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[54] PRODUCTION OF TEXTILE MATERIALS WITH IMPROVED FLAME RETARDANCE

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Related U.S. Application Data

[60] Division of Ser. No. 307,796, Nov. 20, 1972, Pat. No. 3,827,907, which is a continuation-in-part of Ser. No. 220,453, Jan. 24, 1972, abandoned.

[52] **U.S. Cl.** .... **260/231 A;** 8/116 P; 117/136
[51] **Int. Cl.** **C08b 11/04;** C08b 27/70
[58] **Field of Search** .... 117/136, 138; 8/116 P; 260/231 A

[56] **References Cited**

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[57] ABSTRACT

The flame retardant properties of textile materials which have been reacted with phosphorus-containing compounds or salts thereof, are improved by an after-treatment of the textile material with a salt of a heavy metal, for example, titanium tetrachloride. The treatment not only imparts increased flame retardance to treated textile materials but protects the imparted flame retardance against subsequent impairment of ion exchange with calcium and other elements in water. Consequently, the treatment extends the effective life of flame retardance over a large number of launderings. The treatment is applicable to cellulosic fibers, e.g., cotton or rayon, as well as to wool, silk and other natural and man-made fibers.

2 Claims, No Drawings

PRODUCTION OF TEXTILE MATERIALS WITH IMPROVED FLAME RETARDANCE

RELATED APPLICATION

This application is a divisional application of Ser. No. 307,796, filed Nov. 20, 1972, now U.S. Pat. No. 3,827,907, which application in turn is a continuation-in-part of Ser. No. 220,453, filed Jan. 24, 1972 and now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to a novel method for imparting improved flame retardance to textile materials which have been treated with flame retardant phosphorus-containing compounds, and for improving the durability of such flame retardance during laundering.

It has become a widely accepted practice in the textile industry to treat textile materials, especially cellulosic materials such as cotton or rayon, but also wool, silk and various synthetic fibers, for the purpose of rendering the material resistant to the action of flame and heat. Such practice has assumed increasing importance with the adoption of legislation designed to protect the public against the hazards of inflammable fabrics in articles of clothing, toys, household articles such as curtains and drapes, and the like.

A broad group of flameproofing agents or flame retardants which have received extensive attention is represented by the inorganic and the organic phosphorus compounds. One theory to explain why such phosphorus compounds function as flame retardants for substrates, especially organic substrates such as cellulose, is that they produce phosphorus pentoxide during exposure to flame. The liberated P_2O_5, which is a Lewis acid, thereupon acts on the organic fiber substrate to dehydrate it, making it less flammable. Another theory is that the phosphorus compounds change the path of degradation to prevent the formation of levoglucosan, to increase the amount of carbon, water and carbon dioxide and to reduce the amount of flammable, volatile gases and flammable tars. Examples of agents which have been employed in the prior art for this purpose include salts of orthophosphoric acid and other acids of phosphorus, such as diammonium phosphate, and salts formed from mixtures of an aliphatic organic base and an acid of phosphorus. The acids of phosphorus which have been used to form salts with organic bases include, for example, orthophosphoric acid, phosphorous acid, pyrophosphoric acid, and methyl phosphonic acid. Typical organic bases include cyanamide and urea. These salts may be employed per se, or in association with haloalkyl phosphonic acid derivatives and phosphate esters, which are also flame-proofing agents.

Another type of phosphorus-containing flameproofing agents comprises the haloalkylphosphonic acids and their salts, such as chloromethylphosphonic acid. These compounds react with a portion of the hydroxyl groups of the cellulose of other hydroxyl-containing fiber molecule, thereby forming ethers and chemically modifying the textile material by incorporating phosphorus into the fibers.

One of the drawbacks of such phosphorus-containing flame retardants has been their ability to undergo ion exchange when the textile material is laundered in water containing alkali metal or alkaline earth metal compounds which causes a loss of fire retardance. Thus, textiles can be rendered fire retardant by the application of a compound such as diammonium phosphate to form a monophosphate ester of cellulose, CellO—P(O)—(OH)_2, or an ammonium salt thereof. However, this fire retardance can be lost in a single laundering in water containing even small amounts of alkali metal or alkaline earth metal compounds, because of the conversion of this readily decomposable monophosphate ester or ammonium salt into an alkali metal or alkaline earth metal salt which does not decompose readily into P_2O_5 when heated.

These ion exchange properties are exhibited by a number of phosphorus flame retardants. The phosphorus can be in a compound linked chemically to the cellulose or in a compound which is deposited as an insoluble deposit in or on the textile fibers. The groups which are usually associated in ion exchange properties are acidic OH groups. But, ion exchange can take place with other groups which are capable of linking with metal ions such as alkali metal and alkaline earth metal ions. The groups can be attached to the phosphorus atoms or attached to other atoms which are on the textile.

Normally the metal ions that cause the most trouble during laundering are the so-called hard water ions such as calcium and magnesium. We will refer to hard water ions as being the ones causing loss of fire retardance, but it is to be understood that both the usual hard water ions and ions such as sodium and potassium can be ion exchanged by the fire retardant fabric with subsequent loss of fire retardance. The process of this invention protects the fabric not only from hard water ions, but also all of the alkali metal and alkaline earth metal ions.

No matter what the mechanism of the ion exchange, the effect on the fire retardance of the textile laundered in hard water is the same: a loss of fire retardance associated with a pick-up of hard water ions. This is theoretically due to these metals such as calcium tyeing up phosphorus during the combustion process so that the phosphorus may not function as a flame retardant.

Thus, for example, it is known that cellulose can be phosphonomethylated by treatment with the sodium salt of chloromethylphosphonic acid in accordance with the equation:

$$\text{ClCH}_2\text{P(O)(ONa)}_2 + \text{Cell-OH} + \text{NaOH} \rightarrow \text{Cell-OCH}_2\text{P(O)(ONa)}_2 + \text{NaCl}.$$

When the treated textile is acidified with an acid such as hydrochloric acid, the sodium salt is transformed into the acid from of phosphonomethylated cellulose which has two free acid groups on the phosphorus atom. Whether it is in the salt form or in the free acid form, it is capable of picking up calcium ions by ion exchange when it is laundered in hard water, forming a calcium phosphonate salt which does not readily decompose.

A similar tendency toward ion exchange with calcium and other ions in hard water is found in textiles treated with salts of organic bases and phosphoric acid, which present some acid groups for ion exchange.

It has been proposed (see U.S. Pat. No. 2,728,680) to apply a mixed solution of a soluble chloride of tetravalent titanium and a soluble inorganic phosphate to cellulosic material as a flame retardant. The mixture is gelatinized and adhered onto the fabric. The solutions, however, only contain a small amount of phosphorus (0.02 to 0.17 part of phosphorus per part of titanium) and attempts to add higher proportions of phosphorus to such titanium tetrachloride solutions result in precipitation of titanium phosphate. The addition to the solution of antimony trichloride, another known flame retardant agent, is thus recommended in the patent to improve the fire-resistant properties of the treated fabric, particularly after laundering.

GENERAL DESCRIPTION OF THE INVENTION

In accordance with the present invention there is provided a novel method whereby the durability of flame retardant properties of textile materials treated with phosphorus-containing agents affixed to the material in an amount of from about 0.5 to about 5 percent of phosphorus based on the weight of the material is improved by the after-treatment of the textile material with a salt of a heavy metal or a transition metal, i.e., a metal which is in Group I-B or in a Group higher than Group III of the Periodic Table of Elements. If a metal can exist in different valence states, salts wherein the metal is in a higher valence state are usually more effective for the purposes of the present invention than the same metals in a lower valence state.

The treatment of the invention serves to increase the flameproofing effect of the flameproofing agent and protect it against ion exchange or other effects of exposure to hard water, thereby promoting flame resistance and increasing its retention over a large number of launderings.

The materials or substrates to which the invention is applicable include textiles or webs formed of cotton and other cellulosic fibers such as linen, regenerated cellulose, viscose rayon, and partially etherified or esterified cellulosic materials; other forms of cellulose such as paper or wood products; proteinaceous textiles, such as wool, silk, or fiber made from casein; as well as textile blends containing one or several of the foregoing fiber types. The textile materials may be in the form of fibers, yarns, fabrics (woven, non-woven or knitted), webbing and so on. The invention is particularly useful with textile materials having a fabric weight of about 5 or more ounces per square yard.

The practice of the invention will be illustrated with regard to cotton textiles, but it is to be understood that this is for purposes of illustration, and is not to be regarded as limiting.

The invention is especially applicable in conjunction with organic or inorganic phosphorus compounds which are applied to the textile material or other substrate by impregnation and chemical modification and which contain groups such as acid or hydroxy groups, that is, groups which are capable of undergoing ion exchange either in the free acid form or the salt form such as the ammonium or alkali metal salt. Examples of useful inorganic phosphorus compounds include phosphoric acid, H_3PO_4, its salts such as diammonium phosphate, as well as combinations of phosphoric acid with organic bases such as urea, cyanamide or dicyandiamide.

However, the invention is also applicable to cellulose or other substrate which is reacted with a phosphorus compound such as a haloalkyl phosphonic acid derivative, e.g., chloromethylphosphonic acid, to the extent that the resulting product is capable of undergoing further reaction with a transition metal compound, for example, titanium tetrachloride, ferric sulfate, or ammonium molybdate.

Regardless, the substrate is suitably treated to provide a phosphorus content on the substrate from about 0.5 to about 5, preferably from about 0.8 to about 3, percent by weight of the substrate.

The metals whose compounds may be employed to react with the phosphorus-containing flame retardants or with textiles incorporating such retardants generally are those which are bracketed under the heading "Heavy Metals" in the Periodic Chart of Elements, and particularly those heavy metals which fall in Groups I-B, IV-A, IV-B, V-A, V-B, VII-B and VIII of the Chart. As different arrangements of the Periodic Chart of the Elements are known in the art, when the terms "Periodic Chart of the Elements", Periodic Chart or Periodic Table are used in this specification, these terms shall be understood to refer to the particular arrangement which is shown at pages 56–57, Lange's Handbook of Chemistry, Ninth Edition, Handbook Publishers, Inc., Sandusky, Ohio (1956).

More specifically, representative heavy metals whose compounds may be used include copper (I-B), tin (IV-A), lead (IV-A), titanium (IV-B), arsenic (V-A), antimony (V-A), bismuth (V-A), chromium (VI-B), molybdenum (VI-B), tungsten (VI-B), manganese (VII-B), iron (VIII), cobalt (VIII), nickel (VIII), thorium (actinide series), and so on. Salts of titanium are particularly preferred when it is desired to make white or light colored products. However, compounds of other metals are also useful when product color is unimportant or when the salt contributes a color which is actually desired. Thus, for instance, copper and iron salts may sometimes be preferred either because of their relatively low cost or because of the colors or other effects which they produce. In conjunction with chromium they may be used as dyeing, mildew proofing, fire retardant combination finishes. Mixtures of heavy metals are also contemplated although in some cases mixtures of heavy metals suitable when used singly may not be as suitable. The efficacy of a particular mixture may be readily determined by a preliminary, empirical screening test.

The metal in its compounds may be in the cation, as in titanium tetrachloride, or the anion, as in ammonium molybdate. When the metal is the cation, the compound may be a salt or a basic salt such as a chloride, bromide, iodide, fluoride, sulfate, nitrate, or acetate. Examples of other suitable salts include titanium chloride acetate, titanium acetate, titanium sulfate, titanium tetrabromide, titanyl sulfate, chromic chloride, zirconium acetate, ferric sulfate, cupric chloride, stannic chloride, antimony trichloride, thorium tetrabromide, thorium tetrachloride and tungsten tetrachloride. Examples of suitable salts wherein the heavy metal is present in the anion include, for example, ammonium molybdate and sodium molybdate.

In the case of titanium tetrachloride, it has been found especially advantageous to add to it two moles of an alkali metal base, NaOH, making the product $TiCl_2(OH)_2$, a basic salt. In comparison to a strongly acid salt such as $TiCl_4$, the basic salt such as $TiCl_2(OH)_2$ tends to result in better strength retention in the treated substrate. $TiCl_3OH$ and $TiCl(OH)_3$ are other forms of titanium chloride hydroxide which are useful.

The metal compounds or salts can be applied to the pretreated flameproofed textile substrates from any suitable solvent which does not dissolve or otherwise undesirably attack the substrate and in which the particular compound used is soluble. Because of economic reasons and also because of its beneficial swelling effect on substrates such as cellulose, water is usually the preferred solvent in the case of metal compounds which are water soluble, but other solvents such as alcohols are also usable.

The quantity of heavy metal which is desirably applied to the phosphorus pretreated textile substrate is that which is effective in permitting enough of the heavy metal ions to become attached to the ion exchange sites of the flameproofing compound such that there are not sufficient ion exchange sites left unoccupied to cause a loss in fire retardance by picking up calcium during laundering. In practice, such an effective quantity of the heavy metal is readily determined in each case by a limited number of preliminary, empirical screening tests.

As a more quantitative guideline it may be suggested that in a system using a phosphorus compound having two OH groups as the flameproofing agent and a salt such as $TiCl_4$ or $TiCl_2(OH)_2$ as the heavy metal salt, the flameproofing agent will be capable of picking up about one atom of a metal such as titanium per atom of phosphorus. Accordingly, in such a case it is preferred to apply the titanium salt solution to the pretreated textile in a proportion producing an atomic ratio of about 1:1 for Ti to P in the treated textile. However, a satisfactory finish may generally be obtained when the Ti/P atomic ratio is in the range from 0.5:1 to 5:1, preferably from 0.75:1 to 3:1.

Naturally, there is a certain tolerance or range within which the textile material can pick up alkali metal or alkaline earth metals (such as calcium or sodium ions) without significant loss of flame retardance. Only when the calcium or sodium ion pick-up exceeds this tolerance will a significant loss of fire retardance occur. This tolerance varies with the weight of the farbic, its weave and type of finish, the kind of proportion of phosphorus compound used, the kind and proportion of titanium or other heavy metal used, etc. It is because of these many variables that it is best to determine the effective proportions of heavy metal compound by preliminary empirical testing rather than by attempting to derive the needed proportions from a general formula or equation.

In applying the heavy metal compound to the pretreated textile substrate somewhat better metal utilization, better durability of the finish and lower strength loss of the substrate may be obtained with some systems if the phosphorus compound is in the form of an ammonium or an alkali metal salt, preferably the sodium salt, than if the phosphorus compound present on the substrate has free acid groups. More particularly, in applying the present invention, it has been found especially advantageous to wash the cotton cloth or other textile substrate in a dilute sodium carbonate (soda ash) or caustic soda solution after it has been treated with the phosphorus-containing flame retardant and before it is treated with the titanium salt or other heavy metal salt solution.

A still somewhat better metal utilization and better durability of the finish is obtained if the textile substate is steamed or boiled in water after treatment with the phosphorus compound and prior to application of the heavy metal compound.

The application of the heavy metal compound solution to the phosphorus pretreated substrate is conveniently conducted at room temperature, e.g., between 15° and 35°C., although higher or lower temperatures may be used.

After the metal compound is applied to the textile material containing the phosphorus flame retardant, it is allowed to react for a period of time and then the unreacted chemicals are washed out. As noted above, the treated textile material contains from about 0.5 to about 5, preferably from about 0.8 to about 3, weight percent phosphorus.

The fabrics may be washed in water with a little nonionic wetting agent. Basic materials may be added to the wash water if the fabric contains acidic materials to be neutralized. Examples of basic materials that can be used are soda ash, ammonium hydroxide, sodium silicate, sodium phosphate, sodium borate, etc.

The flame retardant properties of relatively lightweight (i.e., below about 5 oz./sq.yd.) materials are particularly enhanced by a process wash or an afterwash in a solution of a sodium phosphate, preferably sodium tripolyphosphate. It has been shown, for example, that some such lightweight fabric materials which are particularly difficult to flame-retard will exhibit greatly improved flame-retardant properties after a process wash or an afterwash in sodium tripolyphosphate-containing solutions or one or more launderings in a sodium tripolyphosphate-containing detergent. Thus, the durability of flame retardant properties may be improved to the extent that these properties increase with such washings or launderings.

The invention is broadly applicable for improving and prolonging the flame retardant properties of any textile material treated with a phosphorus-containing flameproofing agent having ion exchange capability.

Exemplifying the types of flameproofing treatments, but not limited thereto, are the phosphonomethylation of cellulosic textile materials, such as cotton, the production of which is known and described, for example, in U.S. Pat. No. 2,979,374. The cotton fibers, and the like, are reacted with an aqueous solution of an alkali metal salt of chloromethylphosphonic acid, thereby producing a phosphonomethyl ether or cellulose.

Similarly, the flameproofed cellulosic textile material may be one which has been treated with an aqueous solution of cyanamide and phosphoric acid, as described, for example in U.S. Pat. No. 3,567,359, or with dicyandiamide and phosphoric acid, as described in U.S. Pat. No. 3,479,211, or with phosphoric acid and urea, as described in U.S. Pat. No. 3,253,881.

As the result of the treatment of the invention, the flame retardance of the textile material is improved and protected against ion exchange with other metal ions such as calcium and sodium such that the flame retardant properties are maintained through 30 to 50 or more launderings in hard water.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples serve to illustrate the practice of the invention, but are not to be considered as limiting:

EXAMPLE 1 — Part A

Preparation of Phosphonomethylated Cotton

A flameproofing solution of the sodium salt of chloromethylphosphonic acid was prepared as follows:

Chloromethylphosphonic acid	11.2% by weight
Sodium hydroxide	32.0%
Water	56.8%

A 100% cotton sateen weighing about 8 ounces per square yard (about 272 g/m^2) is padded with two dips and two nips to approximately 135% pick-up and dried on pin frames at 110°C. for 30 minutes. The treating solution contains an excess of NaOH (about 25% free caustic). The drying step causes the chloromethylphosphonic acid to react with the hydroxy groups on the cellulose. The excess NaOH in the treating formulation neutralizes the HCl formed. Usually the attachment of about 5 to 7% of the chloromethylphosphonic acid to the cellulose is sufficient to inhibit combustion.

The treated cotton is washed in a 0.017% solution of non-ionic detergent, such as Triton X-100 (an ethoxylated nonyl phenol), rinsed and dried.

The treated fabric is then soaked in a 2% HCl solution for 15 minutes, in order to convert the agent to the acid form, rinsed in deionized water and dried.

When tested by the AATCC Test Method 34-1969 (vertical flame test) the fabric exhibited a char length of 4¼ inches.

After the treated fabric was given a home laundering according to AATCC 124-1969 (Machine Wash B at 120°C.) and tumble drying, the fabric burned the entire length when tested.

EXAMPLE 1 — Part B

Treatment of Phosphonomethylated Cotton

The fabric prepared as described above in Part A is padded with an aqueous solution containing approximately 12.5% $TiCl_4$ by weight to an 85% wet pick-up. The fabric is then aged for 15 minutes and is then washed in a washing machine with water containing 25 grams soda ash to remove acidity. The resulting product contains about 1.2 to 1.7% phosphorus and about 1.8 to 2.6% titanium, the atomic ratio of titanium to phosphorus being somewhat greater than 1:1.

The titanium tetrachloride treatment reaction can be represented by the equation:

$$\text{Cell-O—CH}_2\text{P(O)(OH)}_2 + \text{TiCl}_4 + 2\text{H}_2\text{O} \longrightarrow \text{Cell-O—CH}_2\text{P(O)O}_2\text{Ti(OH)}_2 + 4\text{HCl}$$

The resulting fabric does not exhibit ion exchange properties toward hard water and retains its fire retardance for over 50 launderings. When tested by AATCC 34-1969 the fabric exhibited a char length of 3 inches. After having been laundered and tumble dried 50 times according to AATCC 124-1969, the fabric exhibited a char length of 4 inches.

EXAMPLE 2

Treatment of Phosphonomethylated Cotton

Phosphonomethylated cotton prepared as in Part A of Example 1 is padded to an 85% wet pick-up with a treating bath having the composition:

Titanium tetrachloride	8.0% by weight
HCl	4.5%
Water	87.5%

After aging for 15 minutes, the wet fabric is washed in a washing machine with 25 grams soda ash added to the wash water. The fabric again contains about 1.2 to 1.7% phosphorus and about 1.8 to 2.6% titanium. After rinsing and drying, the fabric exhibits a char length of 3.5 inches when tested by AATCC 34-1969. After 30 home launderings the fabric still has only a 2¾ inch char when tested.

EXAMPLE 3

Treatment with Ammonium Molybdate

Phosphonomethylated cotton prepared as a Part A of Example 1 is padded to an 85% wet pick-up with a treating bath having the composition:

Ammonium molybdate	12%
Water	88%

The fabric is dried and cured in a circulating air oven for 10 minutes at 250°F. It is given an afterwash with 0.01% Triton X-100 detergent in a washing machine. The fabric exhibits a char length of 3¼ inches when tested by AATCC 34-1969, the vertical flame test.

The fabric is laundered in water in which the hardness is raised artificially to 300 PPM. After two such launderings, the char length of the fabric is still 3 inches.

EXAMPLE 4 — Part A

Diammonium Phosphate-Urea-Titanium Tetrachloride Treatment of Cotton

Phosphate Treatment

Cotton twill weighing about 8 ounces per square yard is treated with a bath having the composition:

Diammonium phosphate	16.5% by weight
Urea	33%
Triton X-100	0.1%

A 65% wet pick-up is attained after two dips and two nips. The treated fabric is dried at 225°F. (107°C.) for 5 minutes and cured for 6 minutes at 330°F. (165°C.). It is then given a process wash in about 4 liters of water containing 0.1% Triton X-100 detergent and about 50 grams soda ash. Add-on is about 10% and phosphorus content is about 2%.

EXAMPLE 4 — Part B

Diammonium Phosphate-Urea-Titanium Tetrachloride Treatment of Cotton

Titanium Salt Treatment

The fabric treated as described above in Part A is next padded through an aqueous solution containing 21% $TiCl_4$, with two nips and two dips, to a 72% wet pick-up and aged wet for 2 hours. It is then given another process wash with 0.1% Triton X-100 solution and 0.03% soda ash, rinsed and dried. The fabric now contains about 3% titanium. The laundering durability of its flameproofing finish is determined by submitting representative samples to flame tests and by determining their phosphorus and titanium content after a known number of laundering and tumble drying cycles. Some samples were laundered at 120°F. and other samples at 140°F. The flame test results are shown below in Table I and the chemical analysis results are shown in Table II.

Both the flame test data and the chemical analyses show that the invention produces a flame retardant finish which is durable over 50 or more laundering cycles. It has been observed in this work that this fire retardant finish often shows improved fire retardant properties after extensive launderings. For example, certain fabrics will have shorter char lengths after 30 to 50 launderings than after the first one to ten launderings. The cause for this is not known. It may be due to something picked up by the fabric or lost by the fabric during laundering.

TABLE I

Laundering Durability of Ti-Urea-DAP-Cotton Twill

Sample	30-1		30-2		30-3		30-4	
Launder Temp.	120°F.		120°F.		140°F.		140°F.	
3-Sec. Vertical Flame Test	Char (in.)	A.G.[b] (sec.)	Char (in.)	A.G.[b] (sec.)	Char (in.)	A.G.[b] (sec.)	Char (in.)	A.G.[b] (sec.)
L. + T.D.[c] cycles								
0	2.50	51	2.00	71	2.25	65	4.00	93
5	1.25	20	2.00	15	0.50	22	0.50	24
15	1.25	18	0.75	22	0.75	36	0.50	46
30[a]	0.50	34	1.25	39	1.00	80	1.50	28
50[a]	0.75	51	1.00	50	0.50	83	1.00	90
12-Sec. Vertical Flame Test								
L. + T.D.[c] cycles								
0	4.00	38	4.50	92	4.75	78	4.75	81
5	3.50	21	3.75	21	3.25	20	3.50	50
15	3.25	19	3.75	24	3.00	135	3.25	125
30[a]	3.50	38	3.00	31	3.25	28	3.25	25
50[a]	4.00	210	3.50	70	3.25	230	3.00	200

[a] These samples were tested in bone-dry condition according to DOC-FF-3-71. The other samples were conditioned at 65% R.H. at 70°F.

TABLE II

Analysis of Ti-Urea-DAP Cotton Twill After Laundering

Sample	Launder Temp. °F.	Analysis %	After L + T.D. 0	5	15	30	50
30-1	120	P	1.32	1.86	1.83	1.58	1.56
		Ti	3.42	3.10	2.31	2.97	3.04
30-2	120	P	1.85	1.75	1.98	1.60	1.57
		Ti	3.06	2.91	2.65	2.86	3.20
30-3	140	P	1.94	1.73	1.76	1.32	1.47
		Ti	3.05	2.90	2.69	2.96	2.81
30-4	140	P	1.95	1.72	1.77	1.38	1.39
		Ti	3.39	3.17	3.12	2.96	3.05

EXAMPLE 5

Treatment with $TiCl_2(OH)_2$

Two moles (384 grams) of $TiCl_4$ are dissolved in 900 grams of water. Four moles of NaOH (320 grams of a 50% solution) are added with stirring and cooling to the $TiCl_4$. (Caustic can be added carefully to $TiCl_4$ without precipitation occurring if no more than 3 moles of caustic are added to one mole of $TiCl_4$.)

When 4 moles of NaOH are added to 2 moles of $TiCl_4$, the solution contains 2 moles of $TiCl_2(OH)_2$ and 4 moles of NaCl.

Cotton twill is treated with diammonium phosphate and urea as in Example 4 — Part A. This treated twill is boiled in water for 10 minutes and dried. The dried, treated twill is padded with the $TiCl_2(OH)_2$ treating bath to a 90% wet pick-up. The wet fabric is aged one hour and then given a neutralizing wash in the washing machine with 10 grams of Triton X-100 detergent and 50 grams of concentrated ammonium hydroxide. The fabric is rinsed, dried and subjected to laundering and testing for fire retardance. The fabric contains about 2% phosphorus.

When tested by AATCC 34-1969, the fabric has a char length of 4 inches after 50 launderings and tumble dryings.

EXAMPLE 6

Example 4 is repeated except that the phosphate treatment bath contains 8% by weight diammonium phosphate, 16% by weight urea and 0.1% by weight Triton X-100. The treated fabric contains about 1.2% by weight phosphorus.

When tested by AATCC 34-1969, the fabric shows acceptable flame retardant properties.

EXAMPLE 7

Unmercerized flannelette weighing 3.25 oz./sq. yd. is padded through the phosphate treatment bath of Example 6 with two dips and two nips to a wet pick-up of 95%. The fabric is dried 5 minutes at 250°F. and cured 7 minutes at 330°F., afterwashed in water with a little soda ash and Triton X-100, rinsed and dried.

This treated fabric is padded with an aqueous solution of 25% $TiCl_4$ to a wet pick-up of 140%. The wet fabric is aged for 60 minutes, neutralized in a washing machine with ammonia water, rinsed and dried. The fire retardance is tested by DOC FF 3-71 (vertical flame test) initially and after laundering in a sodium tripolyphosphate-containing detergent and tumble drying.

The results of this testing are:

No. of Launderings	Char Length (inches)
0	Burned entire length
1	9.5
10	6.5
50	5.5

The fire retardance of these lightweight samples increases with increased launderings in detergent which contains sodium tripolyphosphate. Other lightweight samples such as broadcloth (3.25 oz/sq yd fabric weight) which exhibit suitable fire retardance after treatment with the process of the present invention also display increased fire retardance with launderings or process washes with sodium tripolyphosphate.

EXAMPLE 8

Unmercerized flannelette (3.25 oz./sq. yd.) is treated in the same way as in Example 7 except that after the fabric is neutralized in ammonia water, it is washed for 5 minutes in 1% sodium tripolyphosphate, rinsed and dried. This fabric is laundered and tested for fire retardance:

No. of Launderings	Char Length (inches)
0	2.75
1	2.5
10	3.0
50	4.25

Washing the treated fabric with sodium tripolyphosphate improves the initial fire retardance.

EXAMPLE 9

Mercerized flannelette weighing 3.25 oz./sq. yd. is treated the same as the unmercerized flannelette in Example 8. This fabric is laundered and tested for fire retardance.

No. of Launderings	Char Length (inches)
0	5.0
5	4.75
10	3.5
50	4.5

Comparison of Examples 8 and 9 shows that the treatment is effective on either mercerized or unmercerized fabric.

EXAMPLE 10

A sample of 4.1 oz./sq. yd. flannelette is padded through the phosphate treatment bath of Example 6 with two dips and two nips to a wet pick-up of 95%. The fabric is dried 5 minutes at 250°F. and cured seven minutes at 330°F., afterwashed in water with a little soda ash and Triton X-100, rinsed and dried.

The treated fabric is padded through 12.5% $TiCl_4$ with two dips and two nips and immediately neutralized in 15% NH_3 in a beaker. The fabric is rinsed and given a process wash in 1% sodium tripolyphosphate.

The fabric is laundered and tested with the following results:

No. of launderings	Char length (inches)
0	3.75
10	4.25
25	2.75
50	4.00

EXAMPLE 11

After-Treatment With Other Metals

Another batch of cotton twill is treated with the diammonium phosphate-urea solution in the same manner as described in Example 4 — Part A (except as indicated), but instead of the treatment with titanium salt solution, is then treated with solutions of other metal salts. The metal salts used and the fire retardance results obtained are shown in Table III below. The cotton twill has a fabric weight of 8 oz./sq. yd.

The results show that with the exception of zinc chloride, zirconium oxychloride, aluminum chloride, and the mixed titanium chloride-antimony oxide, all the other salt solutions tested have produced a very noticeable improvement in the durability of the fire retardant finish.

It should be understood that the foregoing description of the general nature of the invention and of its representative embodiments is presented primarily for purposes of illustration and should not be considered limiting. The invention for which patent protection is sought is particularly pointed out in the appended claims.

TABLE III

Fire Retardance Durability of PO_4-Cotton Treated With Metal Salt Solutions
Fire Retardance — 12 Second Vertical Flame[1], After L. + T. D. (Laundering and Tumble Drying)

	0		1		5		15		20	
Metal Salt Solution	Char (in.)	A.G. (sec.)	Char (in.)	A.G. (sec.)	Char (in.)	A.G. (sec.)	Char (in.)	A.G. (sec.)	Char (in.)	A.G. (sec.)
None (control)	3.50	0	BEL[3]	0	—	—	—	—	—	—
32% $SnCl_4$	4.00	10	4.00	10	3.25	15	3.00	23	3.30	15
32% $SnCl_4$, 10% HCl	3.75	7	3.00	16	2.50	30	2.75	35	3.00	30
22% $ZrOCl_2$	4.75	2	BEL	8	—	—	—	—	—	—
22% $ZrOCl_2$, 10% HCl	4.50	4	BEL	9	BEL	32	BEL	70	BEL	18
35% $SbCl_3$, 10% HCl	2.75	14	2.50	3	3.50	21	3.25	85	3.50	157
20% $ZnCl_2$, 10% HCl	BEL	0	BEL	0	BEL	0	BEL	0	—	—
20% $CrCl_3$, 10% HCl	5.25	295	6.25	320	5.25	320	5.75	300	5.25	240
20% $AlCl_3$, 10% HCl	BEL	0	BEL	0	BEL	0	BEL	0	-	—
16.7% $AlCl_3$	BEL	0	BEL	0	—	—	—	—	—	—
18% $CuCl_2$	5.00	95	4.25	38	5.75	200	—	—	—	—
23% $Fe_2(SO_4)_3$	5.00	150	6.00	450	6.25	500	6.75	500	6.75	420
12% $TiCl_4$, 6% Sb_2O_3, 12% HCl[2]	3.0	—	—	—	BEL	—	—	—	—	—

[1] Samples conditioned 18 hours at 65% R.H. and 70°F. prior to testing.

[2] Sample is unmercerized flannelette treated with 16% urea and 8% diammonium phosphate as in Example 6. After neutralization, the treated fabric was given an afterwash in 10% sodium tripolyphosphate.

[3] "BEL" = burned entire length

What is claimed is:

1. Titanated phosphonomethyl ether of cellulose.
2. The titanated phosphonomethyl ether of cellulose of claim 1 wherein the atomic ratio of titanium to phosphorous is between about 0.5:1 and 5:1.

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