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[72] Inventors John W. Benimate
Grenada;
Eileen K. Boylston, New Orleans; George L.
Drake, Jr., Metairie; Wilson A. Reeves,
Metairie, all of La.
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[54] IMPARTING FLAME RESISTANCE TO FIBROUS
TEXTILES FROM AN ALKALINE MEDIUM
12 Claims, No Drawings

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138.8 F

[56] References Cited
UNITED STATES PATENTS
2,772,188 11/1956 Reeves et al. ........................ 117/136
3,084,072 4/1963 Dealey .............................. 117/137 X
3,096,201 7/1963 Coates et al. ...................... 117/62.2
3,236,676 2/1966 Coates et al. ........................ 117/137 X
3,276,897 10/1966 Reeves et al. ...................... 117/62.2
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3,335,113 8/1967 Dundon ............................. 117/139.4 X
3,403,044 9/1968 Chance et al. ...................... 117/62.2
3,160,515 12/1964 Goldstein et al. ................. 117/62.1

OTHER REFERENCES
Reeves et al., "Flame Retardant Gels. Trial," Chemical
and Engineering News, Sept. 9, 1968, pp. 42 and 43

Primary Examiner—William D. Martin
Assistant Examiner—Harry J. Gwinnell
Attorneys—R. Hoffman and W. Bier

ABSTRACT: Flame resistance has been imparted to fibrous
textiles by application of an aqueous alkaline solution contain-
ing tris (hydroxymethyl) phosphine (heretofore referred to as
THP) and tetakis (hydroxymethyl) phosphonium hydroxide
(heretofore referred to as THPOH) followed by heat drying to
10-20 percent moisture content, and finally polymerizing the
phosphorous material in the fabric with ammonia vapor. The
invention provides an improved process for flameproofing tex-
tiles, particularly lightweight apparel fabrics whereby the
resulting treated textile materials are rendered flame resistant
with little or no loss in tearing strength and tensile strength or
undesirable change in hand. Cellulosic textiles treated by this
process retain their flame resistant properties after repeated
laundering.
IMPARTING FLAME RESISTANCE TO FIBROUS TEXTILES FROM AN ALKALINE MEDIUM

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This invention relates to an improved process for treating fibrous materials to render them flame resistant. Specifically, this invention relates to the treatment of textiles with an aqueous solution containing an equilibrium mixture of tri(hydroxyethyl)phosphine (hereinafter referred to as THP) and tetrakis(hydroxymethyl)phosphonium hydroxide (hereinafter referred to as THPOM), and said product polymerized on said fibrous materials with ammonia. The process is particularly useful in rendering cellulosic textiles flame resistant. The treated fabrics generally have an improved strength retention, good hand, and flame resistance which is durable to repeated laundering.

The textile treating solution suitable for use in this invention is a water solution containing THP and THPOM as an equilibrium mixture. The product can be prepared by any of several methods. The method of preparation is not a critical feature of this invention. The following two procedures are examples of suitable processes: (a) React phosphine with aqueous formaldehyde to form suitable metal salts or catalysts. This process is fully described in German Pat. No. 1,041,957; (b) React tetrakis(hydroxymethyl)phosphonium chloride, TIPC, with an equivolumar quantity of an organic or inorganic base. The pH of the final solution should be in the range of about 7.1 to 8. For convenience the equilibrium treating solution is referred to as THP. The methylol groups of THP react with ammonia to form water insoluble thermosetting polymers that contain both phosphorus and nitrogen.

In the prior art U.S. Pat. No. 2,772,188 discloses a process wherein flame resistance is imparted to cellulosic materials by treating them with condensation products of a tetrakis(hydroxymethyl)phosphonium salt, and a nitrogen compound containing at least two hydrogen atoms and/or methylol radicals, and subsequently insolubilizing the condensate in the treated cellulosic material with ammonia. Cellulosic fabrics treated by this process, especially lightweight apparel fabrics, are usually stiffened to various degrees, making the “hand” unacceptable. The process of the instant invention differs in that the need to prepare a precondensate for the application to the cellulosic textile before submitting to the ammonia cure is avoided (eliminated). Only the THP solution is applied before the ammonia cure step. Also, the hand of the lightweight fabric treated by the process of the instant invention is not altered, this is, there is no stiffness imparted.

In another patent (U.S. Pat. No. 3,236,676) a process is disclosed for treated cellulosic material with tetrakis(hydroxymethyl)phosphonium salt solution, the pH of which solution is adjusted to about from 3 to 9.5, with a preferred limit of 5.5 to 7.0, the material so treated is dried and heated to a temperature and for a time sufficient to fix the THP salt in the material, then the material is treated with ammonia to produce a substantially insoluble polymer. A preferred time and temperature therein disclosed is 10 minutes employing the range of about from 120° to 130° C.

In accordance with the process of U.S. Pat. No. 3,236,676 the cellulosic material is impregnated and heat fixed at high temperature, or alternately at lower temperature for a longer time period, prior to the ammonia treating step in order to produce an insoluble polymer in the cellulosic material and render it flame resistant.

The process of the instant invention differs from the process of U.S. Pat. No. 3,236,676 in that once the cellulosic material is impregnated with the THP solution no heat fixing step is necessary prior to the ammonia curing step. The process of the instant invention requires only that the THP solution impregnated cellulosic material be dried at a low temperature to a residual moisture content of about 10 to 20 percent prior to the ammonia cure step.

It is therefore an object of the instant invention to provide an improved process for treating organic fibrous materials and more particularly cellulosic fibrous materials to render them substantially flame resistant.

A second object of this invention is to provide an improved process for flameproofing textiles, whereby said textiles are treated with an aqueous alkaline solution containing THP followed by heat drying to reduce the moisture content of the impregnated material to 10 to 20 percent and finally causing polymerization of the phosphorus material in the fabric with ammonia.

A third object of this invention is to provide a treatment which does not require high temperature or prolonged lower temperature heat fixing of the impregnated material prior to the ammonia treating step.

A fourth object of the invention is to provide an improved process for flameproofing very lightweight cellulosic fabrics used in apparel garments, whereby the resulting treated textile fabrics are made durably flame retardant and undergo substantially no reduction in tear strength or tensile strength and no undesirable change in hand.

Still another object of this invention is to provide a method of producing textiles which retain their improved flame retardant properties after frequent washings.

These and other objects of this invention will be apparent to those skilled in the art of making flame retardant cellulosic materials.

The procedure in accordance with the invention comprises the following steps:

1. A tri(hydroxymethyl)phosphine aqueous treating solution with a pH preferably in the range of 7.5 to 7.9 is prepared. The concentration of the treating solution can be varied depending on the amount of phosphorus-containing polymer that is desired in the final treated textile.

2. The cellulosic material is impregnated with the THP solution described above.

3. The impregnated cellulosic material is dried with moderate heat to a moisture content of about 10 percent to 20 percent.

4. The partially dried cellulosic material is then exposed to ammonia gas to form an insoluble polymer with the phosphonium reaction product within the fibrous cellulosic or other textile material. The ammonia treated material is then washed and dried.

In accordance with this invention, any fibrous material such as cotton, rayon, wool, paper, jute, ramie, wood, and certain blends can be treated, but the invention is particularly effective when applied to the treatment of fibrous cellulosic textiles.

A fibrous cellulosic textile is impregnated with the aqueous THP solution by padding, although other impregnating techniques may be used; the excess solution is removed by passing the textile through squeeze rolls, centrifuging, or other methods. The cellulosic material is then dried to a residual moisture content ranging from 10 to 20 percent. The drying temperature can vary from room temperature to 100°C, although 80° to 90°C is preferred. The drying time varies from one-half minute to very lightweight materials to 6 minutes for heavyweight or bulky materials. The moisture content of the dried cellulosic material is measured by a conventional moisture meter.

The dried impregnated cellulosic material is exposed to gaseous ammonia in an enclosed chamber to form an insoluble flame retardant polymer within the material. The chemical curing is carried out for a period of time sufficient to effect substantially complete polymerization and curing of the impregnated composition. In many instances, curing times within the range of 1 minute to 6 minutes have been found to be typical depending on the amount of resin add-on in the treated material, as well as the nature of the cellulosic material itself. The treated cellulosic materials are then washed and dried.

The cellulosic materials treated in accordance with the procedures which have been described above are found to be
durable flame retardant even after repeated launderings. Additionally, these materials are found to have a tear strength, tensile strength and hand substantially unchanged from those of untreated materials. Moreover, very lightweight cellulosic textile fabrics treated by this process are found to have the good properties mentioned above, particularly the retention of a good hand. Prior art methods utilizing a chemical cure operation in most instances have imparted undue stiffness to very lightweight materials.

To summarize, the instant invention discloses a process for imparting flame resistance to lightweight fibrous textiles, and the products obtained by said process, wherein the process is a series of steps comprising:

a. impregnating a fibrous textile selected from the group consisting of cotton, wool, paper, jute, rayon-cotton blend, and polyester-cotton blend with a THP solution having a pH of about 7.5 to 7.9 and from about 10 to 40 percent, to a wet pickup of about from 70 percent to 100 percent,

b. drying the wet impregnated fibrous textile to a moisture content of about from 10 percent to 20 percent,

c. treating the partially dried fibrous textile with a high concentration of ammonia gas in a suitable chamber for about from 2 to 6 minutes of time at room temperature, to deposit within and on the fibrous structure of the textile a polymerized phosphorus-containing substance which is relatively insoluble to common solvents, and

d. washing and drying the polymer-containing fibrous textile to remove unreacted substances to obtain a flame resistant product.

The following examples illustrate the methods of carrying out the invention but the invention is not restricted to these examples. Treated fabrics were tested by the standard methods of the American Society for Testing Materials, Philadelphia. Breaking strength was determined by the 1-inch strip method (ASTM Method 39–49), tearing strength by the Elmendorf method (ASTM Method D1424–57), and flame resistance by the standard vertical test (AATCC Test Method 34–1966NaOH to THPC employed in the examples is 1:1.

EXAMPLE 1
An aqueous solution containing 30 percent THP was prepared by slowly adding with continuous stirring a solution of 0.5 parts NaOH dissolved in 152 parts of water to 125 parts of an 80 percent THPC solution. The pH of the treating solution was 7.8. A piece of 8.5 oz. carded cotton sateen was impregnated with this solution and passed through squeeze rolls to give about a 75 percent wet pickup. The impregnated fabric was dried in an electrically heated forced air oven for 3 minutes at 85°C. The moisture content of the fabric after drying was about 15 percent. The fabric was then exposed to gaseous ammonia in an enclosed chamber for 6 minutes. The treated fabric was thoroughly washed in hot water and dried. The treated fabric had a weight increase of 16.1 percent and passed the standard vertical flame test with a char length of 4.2 inches. The treated fabric had a warp breaking strength of 143.8 pounds as compared to a warp breaking strength of 124.4 pounds for an untreated fabric. A 3-hour boil in an aqueous solution containing 0.2 percent anhydrous sodium carbonate and 0.5 percent soap, the treated fabric was still flame resistant passing the vertical flame test with a 3.5 inch char length. The hand of the treated fabric was excellent.

EXAMPLE 2
An aqueous solution containing 30 percent THP was prepared in the manner described in Example 1. A piece of 2.8 oz. 87×51 cotton gingham, a very lightweight apparel fabric, was impregnated with the solution and passed through squeeze rolls to give about a 100 percent wet pickup. The impregnated fabric was dried for 1 minute at 85°C. to a moisture content of about 15 percent. The fabric was then exposed to gaseous ammonia for 6 minutes then thoroughly washed in hot water and dried. The treated fabric had a weight increase of 17.4 percent and passed the standard vertical flame test with a char length of 4.4 inches. The treated fabric had a warp breaking strength of 47.9 pounds as compared to a warp breaking strength of 47.3 pounds for an untreated fabric. After a 3-hour boil in a soap-soda solution (described in Example 1) the treated fabric was still flame resistant passing the vertical flame test with a 4.2 inch char length. The hand of the fabric was very good.

EXAMPLE 3
An aqueous solution containing 30 percent THP was prepared in the manner described in Example 1. A piece of white napped cotton sheeting, a fabric commonly used for blankets, was impregnated with the solution and passed through squeeze rolls to give about a 110 percent wet pickup. The impregnated fabric was dried for 75 seconds at 85°C. to a moisture content of about 15 percent. The impregnated fabric was exposed to gaseous ammonia then thoroughly washed and dried. The treated fabric had a weight increase of 22 percent and passed the standard vertical flame test with a char length of 4.2 inches. The treated fabric had a warp breaking strength of 42.2 pounds as compared to a warp breaking strength of 30.9 pounds for an untreated fabric. After a 3-hour boil in a soap-soda solution (described in Example 1) the treated fabric was still flame resistant passing the vertical flame test with a 4.5 inch char length. The hand of the treated fabric was very good.

EXAMPLE 4
An aqueous solution containing 15 percent THP was prepared by slowly adding with continuous stirring a solution of 7 parts NaOH dissolved in 151 parts of water to 42 parts of an 80 percent THPC solution. The pH of the treating solution was 7.9. A piece of 8.5 oz. carded cotton sateen was impregnated with this solution and passed through squeeze rolls to give a wet pickup of 70 percent and processed according to the procedure described in Example 1. The treated fabric had a weight increase of 8.4 percent and passed the standard vertical flame test with a char length of 4.5 inches. After a 3-hour boil in soap-soda solution (described in Example 1) the treated fabric was still flame resistant passing the vertical flame test with a 3.8 inch char length. The phosphorous content of the treated fabric was 3.9 percent before and 3.5 percent after the soap-soda boil.

EXAMPLE 5
An aqueous solution containing 40 percent THP was prepared by slowly adding with continuous stirring a solution of 18.7 parts of NaOH dissolved in 68.5 parts of water to 11.8 parts of an 80 percent THPC solution. The pH of the treating solution was 7.9. A piece of 8.5 oz. carded cotton sateen was impregnated with this solution and passed through squeeze rolls to give about a wet pickup of 90 percent, and processed according to the procedure described in Example 1. The treated fabric had a weight increase of 24.1 percent and passed the standard vertical flame test with a char length of 4.6 inches. The warp breaking strength of the treated fabric was 156.8 pounds as compared to a warp breaking strength of 124.4 pounds for an untreated fabric.

EXAMPLE 6
A piece of 8.5 oz. carded cotton sateen was impregnated with a 30 percent THP solution described in Example 1 and processed according to the procedure described in Example 1 with the exception that the impregnated, dried fabric was exposed to gaseous ammonia for 2 minutes instead of 6 minutes. The treated fabric had a weight increase of 18.3 percent and passed the standard vertical flame test with a char length of 4.4 inches. After a 3-hour soap-soda boil, the treated fabric
was still flame resistant passing the vertical flame test with a 3.7 inch char length.

EXAMPLE 7

A piece of 2.8 oz. 87x51 cotton gingham, a very lightweight apparel fabric, was impregnated with a 30 percent THP solution described in Example 2 and processed according to the procedure described in Example 2. The treated fabric had a weight increase of 22.9 percent and passed the standard vertical flame test with a char length of 4.5 inches. The phosphorous content of the treated fabric was 5.3 percent. The treated fabric was washed 25 consecutive times in an agitation-type washing machine under normal wash settings for cottons using a commercial synthetic detergent. The treated fabric was still flame resistant after 25 home laundering cycles and passed the vertical flame test with a 3.4 inch char length. Phosphorous content of the treated fabric after 25 laundering cycles was 4.2 percent.

EXAMPLE 8

An aqueous solution containing 25 percent THP was prepared by slowly adding with continuous stirring a solution of 17.7 parts NaOH dissolved in 177.6 parts of water to 104.7 parts of an 80 percent THPC solution. The pH of the solution was 7.5. Samples of fibrous materials consisting of wool fabric, linen fabric, burlap fabric, rayon-cotton blend fabrics, and blotter paper were impregnated with this solution and passed through squeeze rolls to remove excess solution. The samples were dried at 85°C in an electrically heated forced air oven to reduce the moisture content to about 15 to 20 percent. The samples were exposed to gaseous ammonia and then washed thoroughly in hot water and dried. Data appears in Table I.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wet Pickup %</th>
<th>Drying Time (min.)</th>
<th>NH₃ Exposure time (min.)</th>
<th>Weight Gain %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wool</td>
<td>96.5</td>
<td>2</td>
<td>7</td>
<td>15.8</td>
</tr>
<tr>
<td>Linen</td>
<td>74.8</td>
<td>1</td>
<td>7</td>
<td>10.1</td>
</tr>
<tr>
<td>Burlap (jute)</td>
<td>75.0</td>
<td>2</td>
<td>7</td>
<td>12.5</td>
</tr>
<tr>
<td>Rayon-cotton</td>
<td>63.4</td>
<td>1</td>
<td>5</td>
<td>15.9</td>
</tr>
<tr>
<td>(50-50)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blotter paper</td>
<td>101</td>
<td>4</td>
<td>10</td>
<td>27.2</td>
</tr>
</tbody>
</table>

All treated samples were flame resistant and had good strength properties.

EXAMPLE 9

An aqueous solution containing 40 percent THP was prepared by slowly adding with continuous stirring a solution of 18.7 parts of NaOH dissolved in 68.5 parts of water to 111.8 parts of an 80 percent THPC solution. The pH of the treating solution was 7.9. A lightweight fibrous textile fabric consisting of polyester and cotton in a 50—50 ratio blend was impregnated with this solution and passed through squeeze rolls to remove excess solution. The sample was dried at 85°C in an electrically heated forced air oven to reduce the moisture content to about 15 to 20 percent. The sample was exposed to gaseous ammonia then washed thoroughly in hot water and dried. The treated fabric had a weight increase of 23.5 percent and passed the standard vertical flame test with a char length of 5.3 inches. After a 3-hour boil in soap-soda solution (described in Example 1) the treated fabric was still flame resistant, passing the vertical flame test with a 5.2 inch char length.

We claim:
1. A process for imparting flame resistance to a lightweight, fibrous, cellulose-containing or wool textile material, said process consisting of:
   a. impregnating the textile material with a solution having a pH of about from 7.5 to 7.9 and a total monomeric tris(hydroxymethyl)phosphine content of about from 10 percent to 40 percent, to a wet pickup of about from 70 percent to 100 percent;
   b. drying the thus-impregnated textile material to a moisture content of about from 10 percent to 20 percent;
   c. treating the thus-dried textile material with a high concentration of ammonia gas for about from 2 to 6 minutes at room temperature to deposit within and on the fibrous structure of the textile material a polymerized phosphorus-containing material; and
   d. washing and drying the resulting polymer-containing textile material to remove unreacted substances.
2. The process of claim 1 wherein the textile material is a cellulose-containing material.
3. The process of claim 2 wherein the cellulose-containing material is cotton, paper, jute, rayon-cotton blend, or polyester-cotton blend.
4. The process of claim 3 wherein the textile material is wool.
5. The process of claim 3 wherein the cellulose-containing material is cotton.
6. The process of claim 3 wherein the cellulose-containing material is paper.
7. The process of claim 3 wherein the cellulose-containing material is jute.
8. The process of claim 3 wherein the cellulose-containing material is rayon-cotton blend.
9. The process of claim 3 wherein the cellulose-containing material is polyester-cotton blend.
10. The product produced by the process of claim 2.
11. The product produced by the process of claim 4.
12. The product produced by the process of claim 5.