FLAME RETARDANT FIBROUS MATERIAL HAVING IMPROVED DIMENSIONAL STABILITY

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ABSTRACT

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

\[
\begin{align*}
\text{HO} & \quad \text{R}^1 \quad \text{OR}^2 \\
\end{align*}
\]

wherein \( R^1 \) represents a divalent organic radical such as methylene or ethylene, \( X \) represents a covalent bond, \(-\text{POOR}^2-\) or \(-\text{CO-}\); and \( R^2 \) and \( R^3 \) represent a monovalent radical such as hydrogen or methyl. Mixtures of these phosphonic acids with other phosphonic acids such as methyl phosphonic acid can give particularly advantageous results. Durability of the flame retardancy to repeated hard water washing may be improved through a subsequent treatment with additional cyanamide, with N-methylol compounds, or by methylation with diazomethane. Durable press properties of cellulosic textiles are also improved by the subsequent treatment with additional cyanamide. A particularly high degree of flame retardancy is imparted to mercerized cotton cloth.

21 Claims, No Drawings
FLAME RETARDANT FIBROUS MATERIAL HAVING IMPROVED DIMENSIONAL STABILITY

CROSS REFERENCE TO RELATED APPLICATIONS

This is a continuation in part of copending application Ser. No. 259,350, filed June 2, 1972, now abandoned, which in turn is a continuation of application Ser. No. 153,094, filed June 14, 1971, now abandoned, which in turn is a continuation of Ser. No. 862,509, filed Sept. 30, 1969, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to flame retardant fiber-containing material having improved dimensional stability 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 has inhibited their wider use in certain instances. A great number of flame retardants have been proposed for use with cellulosic 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 cellulosic 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 "Cyamidine-Based Durable Flame-Retardant Finish for Cotton," Textile Research Journal, March 1968, pp. 256-266. This article describes imparting flame retardancy to cellulosic 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 Patents 15,357 and 18,253, and Schifferm et al. in Faserforsch u. Textiltech., 14, (9), 375-86 (1963) describes 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.

Also, many flame retardants are incompatible with crease-proofing agents commonly employed for cellulosic materials; in the past this limitation has discouraged use of flame retardants in conjunction with a crease-proofing operation so as to yield a cellulosic textile material which is wrinkle resistant and dimensionally stable as well as flame retardant.

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 cellulosic textile material such as color, hand and susceptibility to dyeing.

SUMMARY OF THE INVENTION

Accordingly, a primary object of the present invention is to render fiber-containing material flame retardant and impart improved dimensional stability 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 dimensional stability and flame retardancy to cellulosic textile materials which flame retardancy is durable and resistant to multiple household launderings in general and especially in hard water.

Another object is to provide an improved cellulose flame-retarding process requiring only a relatively small add-on or amount of flame retardants.

A still further object is to provide an improved process for rendering cellulose textile material flame retardant which does not adversely affect the other properties of the material. Another object of the present invention is to provide a cellulose flame-retarding process having improved efficiencies of reaction between the flame retardants and the cellulosic material.

Yet another object is to provide an improved process for rendering cellulose textile material both flame retardant and wrinkle resistant, with improved dimensional stability.

Yet another object is to provide by these processes flame resistant fibrous products having improved dimensional stability.

Additional objects and advantages of the present invention will be apparent to those skilled in the art by reference to the following summary of the characteristics features of the present invention and the subsequent description of the preferred embodiments:

In accordance with a primary aspect of the present invention, a process is provided for rendering or imparting flame retardancy and improved dimensional stability to cellulosic and wool fiber-containing material comprising contacting the material with cyanamide and at least one phosphonic acid represented by the structural formula:

\[
\begin{align*}
\text{O} & \quad \text{OH} \\
\text{H} & \quad \text{OXRP}^- & \quad \text{OR}^2
\end{align*}
\]

to deposit or fix on the material a flame-retarding and dimensional stability-improving amount of the phosphonic acid with cyanamide. In the above formula $R^1$ represents a divalent organic radical such as lower alkylene, lower alkylidene or lower alkylidyne; $X$ represents a covalent bond, $-\text{POOR}^2-$ or $-\text{CO}-;$ and $R^2$ and $R^3$ represent the same or different monovalent radical such as hydrogen or lower alkyl.

A central feature of the present invention is the discovery that cyanamide and the above described phosphonic acids can impart durable, hard water wash-resistant, flame retardancy to cellulosic fiber-containing material, particularly mercerized cotton cloth, while concurrently improving dimensional stability. In addition, the fire retardancy-imparting systems of the present invention have improved efficiencies in terms of efficiency of reaction between the flame retardants and the cellulose, and in terms of fire retardancy per unit add-on of phosphorus.

In accordance with another aspect of the present invention, the fibrous material rendered flame-retardant as indicated above is subsequently treated to improve the durability of flame retardancy to repeated hard water washing by contacting the material with additional cyanamide. Also, this subsequent treatment with
additional cyanamide has been found to improve durable press properties of cellulosic textile material.

In accordance with yet another aspect of the present invention, durability of the flame retardancy of the fibrous material to repeated hard water washing is improved by methylation of the acid form of the phosphonic acid residue on the fibrous material. In a preferred embodiment described below, such methylation is accomplished by contacting the fibrous material with diazomethane.

In accordance with another aspect of the present invention, the fibrous material rendered flame retardant by the phosphonic acid and cyanamide as indicated above is subsequently treated to improve the durability of flame retardancy to repeated hard water washing by contacting the material with at least one water-soluble compound possessing reactive N-methylol groups, and thereafter curing the material to fix or insolubilize the compound on the material.

Other aspects and advantages of the present invention will be apparent to one skilled in the art from the following:

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

As indicated above, cyanamide (HNCHN or H₂N-CN), also known as carbodiimide, is used along with certain phosphonic acids to impart the wash-resistant flame retardancy to the fibrous or fiber-containing material.

The phosphonic acids which may be suitable can be represented by the general structural formula:

\[
\begin{align*}
O & \quad \text{R}^1 \\
\text{HOX} & \quad \text{R}^2
\end{align*}
\]

where \(\text{R}^1\) represents a divalent organic radical such as lower alkylene, lower alkylidene or lower alkylidyn; \(\text{X}\) represents a covalent bond, \(-\text{POOR}^2\) or \(-\text{CO}^1;\) and \(\text{R}^2\) and \(\text{R}^2\) represent the same or different monovalent radicals 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 above-described structural formula and which may be used according to the process of the present invention include hydroxymethyl phosphonic acid, hydroxymethyl phosphonic acid monoalkyl ester, hydroxyethyl phosphonic acid, hydroxyethyl phosphonic acid mono-t-butyl ester, methylene dihydrophosphonic acid, ethylenediophosphonic acid, tetramethylene dihydrophosphonic acid, carboxyethyl phosphonic acid, carboxyethyl phosphonic acid and carboxyethyl phosphonic acid monoalkyl ester. Mixtures of two or more of the phosphonic acids may be used if desired.

Mixtures of at least one of the above phosphonic acids with other substituted phosphonic acids are also contemplated. Such other substituted phosphonic acids may include lower alkyl phosphonic acids such as methyl, ethyl, isopropyl and t-butyl phosphonic acids, lower alkoxyalkyl phosphonic acids such as methoxymethyl phosphonic acid, halosubstituted lower alkyl phosphonic acids such as chloromethyl and bromoethyl phosphonic acids, as well as vinyl phosphonic acid, and mono lower alkyl esters thereof as ethyl phosphonic acid monoethyl ester and methyl phosphonic acid monomethyl ester.

The more preferred single phosphonic acid systems are hydroxymethyl phosphonic acid, hydroxyethyl phosphonic acid, ethylene dihydrophosphonic acid and carboxyethyl phosphonic acid; and the more preferred mixed phosphonic acid systems are a mixture of at least one of the above with methyl phosphonic acid, insofar as these particular systems have been found to give or impart the most durable flame retardancy to the fibrous materials, while concurrently improving dimensional stability.

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

The cellulosic or wool fiber-containing material which may be treated according to the present invention are generally any of those which have been previously employed in conjunction with known flame retardants. The fiber-containing or textile material can have a wide variety of physical forms and can be fibers, filaments, yarns, threads, and particularly woven and non-woven cloth. The cellulosic fiber material can be cotton, flax, linen, hemp, or regenerated cellulose such as rayon (e.g., viscose 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 66,6) polyester (e.g., polyethylene terephthalate), acrylics (e.g., polyacrylonitrile), polyolefins (e.g., polypropylene), polyvinyl chloride, polyvinylidene 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 and improved dimensional stability can be imparted to fibrous material by contacting or impregnating the material with the phosphonic acid and cyanamide under widely varying conditions of temperature and pH. Yet, durable, i.e., wash resistant, flame retardancy and improved dimensional stability are imparted by 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 and to improve dimensional stability, 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 6.0. Naturally, in the latter case the pH of the pad bath may be quite different from 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 hydroxymethyl phosphonic acid, or ammonium hydroxymethyl 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 and improving dimensional stability 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 1:2 to 3:1, and most preferably 1:2 to 2:1. 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 and is conducted 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 cellulosic 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 and improved dimensional stability. 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 hydroxymethyl phosphonic acid and monomethyl ester, or mono-d-ammonium hydroxymethyl phosphonic acid. Another method involves thermally decomposable esters which upon heating yield the above-described phosphonic acids can be employed. A third 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.

The fibrous material rendered flame retardant as indicated above may be subsequently processed to improve durability of the flame retardancy by treating the material with additional cyanamide, or diazomethane (methylamine), or water-soluble compounds possessing reactive N-methyl 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 dichloro 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.,
And generally, for a given phosphonic acid the order of flame retardant efficiency (char length) is acid &gt; monomethyl ester &gt; calcium salt. It is thought that this subsequent treatment with cyanamide causes further reaction of the phosphonic acid residue with the fiber-containing material, which further reaction lowers ionicity and therefore lowers 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.

In the case of cellulosic textile materials, the further reaction of the phosphonic acid by the cyanamide is thought to be in the nature of a crosslinking reaction insofar as, surprisingly, dimensional stability or shrinkage control, durable press properties (wrinkle resistance), and overall shape retention and wash/wear properties are also demonstrably improved.

When cyanamide is used in this 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 soured fibrous material is then contacted or impregnated with cyanamide as generally indicated above for the initial flame retardancy treatment. For example, the material may be contacted with a solution of cyanamide. Examples of suitable solvents include methanol, ethanol, dioxane and, most preferably, water. The cyanamide is present in the solution or pad bath in an amount sufficient to correct flame retardancy (or reduce ionicity) as discussed above. For example, the concentration of cyanamide in solution may range from about 1 to 50 weight percent, and more typically, from 10 to 20 weight percent. Higher or lower concentrations may be used if desired.

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 preferably from 20° to 150°C. The material with the cyanamide is then heated in order to further react the phosphonic acid residue on the fibrous material. Broadly, any temperature can be employed above which the phosphonic acid residue is further reacted with the material by the cyanamide and below which undesirable thermal degradation of the material begins, and generally from about 50° to 400°C, preferably from 100° to 300°C, and most preferably from 20° 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.

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

When diazomethane is 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 soured fibrous material is contacted with diazomethane as generally indicated above for subsequent treatment with cyanamide. For example, the fibrous material may be contacted, e.g., immersed, in an ether solution of diazomethane for about 1 to 2 hours at 0° to 30°C. Such treatment with diazomethane is thought to bring about methylation of the phosphonic acid residue, thus reducing ionicity and calcium pickup (increasing resistance to ion exchange), and improving flame retardancy, especially durable flame retardancy. Other methylating agents such as orthoesters, e.g., trimethyl orthoformate, may also be used to bring about methylation of the phosphonic acid residue. These methylating agents are well known per se and their production or derivation is not part of the present invention.

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 soured fibrous material is contacted with the N-methylol compound and is thereafter cured 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 mono-, di-, tri-, tetra-, penta-, or hexa-methylol 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 the kind include Aerotex 23, an alkylated melamine-formaldehyde precondensate, Aerotex M-3, a dimethoxymethyl hydroxy-methyl 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 Reslloon 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 soluble 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-acting 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 in the fiber 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 in 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°C 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°C 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°C to 300°C, and most preferably from 120°C 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 dihydroxy ethylene urea have been found not to increase significantly the durability to flame retardancy.

If desired, more than one subsequent treatment with additional cyanamide or diazomethane or N-methylol compound may be used. Combinations of subsequent treatments with diazomethane and N-methylol compound and retreatments with cyanamide may also be used if desired.

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 designed 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 hydroxethyl phosphonic acid (HEPA) or HEPA-methyl phosphonic acid (MPA) acid mixture (runs 1 and 2, respectively) in aqueous solutions as shown in TABLE 1. Comparison run 3 was also made using cyanamide and methyl phosphonic acid (MPA) in aqueous solutions as shown in TABLE 1.

For each run, a weighed piece of cotton twill measuring 12 x 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 the 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 in the rinses. In this example, the term "hard water" refers to Irvine, Calif., 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) procedure 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. Dimensional stability was determined by measuring percent shrinkage in the warp direction.

As may be seen from TABLE I, the HEPA:cyanamide system (run 1) imparted a flame retardance durable for at least 40 washes, and vastly improved dimensional stability at 50 washes as compared to the MPA:cyanamide system (run 3) or the untreated control.

The mixed acid system, HEPA-MPA: cyanamide (run 2), imparted a flame retardance durable for at least 50 washes, and improved dimensional control to a degree similar to that obtained in run 1 with HEPA.

| TABLE I
<p>| THE EFFECT OF PHOSPHONIC ACID/CYANAMIDE SYSTEMS ON FLAME RETARDANCE AND DIMENSIONAL STABILITY |</p>
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Acid Used</th>
<th>Cyanamide in Bath (%)</th>
<th>Acid:Cyanamide Ratio</th>
<th>Add-on Acid (%)</th>
<th>P (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HEPA</td>
<td>16</td>
<td>1:2</td>
<td>18.5</td>
<td>2.88</td>
<td>0.95</td>
</tr>
<tr>
<td>2</td>
<td>HEPA-MPA</td>
<td>16</td>
<td>(0.5-0.5):2</td>
<td>18.4</td>
<td>2.76</td>
<td>0.91</td>
</tr>
<tr>
<td>3</td>
<td>MPA</td>
<td>16</td>
<td>1:2</td>
<td>17.7</td>
<td>3.28</td>
<td>0.61</td>
</tr>
</tbody>
</table>
TABLE I -Continued

THE EFFECT OF PHOSPHONIC ACID/CYANAMIDE SYSTEMS ON FLAME RETARDANCE AND DIMENSIONAL STABILITY

<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>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2% (-)</td>
<td>3.5% (-)</td>
<td>3% (-)</td>
<td>7% (-)</td>
<td>BEL</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>1.5% (+)</td>
<td>2 (-)</td>
<td>2% (+)</td>
<td>2% (+)</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>1% (+)</td>
<td>2 (-)</td>
<td>2% (+)</td>
<td>2% (+)</td>
<td>1</td>
<td>5</td>
</tr>
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</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 Velsamine 3800 polyethylene softener.

EXAMPLE II

This example illustrates certain embodiments of the present invention employing cyanamide with hydroxymethyl phosphonic acid (HMPA) alone (run 4) and admixed with certain other phosphonic acids (runs 5 to 8) or orthophosphoric acid (run 9) and gives a comparison to the use of cyanamide with such other phosphonic acids alone (runs 10 to 13) or vinyl phosphonic acid (VPA) alone (run 14).

The procedure of Example I was repeated employing the same quantities of the same ingredients and the same times, procedures and conditions except with the various systems shown in TABLE II which includes data and test results for the runs.

As may be seen from TABLE II, runs 4 to 9 utilizing systems of the present invention imparted flame retardance and improved dimensional stability to the cotton fabric.

TABLE II

THE EFFECT OF PHOSPHONIC ACID/CYANAMIDE SYSTEMS ON FLAME RETARDANCE AND DIMENSIONAL STABILITY

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Acid Mixture</th>
<th>Add-On (%)</th>
<th>P (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>HMPA</td>
<td>18.9</td>
<td>3.04</td>
<td>0.53</td>
</tr>
<tr>
<td>5</td>
<td>MPA-HMPA</td>
<td>15.6</td>
<td>2.88</td>
<td>0.73</td>
</tr>
<tr>
<td>6</td>
<td>EPA-HMPA</td>
<td>15.4</td>
<td>2.61</td>
<td>0.71</td>
</tr>
<tr>
<td>7</td>
<td>CMPA-HMPA</td>
<td>16.7</td>
<td>2.74</td>
<td>0.93</td>
</tr>
<tr>
<td>8</td>
<td>MMPA-HMPA</td>
<td>16.7</td>
<td>2.62</td>
<td>0.75</td>
</tr>
<tr>
<td>9</td>
<td>EDPA-HMPA</td>
<td>18.4</td>
<td>3.09</td>
<td>0.76</td>
</tr>
<tr>
<td>10</td>
<td>Li,HPO₄-HMPA</td>
<td>20.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>MPA</td>
<td>17.7</td>
<td>3.28</td>
<td>0.61</td>
</tr>
<tr>
<td>12</td>
<td>EPA</td>
<td>16.3</td>
<td>2.71</td>
<td>0.49</td>
</tr>
<tr>
<td>13</td>
<td>CMPA</td>
<td>2.61</td>
<td>1.34</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>VPA</td>
<td>17.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

EXAMPLE III

This example illustrates the process of the present invention employing cyanamide and carboxymethyl phosphonic acid (runs 15 and 16) or carboxyethyl phosphonic acid (runs 17 and 18) in solutions of varying acid: cyanamide ratio. The procedure of Example I was repeated employing the same quantities of the same ingredients and the same times, procedures and conditions except with the various systems shown in TABLE III which includes data and test results for the runs; and with the exception that, instead of Irvine water, Menlo Park, Calif., water having a hardness equivalent to 32 ppm calcium carbonate was used in the wash and rinse cycles.

As may be seen from TABLE III, runs 15 to 18 utilizing systems of the present invention imparted flame retardance and improved dimensional stability to the cotton fabric.

TABLE III

EFFECT OF CARBOXY PHOSPHONIC ACIDS/CYANAMIDE SYSTEMS ON FLAME RETARDANCE AND DIMENSIONAL STABILITY

<table>
<thead>
<tr>
<th>Note</th>
<th>C₆ Acid</th>
<th>HOOC CH₂PO(OH)₂</th>
<th>C₇ Acid</th>
<th>HOOCCH₂CH₂PO(OH)₂</th>
<th>Acid % in Bath</th>
<th>Acid/Cyanamide Ratio</th>
<th>Add-On on</th>
<th>% P One Wash</th>
<th>% N One Wash</th>
<th>% P Fifty Washes</th>
<th>% N Fifty Washes</th>
<th>Flame Retardance</th>
<th>Shrinkage % Fifty Washes</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>C₆</td>
<td>25</td>
<td>1:2</td>
<td>19.0 2.40 1.04 2.20 1.13 2(+3) 3(-) 3(-)</td>
<td>7.0 0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>C₆</td>
<td>25</td>
<td>1:3</td>
<td>19.6 2.46 2.04 2.36 1.64 2(+3) 2(+3) 2(+3)</td>
<td>6.0 0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>C₆</td>
<td>25</td>
<td>1:2</td>
<td>16.0 1.80 0.03 1.93 0.86 2(-) 2(-) 2(-)</td>
<td>15.0 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>C₆</td>
<td>25</td>
<td>1:3</td>
<td>15.9 1.93 0.86 2(-) 2(-) 2(-) 2(-) 2(-)</td>
<td>10.0 1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Untreated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Twill—Control</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
EXAMPLE IV

This example illustrates certain preferred embodiments of the present invention employing cyanamide with a mixture of hydroxyethyl phosphonic acid (HEPA) and methyl phosphonic acid (MPA) 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 unmercerized flannel cloth (Barium No. - 100) was used for run 19 and mercerized flannel cloth (Barium No. - 154) was used in run 20. Also, Menlo Park water having a hardness equivalent of 24 ppm calcium carbonate was used instead of the Irvine water. The results are recorded in TABLE IV.

As may be seen from TABLE IV, the flame retardancy for the mercerized flannel (Run 20) was durable for at least 50 washes.

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 retardant-reacting 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 V

This example illustrates certain preferred embodiments of the present invention employing cyanamide and hydroxyethyl phosphonic acid with one or more diazomethane (CHN$_2$) retreatments to improve durable flame retardance.

The procedure of Example V is repeated employing the same quantities of the same ingredients and the same times, procedures and conditions with the exception that diazomethane retreatments are used on the fabric samples instead of the cyanamide retreatment. The diazomethane retreatment consists of soaking the soiled fabric sample in an ether solution containing about 2.5 weight percent diazomethane for approximately 12 hours at about 25°C. Improvement in durability of flame retardancy is observed.

EXAMPLES VII-VIII

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

The procedure of Example I (run 1) is repeated employing 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 and improved dimensional stability are observed for each of the treated fabrics.

**EXAMPLE IX**

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 the hydroxyethyl phosphonic acid is replaced by ethylene diphosphonic acid, with the pad bath containing 10% ethylene diphosphonic acid, 18% methyl phosphonic acid and 19% cyanamide. Flame retardance and improved dimensional stability for the treated fabric are observed.

**EXAMPLE X**

This example illustrates the present invention when cyanamide, methyl phosphonic acid and hydroxyethyl phosphonic acid are applied to a fabric from a pad bath which also contains ammonium hydroxide to increase the otherwise autogenous pH of the path to a pH of 3.

The procedure of Example IV (run 20) was repeated employing the same quantities of the same ingredients and the same times, procedures and conditions with the exception that the pH of the pad bath in the run was adjusted to a pH of 3 with ammonium hydroxide, and the fabric sample was washed at about 65°C for 8 minutes and cured at about 160°C for 5 minutes, and reactant ratios were as shown in TABLE X. The resulting flame retardance values are also shown in TABLE X.

As may be seen from TABLE X, good flame retardancy was achieved.

**TABLE XI**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>N-methyl Compound in Bath (%)</th>
<th>Flame Retardance</th>
<th>Analysis (One Wash) % N</th>
<th>Iodine (One Wash) mg/gm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none (control)</td>
<td>1% (+)</td>
<td>2 (+)</td>
<td>1.17</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>1¼ (+)</td>
<td>1¼ (+)</td>
<td>5.22</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>1¼ (+)</td>
<td>1¼ (+)</td>
<td>6.30</td>
</tr>
<tr>
<td>4</td>
<td>7.5</td>
<td>1¼ (+)</td>
<td>1¼ (+)</td>
<td>0.82</td>
</tr>
</tbody>
</table>

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 imparting flame retardance and improved dimensional stability to cellulosic and wool fiber-containing material, which process comprises contacting the material with cyanamide and at least one phosphonic acid represented by the structural formula:

   \[
   HOXRP \rightarrow OH \quad OR\quad OH
   \]
wherein $R^1$ represents a divalent radical selected from the group consisting of lower alkylene, lower alkylidene and lower alkylidyne; $X$ represents a covalent bond,

$$\begin{align*}
&\text{O} \\
&\text{P} - \text{OR}^2 \\
&\text{OH} \\
&\text{OR}^1
\end{align*}$$

or $-\text{CO}-$, and wherein $R^2$ and $R^3$ represent monovalent radicals selected from the group consisting of hydrogen and lower alkyl; to deposit on the material a flame retarding and dimensional stability-improving amount of the phosphonic acid with cyanamide.

2. A process according to claim 1 wherein the material is cellulosic and is contacted with hydroxyethyl phosphonic acid, ethylene diphosphonic acid, carboxymethyl phosphonic acid, or a mixture of at least one thereof with methyl phosphonic acid.

3. A process according to claim 1 for imparting flame retardance and improved dimensional stability to cellulosic fiber-containing material, which process comprises contacting and fixing on the material with cyanamide a flame-retarding and dimensional stability-improving amount of at least one phosphonic acid represented by the structural formula:

$$\begin{align*}
&\text{O} \\
&\text{P} - \text{OH} \\
&\text{OR}^1 \\
&\text{R}^1 \text{OR}^2
\end{align*}$$

wherein $R^1$ represents a divalent radical selected from the group consisting of methylene and ethylene; $X$ represents a covalent bond or

$$\begin{align*}
&\text{O} \\
&\text{P} - \text{CO} - \\
&\text{OR}^2
\end{align*}$$

and wherein $R^2$ represents a monovalent radical selected from the group consisting of hydrogen and methyl; and wherein during contacting the molar ratio of phosphonic acid to cyanamide is from 1:10 to 10:1.

4. A process according to claim 3 wherein the material is fixed by heating the material for a period of time and at a temperature at least sufficient to give an add-on of from 1 to 30%; wherein the phosphonic acid and cyanamide are in solution when contacted with the material; wherein the pH at fixation is less than 2.5; and wherein the cellulosic fiber-containing material is cotton cloth.

5. A process according to claim 3 wherein the cellulosic fiber-containing material is fixed by contacting the material with the phosphonic acid and cyanamide and then heating the material at a temperature between about 100°C and 300°C.

6. A process for imparting flame retardance and improved dimensional stability to cellulosic textile material comprising in sequence the steps of:

I. contacting the material with an aqueous solution of cyanamide and at least one phosphonic acid selected from the group consisting of ethylene diphosphonic acid, carboxymethyl phosphonic acid and hydroxyethyl phosphonic acid, wherein the molar ratio of phosphonic acid:cyanamide is 1:10 to 10:1 and

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

7. A process according to claim 6 for imparting durable flame retardance and improved dimensional stability to cellulosic fiber-containing textile material, which process comprises in sequence the steps of:

I. contacting the material with an aqueous mixture of cyanamide with the phosphonic acid wherein the molar ratio of phosphonic acid:cyanamide is 1:10 to 10:1; and,

II. fixing the retardancy in the material at a pH less than 1.5 by heating the material until a dimensional stability-improving add-on of between about 1 and 30% is achieved and the flame retardancy becomes durable to at least 30 hard water washes.

8. A process according to claim 7 wherein the cellulosic material is mercerized cotton cloth and the aqueous solution further includes methyl phosphonic acid, and the flame retardancy is durable to at least 50 hard water washes.

9. A process according to claim 7 wherein the aqueous mixture of cyanamide and phosphonic acid further contains ammonium hydroxide, and an ammonium salt of the phosphonic acid is deposited on the textile material.

10. A process for imparting durable flame retardance and improved dimensional stability to cellulosic and wool fiber-containing material, which process comprises the steps of:

I. contacting the material with cyanamide and at least one phosphonic acid represented by the structural formula:

$$\begin{align*}
&\text{O} \\
&\text{P} - \text{OH} \\
&\text{OR}^1 \\
&\text{R}^1 \text{OR}^2
\end{align*}$$

wherein $R^1$ represents a divalent radical selected from the group consisting of lower alkylene, lower alkylidene and lower alkylidyne; $X$ represents a covalent bond,

$$\begin{align*}
&\text{O} \\
&\text{P} - \text{CO} - \\
&\text{OR}^2
\end{align*}$$

and wherein $R^2$ and $R^3$ represent monovalent radicals selected from the group consisting of hydrogen and lower alkyl; to deposit on the material a flame retarding and dimensional stability-improving amount of the phosphonic acid with cyanamide; and subsequently

II. contacting the material with at least one member selected from the group consisting of cyanamide, diazomethane and water-soluble compounds possessing reactive N-methylol groups, in an amount sufficient to improve the durability of the flame retardancy of the material to repeated hard water washing.

11. A process according to claim 10 wherein in step (I) the phosphonic acid and the cyanamide are in solution when contacted with the material and the molar ratio of phosphonic acid to cyanamide is from 1:10 to 10:1; and in step (II) the cyanamide is in solution when contacted with the material, and the material is thereafter heated to give a total add-on of from 1 to 30%.
A process for rendering cellulosic textile material durably flame retardant, dimensionally stable and wrinkle resistant, which process comprises the steps of:

I. contacting the material with an aqueous mixture of cyanamide and at least one phosphonic acid selected from the group consisting of ethylene di-phosphonic acid, carboxymethyl phosphonic acid and hydroxyethyl phosphonic acid, wherein the molar ratio of phosphonic acid:cyanamide is 1:10 to 10:1, and

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

III. contacting the material with an aqueous solution of cyanamide and heating the material to improve the durability of the flame retardancy, dimensional stability, and durable press properties of the material

A process according to claim 12 for rendering cotton fiber-containing textile material durably flame retardant and for simultaneously improving the dimensional stability and durable press properties of the textile material, which process comprises in sequence the steps of:

I. contacting the material with an aqueous solution of cyanamide with the phosphonic acid wherein the molar ratio of phosphonic acid:cyanamide is 1:10 to 10:1,

II. 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 30 hard water washes; and

III. regenerating an acid form of fixed phosphonic acid residue on the material and then contacting the material with an aqueous solution of the N-methylol compound, and heating the material to improve the durability of the flame retardancy to at least 50 hard water washes, and to improve dimensional stability, and durable press properties of the material.

A process for rendering cellulosic textile material durably flame retardant, dimensionally stable and wrinkle resistant, which process comprises the steps of:

I. contacting the material with an aqueous solution of cyanamide and at least one phosphonic acid selected from the group consisting of ethylene di-phosphonic acid, carboxymethyl phosphonic acid and hydroxyethyl phosphonic acid, wherein the molar ratio of the phosphonic acid:cyanamide is 1:10 to 10:1, and

II. 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

III. contacting the material with an aqueous solution of at least one water-soluble compound possessing reactive N-methylol groups and curing the material to improve the durability of the flame retardancy of the material.

A process according to claim 14 for rendering cotton fiber-containing textile material durably flame retardant and for simultaneously improving the dimensional stability and durable press properties of the textile material, which process comprises in sequence the steps of:

I. contacting the material with an aqueous mixture of cyanamide with the phosphonic acid wherein the molar ratio of phosphonic acid:cyanamide is 1:10 to 10:1,

II. 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 30 hard water washes.

A process according to claim 15 wherein the textile material is mercerized cotton cloth, and wherein the aqueous mixture of cyanamide and phosphonic acid further contains ammonium hydroxide, and an ammonium salt of the phosphonic acid is deposited on the textile material.

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

A durably flame retardant material having improved dimensional stability produced according to the process of claim 7.

A durably flame retardant material having improved dimensional stability produced according to the process of claim 10.

A durably flame retardant and wrinkle resistant material produced according to the process of claim 13.

A durably flame retardant material having improved dimensional stability produced according to the process of claim 15.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,892,906 Dated July 1, 1975

Inventor(s) Ronald Swidler et al.

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

IN THE CLAIMS

Column 18, line 45, delete the formula and insert

\[ \frac{0}{P} \frac{1}{OR^3} \]

Signed and Sealed this fourteenth Day of October 1975

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks
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[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks