.e., reacting, the phosphonic acid with the cyanamide on the material. This fixing or “curing” is generally accomplished by heating the treated material at superambient temperatures and at low pH. Broadly, any temperature can be employed above which the phosphonic acid and cyanamide are fixed or reacted on the material and below which undesirable thermal degradation of the material begins, and generally from 20° to 400°C and preferably from 100° to 300°C. Optimum results are obtained at 120° to 180°C.

Durable flame retardance is imparted if, concurrently with the above described heating, the pH of the reacting mixture on the material is low, i.e., typically less than 2.5 and preferably less than 1.5, e.g., about 1.0. While these pH's are believed to be critical to durability it is generally valid to assume that the pH of the reacting mixture on the material is the same as the pH of the mixture of phosphonic acid, cyanamide, and solvent when present, except as indicated below for the in situ generation of the reactants.

The fibrous material may be contacted with a simple mixture of the phosphonic acid and cyanamide; and a solvent is preferably present. The solvent can be employed in any amount up to infinite dilution as long as the final treated material has an add-on sufficient to impart flame retardancy, which add-on may be, for example, from 2 to 15 weight percent. Add-on is defined and used herein as the increase ("dry" basis) in weight of the fibrous material due to the addition of the flame retardant as a percentage of the weight of the untreated fibrous material. Examples of suitable solvents include lower alkanols such as methanol and ethanol, lower alkylene or alkyl ethers such as dioxane and ethyl ether, or, most preferably, water. Such solutions are termed pad baths.

The fibrous material can be contacted with the phosphonic acid and cyanamide sequentially but is preferably contacted with both simultaneously.

This mixture of phosphonic acid and cyanamide can be employed at autogenous pH which is generally about 0.8 or at a slightly higher pH, e.g., about 1.0 to 1.5, except as indicated below for the in situ generation of the reactants where the pH of the pad bath may vary up to about 6.0. Naturally, in the latter case the pH of the pad bath may be quite different than the pH on the material at fixation.

A method by which the above described phosphonic acids can be formed in situ is by the thermal degradation of the corresponding ammonium salt such as mono- or di-ammonium chloromethyl phosphonic acid, or ammonium chloromethyl phosphonic acid monomethyl ester. For example, ammonium hydroxide can be added to a pad bath containing the phosphonic acid (which would, of course, raise the pH, typically to about 3.0). Thus, in the fixing step there is initially present, on the fibrous material, cyanamide and an ammonium salt of the phosphonic acid. Upon heating to fixation, the ammonium salt would decompose to ammonia and the corresponding phosphonic acid (resulting in a lowered pH). Usage of such ammonium salts and the inherent raising of the pH of the pad bath can be advantageous where lower pH (higher acidity) pad baths are not desired due to corrosion and personnel handling considerations.

In a preferred process for rendering fibrous materials such as cellulosic textile materials flame retardant according to the present invention, the material is first contacted with an aqueous solution comprising a mixture of phosphonic acid and cyanamide at the desired pH in a molar ratio of 1:10 to 10:1 preferably 1:3 to 3:1. The excess solution is then removed from the material by any suitable means such as by passing the material between the nip of two rollers. The material is then dried to remove excess water. The drying can be accomplished at any temperature but is generally accomplished at superambient temperatures and preferably from 20° to 150°C. The material is then heated in
order to fix the phosphonic acid and cyanamide on the material at the above described fixation temperatures. The heating is conducted for at least several seconds and up to several hours, more typically from one to 15 minutes. In certain instances, the fixing may be generally complete in within 2 to 10 minutes. The drying and heating steps can be conducted simultaneously but are preferably conducted sequentially. The fixing of the phosphonic acid with the cyanamide on cellulose material is presently thought to occur in the form of a reaction product which then reacts with the hydroxyl groups of the cellulosic material.

The treated fibrous material preferably has sufficient add-on such that it exhibits the desired degree of flame retardancy. Such materials generally have add-ons of 1 to 30, and preferably 10 to 20 percent.

It is only critical to the present invention that the above described phosphonic acids and cyanamide be present on the fibrous material. Therefore, according to another embodiment of the present invention many of these compounds can be formed in situ. A preferred method by which the above described phosphonic acids can be formed in situ is by the above-described thermal degradation of the corresponding ammonium salt such as ammonium chloromethyl phosphonic acid, monomethyl ester, or mono- or di-ammonium chloromethyl phosphonic acid. Another method may be by the use of metal salts of the phosphonic acids together with means for creating the low pH's necessary to effect fixation. For example, the pH of the pad bath may be increased with sodium hydroxide, followed by the addition of ammonium chloride. Thus, in the fixing step there would be present on the cellulosic material: cyanamide, a sodium salt of the above described phosphonic acids, and ammonium chloride. Upon heating, the ammonium chloride would decompose to ammonia and hydrochloric acid converting the sodium salt to the free acid to accomplish fixation. Naturally, in these cases the pH of the pad bath may be quite different than the pH on the material.

The solution of phosphonic acid and cyanamide into which the cellulosic material is dipped may also contain, if desired, conventional softeners, lubricants, stiffeners, brighteners, water-repellants, soil release agents, and dyes.

In accordance with another aspect of the present invention, the fibrous material rendered flame retardant as indicated above is subsequently treated to improve flame retardancy by contacting the material with one or more water-soluble compounds possessing reactive N-methylol groups. When such further processing or "retreatments" are employed, the acid form of the phosphonic acid residue typically needs to be regenerated such as by contacting or "souring" with a dilute hydrochloric acid solution. Such regeneration is typically necessary due to what is thought to be inherent chemical breakdown of cyanamide to produce eventually ammonia in the curing or fixation stage, which results in an ammonium salt form of the phosphonic acid residue on the fabric. And after hard water washing, the phosphonic acid residues may inherently be present on the fabric as their calcium salts, as further explained hereinbelow.

After laundering in hard water, the phosphonic acid residues are thought to be at least in part present on the fabric as their calcium salts, e.g.,

It is thought that this subsequent treatment with N-methylol compounds causes lowered ionicity and therefore lower susceptibility to calcium pickup (increases resistance to ion exchange) during hard water washings. As a consequence, flame retardance, and especially the durability of flame retardance, is improved.

When one or more N-methylol compounds are used in the subsequent treatment, the acid form of the phosphonic acid residue should be regenerated such as by contacting or "souring" with a dilute hydrochloric acid solution, and the soiled fibrous material is contacted with the N-methylol compound and is thereafter curbed to fix or insolubilize the compound on the material.

The water-soluble compounds possessing reactive N-methylol groups, sometimes referred to herein as N-methylol compounds, include the substantially water soluble precondensates which are obtained by condensation of formaldehyde with a compound such as melamine, or a lower alkyl-substituted melamine, or a urea.

The resulting methylol-containing compound or precondensate may be further etherified by reaction with a lower alkanol such as methanol or butanol. As is well known in the fabric treating art, these precondensates are capable of being applied to fibrous materials from an aqueous solution. Good results may be obtained, for example, using precondensates obtained by condensing 1 mole of melamine or an alkyl substituted melamine with 1 to 6 moles of formaldehyde, i.e., using monomethylol, dimethylol, trimethylol, tetramethylol, or hexamethylol melamine. Such products function well to increase flame retardance durability and can be readily fixed or cured on fibrous material by heating as described herein. Commercially available products of this kind include Aerotex 23, an alkylated melamine-formaldehyde precondensate, Aerotex M-3, a dimethoxymethyl hydroxyethyl melamine: Aerotex P-225, a hexakis (methoxymethyl) melamine; Aerotex 19, which is a less completely fractionated modification of Aerotex P-225, and Aerotex 92 which is a melamine having an average of about 1.5 methylol groups. These Aerotex products are supplied by American Cyanamide Company. Equivalent products are commercially available from other manufacturers such as Monsanto Company which produces Resloom HP, which is a melamine having an average of about 2 to 3 methylol groups. To be applied by padding, one or more of the aforementioned N-methylol compounds may be dissolved in water to form a solution containing from about 1 to 50%, preferably about 5 to 20%, N-methylol compound. To facilitate insolubilization or formation of polymer on the fabric in a desired amount, it may be desirable in certain cases to add to the padding solution, a catalyst such as formic acid, citric acid, hydrochloric acid, or, particularly, an acid reacting salt such as zinc nitrate, zinc chloride, magnesium chloride, ammonium chloride, aluminum chloride, sodium hydrogen phosphate, or sodium dihydrogen phosphate. Such a catalyst may be added to the pad bath in a concentration of between
about 0.1 and 10% by weight of the N-methylol compound. Formation of the insoluble form of the N-methylol compound on the fibrous material is typically aided by heat in addition to acidity. After application of the N-methylol compound to the fibrous material, the latter is dried and finally cured under conditions essentially the same as or similar to those described earlier herein in connection with the subsequent treatment with cyanamide.

Application of the N-methylol compound-containing solution to the fibrous material may be done by conventional padding using customary equipment, or by other processes well known to the art. Typically, the solutions are applied to the fibrous materials in a wet pickup of from about 40 to 120%, so as to give upon fixation a total add-on of between about 1 and 15%, based on dry fabric weight. The padding may be conducted at ambient temperature, e.g., between about 10° and 30°C. As in the initial treatment, any excess solution may then be removed from the fibrous material by any suitable means such as by passing the material between the nip of two rollers. The material may then be dried to remove excess water. The drying can be accomplished at any temperature but is generally accomplished at ambient or superambient temperatures, and typically from 20° to 100°C. The material with the N-methylol compound is then heated in order to fix or insolubilize the N-methylol compound on the fibrous material. Broadly, any temperature can be employed above which the N-methylol compound is reacted on the material and below which undesirable thermal degradation of the material begins, and preferably from 100° to 300°C, and more preferably from 120° to 180°C. The heating is conducted for at least several seconds up to several hours, more typically from about 10 seconds to 2 hours and preferably from about 1 to 15 minutes. The drying and heating steps can be conducted simultaneously but are preferably conducted sequentially.

Such treatment with N-methylol compounds has been found to reduce ionicity and calcium pickup (increasing resistance to ion exchange), thus improving durable flame retardancy. Increased durability of flame retardancy through such subsequent treatment with N-methylol compounds was unexpected insofar as the utilization of such compound in the initial pad baths containing the phosphonic acid and cyanamide reduced flame retardancy. Moreover, other conventional creaseproofing agents such as dimethyl dihydroxyethylene urea have been found not to increase significantly the durability of flame retardancy.

If desired, more than one subsequent treatment with additional N-methylol compound may be used.

The present invention is further illustrated by the following examples; all parts and percentages in the examples as well as in other parts of the specification and claims are by weight unless otherwise indicated. These non-limiting examples are illustrative of certain embodiments designated to teach those skilled in the art how to practice the invention and to represent the best mode contemplated for carrying out the invention.

EXAMPLE I

This example illustrates the process of the present invention employing cyanamide and chloromethyl phosphonic acid (CMPA) in aqueous solutions of varying acid to cyanamide molar ratios as is shown in TABLE I.

For each run, a weighed piece of cotton twill measuring 12 inches × 12 inches was dipped into the aqueous solution or "pad bath" of cyanamide and phosphonic acid and then passed between the nip of two rollers to remove the excess solution. The cloth was then dried in an oven for 10 minutes at 80°C and then cured (fixed) in a second oven for 15 minutes at 160°C. The fabric was then washed once as described below, dried, conditioned at 65% relative humidity at 21°C and reweighed. The difference between the initial weight of the sample prior to the contact with the solution and final weight of the cloth after one wash divided by the initial weight of the cloth times 100 is recorded in TABLE I as "add-on." This procedure was repeated for each of the remaining solutions.

Each of the samples was then washed the indicated number of times in an automatic home laundering machine having one wash and two rinses with intermediate spin dry operations. A hard water solution of household laundry detergent, commercially available as "ALL Laundry Detergent," was employed as the wash water (pH 8.5). Hard water was employed in the rinses. In this example, the term "hard water" refers to Irvine, California, water containing a degree of hardness equivalent to 350-380 ppm of calcium carbonate. Total dissolved solids amount to 750-850 ppm. The flame retardancy was then measured according to American Association of Textile Chemists and Colorists (AATCC) procedures 34-1966 and the char length in inches is shown in TABLE I. (The greater the char length, the less the flame retardancy.) A qualitative pass (+)/fail (−) vertical strip-match test was also given to each of the treated samples. In TABLE I the physical testing values are calculated by the formula:

<table>
<thead>
<tr>
<th>Fill</th>
<th>Strength before treatment</th>
<th>Strength after treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retention =</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Fill</td>
<td>Strength</td>
<td>Retention</td>
</tr>
</tbody>
</table>

The values of tensile strength are determined according to ASTM D1682-59T, and the values of tear strength are determined according to ASTM D1424-59. Both are measured in the "fill" direction of the material. The fill direction is also known as the direction parallel to the wool threads.

AS may be seen from TABLE I, at a CMPA/cyanamide ratio of 1:3 (run 3) the retardance is durable for at least 80 washes.
TABLE I

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Acid Used</th>
<th>Cyanamide in Bath (%)</th>
<th>Acid:Cyanamide Ratio</th>
<th>Add-On (%)</th>
<th>P (%)</th>
<th>N (%)</th>
<th>CI (%)</th>
<th>Fill Strength Retention (%)</th>
<th>Tear</th>
<th>Tensile</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CMPA</td>
<td>8</td>
<td>1:1</td>
<td>12.2</td>
<td>1.89</td>
<td>0.70</td>
<td>1.95</td>
<td>71</td>
<td>43</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>CMPA</td>
<td>16</td>
<td>1:2</td>
<td>16.8</td>
<td>2.49</td>
<td>0.91</td>
<td>2.24</td>
<td>57</td>
<td>67</td>
<td>65</td>
</tr>
<tr>
<td>3</td>
<td>CMPA</td>
<td>24</td>
<td>1:3</td>
<td>17.8</td>
<td>2.33</td>
<td>0.92</td>
<td>1.60</td>
<td>87</td>
<td>56</td>
<td>56</td>
</tr>
<tr>
<td>4</td>
<td>CMPA</td>
<td>32</td>
<td>1:4</td>
<td>20.4</td>
<td>2.46</td>
<td>0.72</td>
<td>1.22</td>
<td>72</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>5</td>
<td>CMPA</td>
<td>48</td>
<td>1:6</td>
<td>24.0</td>
<td>2.25</td>
<td>0.30</td>
<td>1.08</td>
<td>77</td>
<td>60(50)</td>
<td>60(50)</td>
</tr>
</tbody>
</table>

Flame Retardance = Char Length (in.) and Match Test* at Number of Washes Shown ("ALL" Det. Detergent)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>BEL</th>
<th>1% (+)</th>
<th>2% (+)</th>
<th>3% (+)</th>
<th>BEL*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>BEL</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The bath also contained, in addition to the cyanamide and phosphonic acid, 0.1 percent Triton X-100 non-ionic wetting agent and 5 percent Velvamine 380 polyethylene softener.

**Value in parentheses measured in area of char.

†w = passed match test; ↓ = failed match test; ♦ = burned greater than 3 inches but not entire length.

‡In a substantially duplicate run where higher percentages of P, N and Cl were recorded, as well as a lower degree of ionicity, the flame retardance at fifty washes was 2% (−).

COMPARISON

Experiments from East German Pat. Nos. DDRP 25 18,253 and 15,357 were carried out. The results are summarized below, the fabric (cotton twill) properties being measured after a hot wash (no detergent or soap) unless otherwise specified.

18,253—Example 1. Fusion of chloromethyl phosphonic acid (CMPA) and urea at 130°C, followed by fabric treatment with an aqueous solution of the product.

P, 1.75%; N, 0.81%; Cl, 0.87%.

Char length — 5½ in. After an additional detergent wash — BEL.

18,253—Example 2. As 1 but more dilute.

P, 1.55%; N, 0.72%; Cl, 0.71%.

Char length — 7 in. After an additional detergent wash — BEL.

15,357—Example 2. Conventional type pad-dry-cure using CMPA and urea.

P, 0.31%; N, 0.32%; Cl, 0.16%.

Char length — BEL.

15,357—Example 3. Soaking fabric in a solution of CMPA and dicyandiamide at 80°C for 15 min. followed by drying and curing.

P, 1.48%; N, 2.19%; Cl, 0.99%.

Char length — 1½ in. After an additional detergent wash — 6 in.

15,357—Example 4. Fabric treated with a solution of CMPA, dried, and overtreated with a melamine-formaldehyde product.

The fabrics were so stiff that they disintegrated on washing. No measurements made.

EXAMPLE II

This example illustrates certain preferred embodiments of the present invention employing cyanamide with chloromethyl phosphonic acid monomethyl ester.

In this example, the term "hard water" refers to Pasadena, California, water containing a degree of hardness equivalent to 128 ppm of calcium carbonate. Total dissolved solids amount to 236 ppm.

The following quantities of the following ingredients were combined as indicated:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>chloromethyl phosphonic acid monomethyl ester cyanamide</td>
<td>(77.5g of 50 wt. % aqueous solution)</td>
</tr>
</tbody>
</table>

The phosphonic acid and cyanamide were mixed with an amount of water added to the mixture to give a total weight of 162 grams of solution. This solution was divided into three samples and the pH of each adjusted to the value shown in Column 3 of TABLE II of the following table with 50 wt. % NaOH.

For each run, a weighed piece of cotton twill measuring 12 inches X 12 inches was dipped into a solution sample and then passed between the nip of two rollers to remove the excess solution. The cloth was then dried in an oven for 10 minutes at 150°C and then cured in a second oven for 15 minutes at 160°C. The fabric was then washed once as described below, dried, conditioned at 65% relative humidity at 21°C and reweighed. The difference between the initial weight of the fabric sample prior to the contact with the solution and final weight of the cloth after one wash divided by the initial weight of the cloth times 100 is recorded at Columns 4 of TABLE II, as "add-on." This procedure was repeated for each of the remaining solutions.

Each of the fabric samples was then washed the indicated number of times in an automatic laundering machine having one wash and two rinses with intermediate spin dry operations. A dry water solution of alkyl benzene sulfonate, commercially available as "Sears Super-concentrated Laundry Detergent," was employed as the wash water (pH 10.3). Hard water was employed in the rinses. The flame retardancy was then measured according to American Association of Textile Chemists and Colorists (AATCC) procedure 34-1966 and the char length in inches is shown in Columns 4 through 8 of TABLE II. (The greater the char length, the less the flame retardancy.)

As may be seen from TABLE II, at a pH of 1.0 (run 6), flame retardance was durable for at least 20 washes for chloromethyl phosphonic acid monomethyl ester.
TABLE I

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Acid Used</th>
<th>pH</th>
<th>Add On (wt %)</th>
<th>five washes (in)</th>
<th>ten washes (in)</th>
<th>twenty washes (in)</th>
<th>thirty washes (in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>CMPAM</td>
<td>1.0</td>
<td>16.4</td>
<td>2½</td>
<td>3¼</td>
<td>4½</td>
<td>BEL</td>
</tr>
<tr>
<td>7</td>
<td>CMPAM</td>
<td>2.0</td>
<td>11.0</td>
<td>3½</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>CMPAM</td>
<td>3.0</td>
<td>9.0</td>
<td>4½</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Legend

CMPAM = chloromethyl phosphonic acid monomethyl ester
BEL = burned entire length

EXAMPLE III

This example illustrates certain preferred embodiments of the present invention employing cyanamide with chloromethyl phosphonic acid (CMPA) and gives a comparison to the effect of mercerization of the cotton (flannel) fabric.

The procedure of Example I, run 2, is repeated employing the same quantities of the same ingredients and the same times, procedures and conditions with the exception that mercerized flannel cloth (Barium No. — 154) is used instead of unmercerized flannel cloth (Barium No. — 100) in this run (9).

The resulting flame retardancy for the mercerized flannel is believed to be more durable than for the unmercerized flannel.

Mercerization of cotton is believed to increase the number of anhydroglucose units available for reaction, i.e., “removes” them from relatively impenetrable crystalline regions of the cellulose. Thus, when a given amount of flame retardancy-imparting reactants is applied to the cellulose, the concentration of reactive sites on a mercerized fabric is greater relative to a similar but unmercerized fabric, and hence, the efficiency of immobilization is increased (i.e., wash-off is decreased). This phenomena is significant insofar as efficiencies of reactants, durability of flame retardancy, and overall process economies are improved.

EXAMPLE IV

This example illustrates certain preferred embodiments of the present invention employing cyanamide and chloromethyl phosphonic acid (CMPA) with subsequent treatments with N-methylol compounds.

The solution samples were prepared by dividing up a master solution into several samples, with the pH of each being adjusted to the value shown in TABLE IV with an ammonium hydroxide solution. The fabric samples were then dried in an oven for 5 minutes at 65°C and then cured in a second oven for 5 minutes at 140°C. The fabric samples were then washed, dried and conditioned as described in Example I except that AATCC standard phosphate detergent, equivalent to “ALL” detergent employed in Example I was used, and the wash and rinse water was Menlo Park, California water containing a degree of hardness equivalent to 56 ppm of calcium carbonate. Three fabric samples were used as controls, while the remaining three fabric samples were subjected to a subsequent treatment with N-methylol compound to improve durable fire retardancy (reduce ionicity). Each subsequent treatment included dipping the fabric sample into an aqueous solution containing 10 weight percent Aerotech 92 methylolated melamine, 0.1 weight percent Triton X-100 non-ionic wetting agent and 5 weight percent Velvamine 380 polyethylene softener. The fabric samples were then dried in an oven for 5 minutes at 65°C and then cured in a second oven for 5 minutes at 140°C. Each of the fabric samples was washed the indicated number of times in an automatic home laundering machine having one wash and two rinses with intermediate spin dry operations. The flame retardancy is then measured according to American Association of Textile Chemists and Colorists (AATCC) procedure 34-1966.

As may be seen from TABLE IV, durable flame retardance is improved by such subsequent treatment with N-methyl compound.

TABLE IV

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Subsequent Treatment</th>
<th>pH of Bath</th>
<th>Flame Retardance (One Wash)</th>
<th>Flame Retardance (Fifty Washes)</th>
<th>% R</th>
<th>% N</th>
<th>% C</th>
</tr>
</thead>
<tbody>
<tr>
<td>11 (control)</td>
<td>No</td>
<td>0.5</td>
<td>2 (+)</td>
<td>BEL</td>
<td>2.73</td>
<td>0.96</td>
<td>2.75</td>
</tr>
<tr>
<td>12</td>
<td>Yes</td>
<td>0.5</td>
<td>1½ (+)</td>
<td>2 (±)</td>
<td>2.40</td>
<td>6.50</td>
<td>2.13</td>
</tr>
<tr>
<td>13 (control)</td>
<td>No</td>
<td>3.0</td>
<td>8½ (+)</td>
<td>2 (±)</td>
<td>2.51</td>
<td>1.15</td>
<td>2.53</td>
</tr>
<tr>
<td>14</td>
<td>Yes</td>
<td>3.0</td>
<td>1½ (+)</td>
<td>4 (±)</td>
<td>2.01</td>
<td>5.61</td>
<td>2.78</td>
</tr>
<tr>
<td>15 (control)</td>
<td>No</td>
<td>4.5</td>
<td>4½ (±)</td>
<td>2½ (±)</td>
<td>2.73</td>
<td>0.96</td>
<td>1.28</td>
</tr>
<tr>
<td>16</td>
<td>Yes</td>
<td>4.5</td>
<td>1½ (+)</td>
<td>2½ (±)</td>
<td>2.73</td>
<td>5.30</td>
<td>1.32</td>
</tr>
</tbody>
</table>

For each run, a piece of cotton flannel was dipped into an aqueous solution sample containing 25 weight percent chloromethyl phosphonic acid, 24 weight percent cyanamide (1:3 acid:cyanamide ratio), 0.1 weight percent Triton X-100 non-ionic wetting agent and 5 weight percent Velvamine 380 polyethylene softener.

EXAMPLES V—VI

These examples illustrate certain preferred embodiments of the present invention employing cyanamide with chloromethyl phosphonic acid on wool and on rayon fabrics.

The procedure of Example I (run 2) is repeated em-
ployn) the same quantities of the same ingredients and the same times, procedures and conditions with the exception that the cotton twill was replaced by bleached, undyed wool in one run, by dyed wool (grey) in another run and by rayon twill in a third run. Durable flame retardance is observed for each of the treated fabrics.

The principles, preferred embodiments and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit of the present invention.

We claim:

1. A process for rendering cellulose and wool fiber-containing material durably flame retardant, which process comprises the steps of:
   (a) contacting the material with cyanamide and at least one phosphonic acid represented by the structural formula:

   \[
   \begin{align*}
   H & \quad O \quad OH \\
   R^1 - C - P & \quad OR^2 \\
   H & \quad OR^2
   \end{align*}
   \]

   wherein \( R^1 \) represents a monovalent radical selected from the group consisting of chloro and bromo; and wherein \( R^2 \) represents a monovalent radical selected from the group consisting of hydrogen and lower alkyl; to deposit on the material a flame retarding amount of the phosphonic acid with cyanamide; and subsequently

   (b) heating the material to fix the phosphonic acid at a pH less than 2.5 with cyanamide on the material to give an add-on of between about 1% and 30%, and

2. A process according to claim 1 for rendering cotton fiber-containing textile material durably flame retardant, which process comprises in sequence the steps of:

   (a) contacting the material with an aqueous solution of cyanamide with chloromethyl phosphonic acid wherein the molar ratio of phosphonic acid:cyamide is 1:10 to 10:1;

   (b) fixing the retardancy in the material at a pH less than 1.5 by heating the material until an add-on of between about 1 and 30% is achieved and the flame retardancy becomes durable to at least 50 hard water washes; and

   (c) regenerating an acid form of fixed phosphonic acid residue on the material and then contacting the material with an aqueous solution of the N-methylo compound, and heating the material to cure and the durability of the flame retardancy is improved to at least 50 hard water washes.

3. A process according to claim 2 wherein the textile material is mercerized cotton cloth, and wherein the aqueous mixture of cyanamide and chloromethyl phosphonic acid further contains ammonium hydroxide, and an ammonium salt of the phosphonic acid is deposited on the textile material.

4. A durably flame retardant material produced according to the process of claim 1.

5. A process according to claim 1 wherein the material is cellulose and the phosphonic acid is chloromethyl phosphonic acid.

6. A process according to claim 5 wherein the cellular solid material is mercerized cotton cloth and the flame retardancy is durable to at least 50 hard water washes.