Flame retardants for cellulosic fabrics, especially polyester blends, comprise a limited phosphine oxide class of N-methylopropionamides, particularly N-methylo-3-(dimethylphosphiny1)propionamide, closely related structurally to N-methylo-3-(dimethylphosphono)propionamide, but markedly more effective as a flame retardant.
FLAME RETARDANT FOR CELLULOSIC FABRICS

BACKGROUND OF THE INVENTION

This invention pertains to a new and limited class of phosphorus- and nitrogen-containing flame retardants for cellulosic materials, especially fabrics.

One of the most interesting advances in the field of flame retardants for cellulosic fabrics in recent years is the class of reactive N-methylo1-3-(dimethylphosphono)propionamides described in U.S. Pat. No. 3,374,292, the pertinent features of which are incorporated herein by reference. One of these, N-methylo1-3-(dimethylphosphono)-propionamide,

\[
\begin{align*}
\text{(CH}_3\text{PO})_2\text{CH}_2\text{CH}_2\text{ONH}_2\text{OH} \\
\end{align*}
\]

has achieved considerable commercial success under the proprietary name of Pyrovatex CP. It is particularly effective because it bonds both phosphorus and nitrogen chemically to the cellulose molecule. Being reactively bonded rather than merely physically coated onto the cellulose, it holds more tenaciously than non-reactive coatings and plasticizers. Besides this advantage Pyrovatex CP, unless it is combined with textile resins, has far less stiffening effect on fabrics than do the various kinds of coating agents.

Pyrovatex CP is not, however, without faults. As a phosphonate ester, it has a potential for hydrolysis under conditions of extended use, as during laundering, weathering, steam ironing, and the like. More important, the efficiency of the reaction between Pyrovatex CP and cellulose is low, thus resulting in considerable loss of expensive reagent during application to fabric. This low efficiency of reaction further manifests itself in the fact that only limited amounts of Pyrovatex CP can be added to cellulosic fibers, a fact which seriously diminishes its utility in fabric blends such as the popular 50/50 polyester/cotton. Being inert to polyester and incapable of heavy add-on to cellulose, Pyrovatex CP cannot be taken up by the blends in amounts sufficient to flameproof them adequately.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a class of flame retardants having a high capacity for bonding chemically with cellulosic fabrics. A further object of the invention is to provide a class of flame retardants effective on polyester/cotton blends.

A further object is to provide flame retardants with exceptional resistance to laundering.

I have found that new compounds, particularly

\[
\begin{align*}
\text{R}_1\text{O} \quad \text{X} \quad \text{O} \\
\text{CH}_3\text{CH}_2\text{ONH}_2\text{OH} \\
\text{R}_2
\end{align*}
\]

where \(\text{R}_1\) and \(\text{R}_2\) are methyl, ethyl, or propyl radicals, and \(\text{X}\) is hydrogen or a methyl radical, are remarkably effective as flame-retardant reagents for cellulosic fabrics and fibers. The most preferred of these reagents is \((\text{CH}_3\text{PO})_2\text{CH}_2\text{CH}_2\text{C(O)}\text{NHCH}_2\text{OH}\). Although obviously analogous to Pyrovatex CP in structure, it is surprisingly different from it in function and efficiency.

As shown hereinafter, the compounds of my invention exhibit high degrees and efficiencies of add-on to cellulosic fabrics and thereby confer a high level of flame resistance upon them. N-methylo1-3-(dimethylphosphonophenyl)propionamide adds so well that it is effective even on 50/50 polyester/cotton blend fabrics.

DETAILED DESCRIPTION

This invention comprises a new class of phosphate oxide derivatives of N-methylo1 propionamides of the general formula

\[
\begin{align*}
\text{R}_1\text{O} \quad \text{X} \quad \text{O} \\
\text{CH}_3\text{CH}_2\text{ONH}_2\text{OH} \\
\text{R}_2
\end{align*}
\]

where \(\text{R}\) represents hydrogen or alkyl of up to six carbon atoms, \(\text{X}\) represents hydrogen or a methyl radical, and \(\text{R}_1\) and \(\text{R}_2\) represent methyl, ethyl, or propyl radicals.

Preferred compounds are those having the formulas

\[
\begin{align*}
\text{R}_1\text{O} \quad \text{X} \quad \text{O} \\
\text{CH}_3\text{CH}_2\text{ONH}_2\text{OH} \\
\text{R}_2
\end{align*}
\]

and

\[
\begin{align*}
\text{R}_1\text{O} \quad \text{X} \quad \text{O} \\
\text{CH}_3\text{CH}_2\text{ONH}_2\text{OH} \\
\text{R}_2
\end{align*}
\]

where \(\text{R}_1\), \(\text{R}_2\), and \(\text{X}\) are as defined above. The most preferred compound is N-methylo1-3-(dimethylphosphonophenyl)propionamide:

\[
\begin{align*}
\text{R}_1\text{O} \quad \text{X} \quad \text{O} \\
\text{CH}_3\text{CH}_2\text{ONH}_2\text{OH} \\
\text{R}_2
\end{align*}
\]

These new compounds may be made by reaction of suitable Grignard reagents with dialkyl phosphites, the resulting dissubstituted phosphate oxides, also known as phosphinous acids, being thereafter treated with acrylamide methacrylamide, and after that with formaldehyde, undergoing reactions comparable to those described in the aforementioned U. S. Pat. No. 3,374,292.

Two particularly surprising features distinguish the phosphate oxide compounds of this invention from compounds known in the art: the high efficiency of their reaction with cellulose, and their superior flame retardant properties. Although neither of these advantages could have been anticipated, they are believed to work together to produce the remarkable overall superiority of these products. From a practical standpoint, the outcome of its particularly favorable combination of properties is that the preferred embodiment of this invention, N-methylo1-3-(dimethylphosphonophenyl)propionamide, hereafter referred to for convenience as MDMP, works effectively as a flame retardant even for
50/50 polyester/cotton blends, an application where Pyrovatex CP falls far short of adequacy. The aforesaid superior flame retardant capabilities of these phosphine oxide compounds are believed to derive from several factors. The principal of these is the fact, taking MDMP versus Pyrovatex CP as an example, that MDMP has so much the greater capacity for bonding to cellulose. This capability is amply demonstrated in the examples. A further factor, perhaps less clearly marked in effect, is the fact that the mode of action of MDMP under the influence of flame seems considerably different from that of Pyrovatex CP. This too is treated further in the examples.

In addition to the foregoing unexpected advantages, these compounds, having no hydrolysis-susceptible phosphonate groups, and being members of the class of phosphine oxides, among the most stable phosphorus compounds known, are free from the potential of many phosphorus-containing flame retardants, including Pyrovatex CP and its homologs, for forming strong and deleterious phosphorus acid groups on exposure to laundering, ironing, weathering, and like hydrolytic influences.

At the same time, these compounds retain all of the advantages mentioned earlier for Pyrovatex: chemical rather than physical bonding to cellulose, simultaneous addition of both nitrogen and phosphorus in a single reagent, and absence of stiffening and like defects commonly associated with flame-retardant coatings.

These compounds may be applied to substrates such as fabrics, yarns, and other forms of cellulose by any known means, such as spraying, dipping, padding, and the like, with preferably aqueous solutions of said compounds. The most convenient, and preferred, is padding, followed by drying in the case of aqueous application. Application to the substrate is followed by a curing of cross-linking step, to effect chemical reaction of the compounds hereof with free hydroxy groups in the substrate. This is preferably followed with a washing step to remove any of the compounds not chemically bound to the substrate. Typically, the reaction or curing step is brought about by application of heat, although other suitable reaction or curing mechanisms may also be utilized. Heat is normally most convenient and therefore is presently preferred. The amount and duration of heat treatment will normally depend on local practice, the type of substrate being treated, etc., and are not presently believed to be critical to the success of this invention. Usually a temperature of from about 150° to 175°C for from about one to several minutes will suffice for the heating step.

It has not as yet been possible to provide reasons for the most truly unexpected advantages of the products of this invention, their remarkable efficiency or their extent of reaction with the fabric substrate. Considering the apparent similarity of the structures of Pyrovatex CP and these compounds, particularly MDMP, it would be expected that Pyrovatex and MDMP would react with cellulosic materials in essentially the same way. The structures differ by only the presence of two extra oxygen atoms in Pyrovatex, and even these are at the opposite end of the molecule from the functional —CH₂OH group. However, the data given below show clearly that there is a remarkable difference in reactivities, in favor of the compounds of this invention.

Not only are differences in reactivities apparent, but even at comparable add-ons and phosphorus contents, blend fabrics treated with MDMP are markedly more resistant to flame than those treated with Pyrovatex CP. It is apparent that, despite their close structural resemblance to each other, MDMP and Pyrovatex CP are actually very dissimilar in effectiveness, and presumably in mechanism of flame-proofing action. These facts are particularly evident when one compares their effects on 50/50 polyester/cotton blends.

It should be recognized that, while the primary emphasis herein is on fabrics of various types including 100 percent cotton, 100 percent rayon, blends of such cellulosics with various man-made fibrous materials, and particularly in blends with polyester, it is understood that these treatments are equally applicable to a broad variety of substrates where flame retardancy may be desired, including yarns, fibers generally, paper, and other cellulosic-containing materials, whether these be made from cotton, rayon, wood pulp, or other sources of cellulose, and whether the articles in which they are incorporated are intended for use in apparel, home furnishings, intermediate, or industrial type products.

In assessing the flame retardancy of both the compounds of this invention and of earlier known products, two methods of evaluation have been utilized. One is the vertical flame test, "Fire Resistance of Textile Fabrics," AATCC No. 34-1966. Greater reliance has been placed in this specification on the measurement of the "Limiting Oxygen Index," LOI, because it offers more potential for indicating the extent of differences between test specimens, particularly those which fail, i.e., "burn entire length" (BEL), in the vertical test and therefore cannot be compared in terms of "char length." It has been found, in general, that fabrics having LOI values above the range of about 0.240-0.260 usually pass the vertical test; i.e., they are self-extinguishing to the degree that they do not burn their entire length, but instead have measurable char lengths.

The LOI values recorded herein were measured on a slightly modified General Electric Oxygen Index Flammability Gate, Cat. No. A4990A, following Instruction Manual 4541K25-001B. (See also ASTM Test D-2863, the standard LOI test used for plastics.) The application of the LOI test to fabrics is discussed in a paper by J. J. Willard and R. E. Wondra, Textile Research Journal, 40, 203-210 (1970).

Modifications to the standard GE instrument (see ASTM Test D-2863, FIG. 1, for the meaning of the following apparatus terms) were as follows: inside diameter of glass cylinder 3 inches instead of 3½ inches; distance from top of screen (4) to top of cylinder 1½ inches instead of 6 inches; distance from bead surface (6) to screen (4) 6⅔ inches instead of 3 inches; fabric length 6 inches instead of 5 inches; cover plate removed.

Flow rate was set at 4 cm/sec. Further details of this invention are given in the following examples.

**EXAMPLE 1**

As an illustration of the invention, N-methyl-3-(dimethylphosphinyl)propionamide, MDMP, was synthesized as follows: Dimethylphosphine oxide was prepared by the method of Hays, J. Org. Chem., 33, 3690 (1968), and distilled before use. To a stirred solution of 271.7 g. 3.48 mol, dimethylphosphine oxide and
247.1 g, 3.48 mol, acrylamide in 319 ml ethanol was added dropwise a freshly prepared solution of sodium ethoxide, made from 8.4 g, 0.365 atom, sodium and 193 ml ethanol. After about one-fourth of the base had been added a vigorously exothermic reaction began. When the reaction subsided the addition was continued at a rate which maintained a temperature of 70°C-80°C. The resulting white slurry was stirred 2 hours longer without heating, cooled, filtered, and the solid 3-(dimethylphosphinyl)-propionamide separated and dried. The yield of product melting 190°-91°C was 483 g.

Analysis:

| % Calc. for C_{3}H_{12}N_{2}O_{5}P | C 40.2, H 8.05, N 9.39, P 20.8 |

% Found: C 39.9, H 7.84, N 9.36, P 21.7

A 95.1-g portion, 0.638 mol, of this intermediate was treated with 157 g, 1.9 mol, of 36.6 percent formaldehyde solution at 60°C. The pH was held at 8.9-9 during the reaction by addition of a few small drops of 50 % NaOH. After 2.5 hours the free formaldehyde content, measured by the sodium sulfite method, was constant. After overnight stirring at room temperature, the solution was analyzed, it being found that the content of N-methylol-3-(dimethylphosphinyl)-propionamide, MDMP, was 0.562 moles in the 141 g of solution.

**EXAMPLE 2**

To illustrate the utility of the invention, in this and following examples the procedure employed was to pad an aqueous solution of reagent, 1 percent curing catalyst (2-amino-2-methylpropanol hydrochloride), and 0.1 percent detergent (nonylphenolpholyethyleneoxyethanol) onto weighed samples of bleached or normally scoured, but otherwise untreated 100 percent cotton sheeting, 50/50 polyester/cotton sheeting, or other cellulosic fabric in a laboratory paddler at 30 psi; dry 4 minutes at 93°C; cure 3 minutes at 175°C; process wash 12 minutes with water containing 0.001 percent detergent in a home washing machine set on “warm;” tumble-dry; and condition overnight at 72°F and 65 percent relative humidity in preparation for final weighing and testing. Except when otherwise indicated, test fabrics were 100 percent cotton sheeting, 3.75 oz/yd², 95 x 84 count, and 50/50 polyester/cotton sheeting, 3.68 oz/yd², 96 x 88 count. Samples for treatment were usually about 10 x 20 inches, weighing before treatment about 18 g for 50/50 polyester/cotton and 16 g for 100 percent cotton. The treatment cycle was repeated more than one time when ever it was desired to increase the extent of modification (add-on) beyond the maximum obtainable in a single treatment. The most superior results were generally obtained when using freshly prepared padding baths.

**EXAMPLE 3**

For comparative purposes, samples of 50/50 polyester/cotton fabrics were padded with 40 percent aqueous solutions of Pyrovatex CP and MDMP by the procedure of Example 2. Though none of the once-treated samples passed the vertical test, those padded with MDMP had slightly but significantly higher LOI readings, as may be seen by comparison of the one-cycle entries in Tables 1 and 2. Two and even three cycles of Pyrovatex CP had almost no further effect on increasing the add-on and the LOI, and all specimens burned their entire lengths in the vertical test. The LOI of the original fabric for all of the samples was 0.168.

**TABLE 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>No. Padding Cycles</th>
<th>Phosphorus % Add-on</th>
<th>LOI</th>
<th>Vertical Char Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>1.32</td>
<td>9.1</td>
<td>0.223 BEL*</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>1.21</td>
<td>9.3</td>
<td>0.220 BEL</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>1.07</td>
<td>10.7</td>
<td>0.231 BEL</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>-</td>
<td>11.0</td>
<td>0.231 BEL</td>
</tr>
<tr>
<td>E</td>
<td>3</td>
<td>1.72</td>
<td>12.5</td>
<td>0.231 BEL</td>
</tr>
<tr>
<td>F</td>
<td>3</td>
<td>1.87</td>
<td>13.9</td>
<td>0.234 BEL</td>
</tr>
</tbody>
</table>

**TABLE 2**

<table>
<thead>
<tr>
<th>Sample</th>
<th>No. Padding Cycles</th>
<th>Phosphorus % Add-on</th>
<th>LOI</th>
<th>Vertical Char Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>1.44</td>
<td>9.6</td>
<td>0.229 BEL</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>1.25</td>
<td>7.8</td>
<td>0.231 BEL</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>2.46</td>
<td>13.4</td>
<td>0.264 7.5*</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>2.73</td>
<td>20.9</td>
<td>0.254 7.5*</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>2.52</td>
<td>18.3</td>
<td>0.256 7.7*</td>
</tr>
<tr>
<td>F</td>
<td>2</td>
<td>2.14</td>
<td>14.0</td>
<td>0.247 BEL</td>
</tr>
<tr>
<td>G</td>
<td>2</td>
<td>2.19</td>
<td>15.0</td>
<td>0.251 3.4*</td>
</tr>
<tr>
<td>H</td>
<td>2</td>
<td>2.67</td>
<td>15.5</td>
<td>0.243 7.1*</td>
</tr>
<tr>
<td>I</td>
<td>2</td>
<td>2.52</td>
<td>15.0</td>
<td>0.236 8.1*</td>
</tr>
</tbody>
</table>

Surprisingly, when MDMP was applied the second time, the additional add-on was usually equal to and sometimes even greater than the original, and the LOI readings were increasing materially. Most significant of all, from a practical standpoint, was the fact that the LOI rose into the 0.240-0.260 range, and that the majority of the test specimens no longer failed the vertical test. (A few did fail, but this was taken as verification of the known impression of the vertical test.)

It is obvious, from the results in these tables, that MDMP displays a remarkably greater capability for bonding with and flameproofing polyester/cotton blends.

**EXAMPLE 4**

To determine what range of polyester/cotton fabrics could be flameproofed with MDMP, samples of 65/35 polyester/cotton sheeting were treated twice with 40 percent MDMP and Pyrovatex CP solutions by the standard procedure of Example 2. Results are given in Table 3.

**TABLE 3**

<table>
<thead>
<tr>
<th>Retardant</th>
<th>% P</th>
<th>% Add-On</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrovatex CP</td>
<td>---</td>
<td>8.2</td>
<td>0.220</td>
</tr>
<tr>
<td>Do.</td>
<td>---</td>
<td>9.1</td>
<td>0.223</td>
</tr>
<tr>
<td>MDMP</td>
<td>1.81</td>
<td>10.6</td>
<td>0.242</td>
</tr>
<tr>
<td>Do.</td>
<td>2.13</td>
<td>13.5</td>
<td>0.247</td>
</tr>
</tbody>
</table>

It's significantly higher LOI values showed that MDMP had effected a significantly greater increase in flame resistance than did Pyrovatex CP.
EXAMPLE 5

For comparative purposes, the procedure of Example 4 was repeated, but this time by padding twice onto 65/35 rayon/polyester sheeting at 40 percent concentration according to the method of Example 2. Two MDMP treated samples gave LOI readings of 0.252 and 0.242, and both samples passed the vertical flame test, giving char lengths of 6.3 and 4.6 inches.

EXAMPLE 6

In using relatively expensive flame retardants such as Pyrovatex CP and MDMP, it is important to achieve a high degree of bonding of the solution padded onto the fabric. Anything removed by the process wash after curing is essentially non-recoverable and wasted. The degree of bonding is expressed as the efficiency, this being calculated from the equation:

\[
\text{Retardant retained after washing/Retardant padded} \times 100 = \% \text{ efficiency}
\]

Samples of 100 percent cotton sheeting were put through one cycle of the process of Example 2, being padded with Pyrovatex CP and MDMP solutions of different concentrations. Data obtained are shown in Table 4.

### TABLE 4

<table>
<thead>
<tr>
<th>Retardant</th>
<th>Conc.</th>
<th>Add-on</th>
<th>% P</th>
<th>Efficiency</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrovatex CP</td>
<td>55</td>
<td>14.9</td>
<td>2.13</td>
<td>39</td>
<td>588</td>
</tr>
<tr>
<td>Do.</td>
<td>45</td>
<td>14.2</td>
<td>1.63</td>
<td>47</td>
<td>586</td>
</tr>
<tr>
<td>Do.</td>
<td>35</td>
<td>12.0</td>
<td>1.58</td>
<td>51</td>
<td>579</td>
</tr>
<tr>
<td>Do.</td>
<td>30</td>
<td>10.2</td>
<td>1.38</td>
<td>51</td>
<td>576</td>
</tr>
<tr>
<td>Do.</td>
<td>25</td>
<td>8.4</td>
<td>0.84</td>
<td>57</td>
<td>571</td>
</tr>
<tr>
<td>Do.</td>
<td>20</td>
<td>6.7</td>
<td>0.94</td>
<td>52</td>
<td>568</td>
</tr>
<tr>
<td>Do.</td>
<td>15</td>
<td>5.1</td>
<td>0.80</td>
<td>54</td>
<td>566</td>
</tr>
<tr>
<td>MDMMP</td>
<td>40</td>
<td>18.5</td>
<td>2.29</td>
<td>62</td>
<td>565</td>
</tr>
<tr>
<td>Do.</td>
<td>33</td>
<td>17.6</td>
<td>2.69</td>
<td>75</td>
<td>560</td>
</tr>
<tr>
<td>Do.</td>
<td>32</td>
<td>17.3</td>
<td>2.52</td>
<td>76</td>
<td>560</td>
</tr>
<tr>
<td>Do.</td>
<td>17</td>
<td>10.4</td>
<td>1.59</td>
<td>88</td>
<td>540</td>
</tr>
<tr>
<td>Do.</td>
<td>11</td>
<td>6.9</td>
<td>0.96</td>
<td>94</td>
<td>520</td>
</tr>
<tr>
<td>Do.</td>
<td>11</td>
<td>7.0</td>
<td>1.12</td>
<td>96</td>
<td>520</td>
</tr>
</tbody>
</table>

From these results it is apparent that the efficiency of addition of MDMMP approaches 100 percent at low concentration, while that of Pyrovatex CP peaks at around 55 percent.

Similar results, shown in Table 5, were obtained when solutions of a range of concentrations were padded onto 50/50 polyester/cotton sheeting in the same manner.

### TABLE 5

<table>
<thead>
<tr>
<th>Retardant</th>
<th>Conc.</th>
<th>Add-on</th>
<th>% P</th>
<th>Efficiency</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrovatex CP</td>
<td>55</td>
<td>8.2</td>
<td>1.17</td>
<td>21</td>
<td>564</td>
</tr>
<tr>
<td>Do.</td>
<td>45</td>
<td>8.0</td>
<td>1.19</td>
<td>27</td>
<td>562</td>
</tr>
<tr>
<td>Do.</td>
<td>35</td>
<td>8.4</td>
<td>1.19</td>
<td>38</td>
<td>560</td>
</tr>
<tr>
<td>Do.</td>
<td>30</td>
<td>7.2</td>
<td>1.11</td>
<td>42</td>
<td>558</td>
</tr>
<tr>
<td>Do.</td>
<td>25</td>
<td>7.0</td>
<td>1.09</td>
<td>46</td>
<td>556</td>
</tr>
<tr>
<td>Do.</td>
<td>20</td>
<td>5.7</td>
<td>0.75</td>
<td>47</td>
<td>553</td>
</tr>
<tr>
<td>Do.</td>
<td>15</td>
<td>4.6</td>
<td>0.70</td>
<td>51</td>
<td>550</td>
</tr>
<tr>
<td>MDMMP</td>
<td>40</td>
<td>9.6</td>
<td>1.44</td>
<td>35</td>
<td>549</td>
</tr>
<tr>
<td>Do.</td>
<td>35</td>
<td>7.7</td>
<td>1.49</td>
<td>35</td>
<td>549</td>
</tr>
<tr>
<td>Do.</td>
<td>32</td>
<td>8.3</td>
<td>1.33</td>
<td>39</td>
<td>548</td>
</tr>
</tbody>
</table>

Efficiency of Addition to 50/50% Cotton and MDMMP at Different Concentrations

From inspection of the last columns of Tables 6 and 7 it is immediately apparent that there is a very large difference of kind in the retention of phosphorus by Pyrovatex-treated versus MDMMP-treated fabrics. Over twice as much Pyrovatex-added phosphorus remains behind. This is interpreted as showing that the mode of flameproofing by MDMMP is such that a far higher percentage of the agent operates in the vapor phase when the fabric is subjected to burning. Evidently this different and wholly unexpected mode of action makes each amount of MDMMP somewhat more effective as a flame retardant than a comparable amount of Pyrovatex CP.
Though it is not desired for this invention to be bound by the limits of any mechanism, it appears probable that the phosphorus liberated into the vapor phase above the burning fabric diminishes the flammability of the vapors, reducing their tendency to engulf the whole fabric in flame. This effect seems particularly advantageous where, as in the present invention, a significant portion of the retardant released by the cotton seems to be in a form more capable of affording maximum protection to the polyester portion of the blend.

EXAMPLE 8

Samples of MDMP-modified cotton and 50/50 polyester/cotton sheeting were subjected to multiple washings in a home washing machine set on "hot," in the presence of 0.15 percent TIDE home detergent. The phosphorus analyses and LOI readings, before and after laundering, are shown in Table 8. It is evident that not only the phosphorus content but also the flame resistance remained constant, within the errors of measurement of the methods.

<table>
<thead>
<tr>
<th>TABLE 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Durability of NDMP-Treated Fabrics to Laundering</td>
</tr>
<tr>
<td>Percent Phosphorus</td>
</tr>
<tr>
<td>Fabric</td>
</tr>
<tr>
<td>Cotton: 100%</td>
</tr>
<tr>
<td>PEI/Cotton: 50/50</td>
</tr>
</tbody>
</table>

where R represents hydrogen or alkyl of up to six carbon atoms, X represents hydrogen or a methyl radical, and R₁ and R₂ represent methyl, ethyl or propyl radicals and thereafter curing the impregnated material under heating conditions.

2. The process of claim 1 wherein the cellulose textile material is a 50/50 polyester/cellulose blended textile fabric, X is hydrogen and R is hydrogen.

3. The process of claim 1 where the cellulose textile material is a polyester/cellulose blended textile material.

4. The process of claim 3 where R is hydrogen and X is hydrogen or a methyl radical.

5. The process of claim 3 where X is hydrogen.

6. The product produced by the product of claim 1.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,816,068 Dated June 11, 1974

Inventor(s) Joseph Rivlin

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

Column 1, line 61, "porpyl" should read --propyl--
Column 2, lines 51-52, "acrylamide methacrylamide"
should read --acrylamide or methacrylamide--
Column 5, line 51, "when ever" should read --whenever--
Column 6, line 29, in the fourth column, "1.50"
should read --15.0--
Column 6, line 57, "CO" should read --CP--
Column 9, line 25, "NDMP" should read --MDMP--

Signed and sealed this 29th day of October 1974.

(SEAL)

Attest:

McCoy M. Gibson Jr. C. Marshall Dann
Attesting Officer Commissioner of Patents
UNIVERSAL STATES PATENT OFFICE
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