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3,744,970

TREATING OF CELLULOSIC FIBER-CONTAINING MATERIAL TO IMPART FLAME-RETARDANCY THERETO

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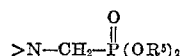
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5 Claims

ABSTRACT OF THE DISCLOSURE

Materials such as cellulosic textile materials are made flame-retardant by treating them with compounds containing methylol groups, nitrogen and phosphorus. Typical such compounds have at least one radical of the formula:



wherein R⁵ is lower alkyl. Typical such compounds also have >NH groups and/or aminomethylol groups of the formula >NCH₂OH.

BACKGROUND OF THE INVENTION

In recent years many technological advances have been made in textile technology towards providing fabrics of improved properties such as crease-resistance and flame-retardancy. A wide variety of flame-retardants have been disclosed, among which are those containing nitrogen and phosphorus. Unfortunately, these prior flame-retardants suffer from a number of disadvantages. Many of these flame retardants are not compatible with conventional crease proofing agents. Others decompose at the temperatures normally employed to fix the crease proofing agents to the fabric to be treated. Still others impart initial flame-retardancy but are ineffective after repeated laundering. Some impart efficient flame-retardancy but adversely affect other properties of the treated material such as tear resistance, tensile strength, hand, color and susceptibility to scorching. Yet others are ineffective when employed with textiles containing cellulosic fibers such as cotton.

Accordingly, it is an object of the present invention to provide treating agents which are substantially free of one or more of the disadvantages of prior agents.

Another object is to provide flame-retardants and/or flame-proofing agents which are compatible with commonly employed crease-proofing agents.

A further object is to provide flame-retardants which do not decompose at the temperatures commonly employed to fix known crease-proofing agents.

A still further object is to provide flame-retardants which are effective after multiple laundering.

Yet another object is to provide flame-retardants which have minimal adverse effect on the treated material in terms of its tear resistance, tensile strength, hand, color and/or susceptibility to scorching.

Still another object is to provide phosphorus and nitrogen containing compounds which contain reactive methylol groups and which can be fixed on cellulosic materials singularly or simultaneously with conventional crease-proofing agents.

Still another object is to provide novel methods for treating fabrics to render them flame-retardant and crease-resistant, and novel fabric treating baths.

Still another object is to provide novel treated fabrics.

Additional objects and advantages of the present invention will be apparent to those skilled in the art by reference to the following detailed description thereof.

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DESCRIPTION OF INVENTION

It has now been discovered that a certain class of compounds containing phosphorus and nitrogen are especially effective as flame-retardants for fibrous materials in general and for cellulosic or cotton fiber containing materials in particular.

NOVEL COMPOUNDS

A typical class of such compounds are those of Formula I:

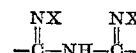


wherein R¹ is a divalent radical of Formula II, III, IV or V:

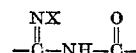
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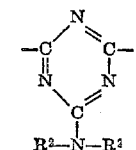
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(IV)

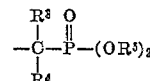


(V)



wherein R² is hydrogen or a monovalent radical of Formula VI or VII:

(VI)



(VII)



with the proviso that at least one R² is a radical of Formula VI and at least one R² is hydrogen or a radical of Formula VII; wherein X is hydrogen or cyano; R³ and R⁴ are independently selected from the group consisting of hydrogen and lower alkyl and R⁵ is lower alkyl. The lower alkyl radicals R³, R⁴ and R⁵ can be substituted with one to three substituents, examples of which include the halogens such as chloro and bromo or lower alkoxy, but are preferably unsubstituted.

Compounds of Formula I wherein R¹ is a radical of Formula V have special characteristics in that they impart a crisp hand to the treated material whereas compounds of Formula I wherein R¹ is a radical of one of the other formulae impart a soft hand and are not subject to the light sensitivity frequently characteristic of the compounds when R¹ is a radical of Formula V.

The compounds of Formula I are synthesized by co-reacting certain polyamines, certain polyalkyl phosphites and certain carbonyl compounds.

The polyamines useful to produce the compounds of Formula I are those of Formula VIII:

(VIII)



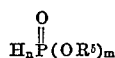
wherein R¹ has the above described meaning. Examples of suitable compounds of Formula VIII include among others melamine, guanidine, guanyl urea, biguanide, and cyanoguanidine. Inorganic acid salts of the compound of Formula I such as guanidinium carbonate and guanidinium chloride can also be employed. The guanidines are preferred because of their high nitrogen to carbon ratio, their reactivity, availability and cost.

The polyalkyl phosphites useful in the present invention are those which are coreactive with polyamines and

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carbonyl compounds. They are generally di- or tri-lower alkyl esters of phosphorus acid and are preferably those of Formula IX.

(IX)



wherein R^5 has the above defined meaning, $n=0$ or 1; $m=2$ or 3 and $n+m=3$. Examples of suitable compounds of Formula IX include among others tris(2-chloroethyl) phosphite, bis(2-bromoethyl) phosphite, triethyl phosphite, trimethyl phosphite, methylethyl phosphite, dibutyl phosphite, di-isopropyl phosphite, diethyl phosphite and dimethyl phosphite. The latter is especially preferred because of the minimum amount of carbon which this compound introduces into the fibrous material or textile.

The carbonyl compounds which are useful in the present invention are those which have heretofore been used in phosphonomethylation reactions such as described in Fields U.S. Pat. 2,635,112, and are generally those of Formula X:

(X)



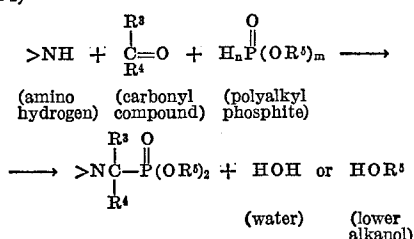
wherein R^3 and R^4 have the above described meanings. Classes of suitable carbonyl compounds include lower alkyl aldehydes and lower alkyl ketones, examples of which include among other acetone, methyl ethyl ketone, glyoxal, butyraldehyde, acetaldehyde and formaldehyde (HCHO). Any source of formaldehyde can be employed in the present invention, but paraformaldehyde and Formalin, the widely available 37 weight percent aqueous solution of HCHO are preferred because of cost, availability and reactivity. Alternate sources of formaldehyde include paraformaldehyde, gaseous formaldehyde, hexamethylene tetramine and methylal.

The reaction can be conducted neat, i.e. in the complete absence of solvents or in the presence of solvents up to infinite dilution. Examples of suitable solvents include among others, water, lower alkanols such as methanol, ethanol and butanol.

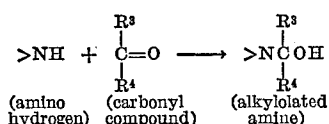
As is well known in the art, the reactivity of compounds of Formula I containing methylol groups can be reduced by capping the methylol groups with lower alkanols such as methanol or n-butanol. The capping can be conducted in situ by the use of the lower alkanol as all or a portion of the solvent or can be conducted as a separate later step.

The amino hydrogens of the polyamine undergo two reactions, a phosphonomethylation reaction according to Equation 1 and an alkylolation reaction according to Equation 2.

(Equation 1)



(Equation 2)



The phosphonomethylation reaction produces water or a lower alkanol depending whether n is 0 or 1. As can be seen by reference to Equation 1 the molar ratio of polyalkyl phosphite to amino hydrogen must be less than 1:1 in order to provide some unreacted amino hydrogen.

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This unreacted amino hydrogen can remain as such or can be alkylolated according to Equation 2. The molar ratio of the carbonyl compound to the polyalkyl phosphite is preferably at least 1:1 in order to react all the polyalkyl phosphite.

The reaction can be conducted at widely varying temperatures from below 20°C . to above 200°C . but generally within this range and preferably between 60 and 120°C . Either subatmospheric or superatmospheric pressures can be employed but atmospheric pressure is preferred for convenience.

In order to produce phosphonomethylated compounds containing amino methylol groups ($>\text{NCH}_2\text{OH}$) at least a portion of the carbonyl compound must be formaldehyde and the equivalent ratio of total carbonyl compound to polyalkyl phosphite must be greater than 1:1 in order to provide some free formaldehyde to react according to Equation 2.

NOVEL BATHS

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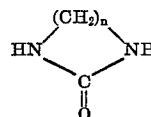
According to another aspect of the present invention there are provided novel material treating baths. These baths can be synthesized by either dissolution of compounds of Formula I or by in situ coreaction of certain reactants.

To form the bath the compounds of Formula I can be dissolved in any solvent but are preferably dissolved in water at any convenient concentration that will provide the treated system with a sufficiently high add-on. For instance the compound of Formula I can comprise from 0.01 weight percent up to the point of saturation, generally from 10 to 70% and preferably from 20 to 60% based on the combined weight of compound and solvent. Naturally compounds of Formula I are suitable whether produced by the above-described process or any other.

According to a preferred embodiment the bath is formed in situ by coreaction of a polyamine, a polyalkyl phosphite and a carbonyl compound at least a portion of which is formaldehyde. In certain cases the bath will naturally contain compounds of Formula I but it will also contain the reaction products of certain competing reactions which surprisingly and unexpectedly do not adversely affect the crease-resistance and the fire-retardance of treated materials.

The term "polyamine" as used herein refers to non-polymeric compounds having a molecular weight of 20 to 300 and preferably 30 to 150, having at least one but preferably a plurality of amino nitrogen atoms each of which has at least one amino hydrogen. The preferred polyamines have at least two $>\text{NH}$ groups and have an atomic ratio of nitrogen to carbon of at least 1:1 and preferably at least 2:1. The polyamines of Formula VIII are the preferred polyamines because of their high nitrogen to carbon ratios and the resistance to laundering exhibited by their compounds. Examples of other suitable polyamines include among others diurea, thiourea, glycoluril, melamine, methyamine, ethylene diamine as well as polyamines of Formulae XI through XIV:

(XI)

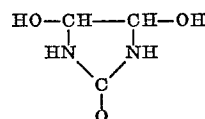


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wherein n is 1 to 4,

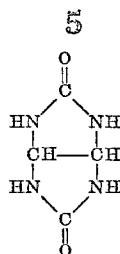
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(XII)

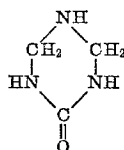


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(XIII)



(XIV)



The reactants can be employed in widely varying ratios but in order to produce a bath that will produce fire-retardant fibrous materials resistant to laundering the reactants must be present in certain critical ratios. For example when the polyamine is one of Formula VIII then the molar ratio of carbonyl compound to polyamine is broadly 1:1 to 10:1 and is preferably 3:1 to 5:1 and the molar ratio of polyalkyl phosphite to polyamine is broadly 0.5:1 to 4:1 and preferably 1.5:1 to 2.5:1. When operating outside the above broad ratios the fire-retardant character of the treated material disappears after one or two launderings whereas within the preferred ratios it is possible to produce treated materials which retain their flame retardant character even after fifty launderings. Adjustments in the above ratios will be readily apparent to those skilled in the art when practicing the present invention with polyamines having greater or lesser number of reactive amino hydrogens, or with polyfunctional polyalkyl phosphites or polyfunctional carbonyl compounds.

According to a preferred embodiment of the present invention the bath further comprises a nitrogen-containing cross-linkable crease-proofing agent and preferably one containing amino methylol groups which are coreactive with amino hydrogens and/or amino methylol groups on the compounds of Formula I and/or on the reaction products of the reactants of the bath and with the hydroxyl groups of cellulose.

Examples of suitable such crease-proofing agents include among others methylolated ureas, methylolated melamines, dimethyloldihydroxy ethylene urea which is commercially available as Permafresh 183, and tetramethylol glycoluril. Tetramethylol glycoluril is preferred because it gives good add-ons and is durable to laundering. Methylolated melamines are also very good and have the advantage of imparting a crisp hand to the treated materials. They are especially useful where light stability is not a problem.

The crease-proofing agent is preferably present in the bath such that the molar ratio of nitrogen to phosphorus in the bath and one the material is 1:1 to 10:1.

TREATING THE FIBROUS MATERIAL

The fibrous material is contacted with the bath by any convenient means such as by spraying the bath on the material or immersing the material in the bath. The excess bath liquid is then removed from the fibrous material by any convenient means such as passing the material through the nip of two rotating rubber rollers. The material is then dried preferably under mild conditions to avoid premature curing and preferably at 20 to 100° C. Finally, when the fibrous material is in the shape desired of the intended end product, it is then heated to a temperature above 100° C. and below the degradation temperature of the material and preferably at 120 to 180° C. to fix the applied compound or compounds on the material. The drying and heating steps can be conducted simultaneously but are preferably conducted sequentially.

The treated fabric preferably has sufficient add-on such that it exhibits the desired degree of flame-retardancy and crease-resistance. Materials generally have add-ons of 1 to 40 and preferably 10 to 30 percent.

GENERAL CONSIDERATIONS

The process is applicable to a wide variety of fibrous materials and especially cellulosic fibrous materials containing cotton or viscose fibers, e.g., fibers, filaments, yarns, threads, and particularly woven and non-woven fabrics. It is especially useful in the manufacture of permanent-press garments, but offers important advantages in the manufacture of other types of cellulosic textile articles as well, whenever good shape retention and fire-retardance are desired, e.g., in the manufacture of tufted cotton carpets, molded cotton batting and so forth. The invention is particularly effective with natural cellulose materials such as cotton and linen but is also applicable to regenerated cellulose such as viscose and high wet modulus (polynosic) rayon. The invention is also useful for fabric blends containing minor amounts of cellulosic fiber, e.g., blends of cotton and polyester (such as polyethylene terephthalate), cotton-and-nylon, etc.

The term "lower" as used herein with lower alkyl, lower alkoxy and the like refers to a carbon atom content of one to four. The term "add-on" as used herein refers to the weight increase due to adhesion of solids from the bath based on the original weight of untreated material. Thus a 100 g. sample of cotton cloth dipped in a bath, dried, cured, washed, dried and conditioned at 65% relative humidity at 70° F. and then found to weigh 125 g. would be said to have a 25% add-on.

The invention is further illustrated by the following examples in which all parts and percentages are by weight unless otherwise indicated. These non-limiting examples are illustrative of certain embodiments and are designed to teach those skilled in the art how to practice the invention and to represent the best mode presently known for carrying out the invention. In the following examples treated materials are tested for flame resistance according to AATCC34-1966 and for crease-resistance according to ATTCC 66-1959T which gives wrinkle recovery angles. Where indicated the laundering is performed in a home-type washing machine using a low-suds detergent.

Example I

This example illustrates the use of a lower alkanol as a solvent.

Guanidinium hydrochloride (57.3 g., 0.6 mole), cyanoguanidine (25.2 g., 0.3 mole), dimethylphosphite (198 g., 1.8 mole) and paraformaldehyde (54 g., 1.8 mole) were combined with 500 ml. of methanol and refluxed 45 hours. To it was added an additional paraformaldehyde (54 g. 1.8 mole) and it was continued heating at reflux temperature for an additional 5 hours. Methanol was removed under reduced pressure to give a viscous, clear liquid aminophosphite condensate.

Pad baths were prepared from this material as follows:

Item	Ingredient	Percent
A	Amino-phosphite condensate	35
B	Catalyst e.g., H_2PO_4 or NH_4Cl	0.5
C	Additive e.g., tetramethylolglycoluril	10
D	Triton X-100-nonionic wetting agent	0.25
E	Mykon SF-polyethylene fabric softener	3

The remainder is water.

Item A is dissolved in an equal weight of water and the pH adjusted to 3.5 with 50% NaOH solution. Items B, C, D, and E are then added and the pH again adjusted to 3.5.

Pad baths were prepared containing 10% of tetramethylolglycoluril and 0.5% NH_4Cl (Bath A) and 10% trimethylolmelamine and 0.5% NH_4Cl (Bath B) and the results of their application to twill are shown in Table 1.

TABLE 1

Bath	Add-on percent	Flame retardance ¹	WRA ² , degree	
			Dry	Wet
A-----	18	20-25	287	216
B-----	20	>50	204	212

¹ i.e., The number of washes before the sample burns $4\frac{1}{2}$ " in the flame test.

² Wrinkle recovery angle.

Example II

This example illustrates the use of trimethylphosphite and dimethyl phosphite.

Cyanoguanidine -----	16.8 g. (0.2 mole).
Guanidinium chloride -----	19.2 g. (0.2 mole).
Paraformaldehyde -----	24.0 g. (0.8 mole).
Dimethyl phosphite -----	66.0 g. (0.6 mole).
Trimethyl phosphite -----	24.8 g. (0.2 mole).

The above reactants, with the exception of the dimethyl phosphite, were mixed and stirred at room temperature, 25 ml. of methanol being added to make stirring easier. After half an hour, an exotherm developed with some effervescence. The mixture was stirred for an additional half hour, and then the dimethyl phosphite added and the solution refluxed for 2 hours.

Paraformaldehyde (12 g.; 0.4 mole) was then added, plus 50 ml. methanol and the solution refluxed for one hour. The solution was evaporated under reduced pressure to give a clear, viscous liquid which was used to prepare pad baths as previously described.

Bath A—10% tetramethylglycoluril+0.5 g. NH_4Cl

Bath B—10% trimethylolmelamine+0.5 g. NH_4Cl

TABLE 2

Bath	Add-on percent	Flame retardance ¹	WRA ² , degree	
			Dry	Wet
A-----	20	35-40	269	202
B-----	20	>50	193	220

^{1 2} See footnotes ^{1 2} bottom of Table 1.

Example III

This example illustrates the synthesis of a bath of the present invention employing guanidinium carbonate, dimethyl phosphite and formaldehyde in aqueous solution.

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

Item	Ingredient	Quantity of—	
		Grams	Gram-moles
A-----	Guanidinium carbonate-----	18	0.1
B-----	Dimethyl phosphite-----	66	0.6
C-----	Formalin-----	40.5	0.5 HCHO

Items A and B are heated rapidly to 90° C. until A dissolves in B forming a solution which is then allowed to cool to 70° C. whereupon the solution is rapidly cooled with Dry Ice to 25° C. Item C is then added dropwise to the solution over a 7 minute period during which the temperature of the reaction mixture rises to 68° C. and then drops to 60° C. The temperature of the reaction mixture is then raised to 80° C. over a 15 minute period and maintained at 80° to 90° C. for a period of one hour.

Example IV

This example illustrates the synthesis of compounds of the present invention from guanidinium hydrochloride, cyanoguanidine, dimethyl phosphite and formaldehyde in aqueous solution.

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

Item	Ingredient	Quantity of—	
		Grams	Gram-moles
A-----	Guanidinium hydrochloride-----	57.3	0.6
B-----	Cyanoguanidine-----	16.8	0.2
C-----	Dimethyl phosphite-----	176	1.6
D-----	Formalin-----	260	3.2 HCHO

Items A and B are added to Item C at room temperature to form a reaction mixture which is then rapidly heated to 90° C. and cooled. Item D is added and heated to reflux over a period of 10 minutes and maintained at a reflux temperature of 78–100° C. for an additional 50 minutes to give a clear pale yellow solution.

Example V

This example illustrates the synthesis of compounds of the present invention and fabric treating baths employing such compounds produced from guanidinium carbonate, cyanoguanidine, dimethyl phosphite and formaldehyde.

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

Item	Ingredient	Quantity of—	
		Grams	Gram-moles
A-----	Guanidinium carbonate-----	54	0.3
B-----	Cyanoguanidine-----	16.8	0.2
C-----	Dimethyl phosphite-----	176	1.6
D-----	Formalin-----	260	3.2 HCHO

Items A, B, and C are mixed and heated rapidly to 85° C. over a period of 10 minutes and then allowed to cool to 50° C. whereupon a clear pale yellow liquid results. To this liquid is added Item D dropwise over a 25 minute period. The temperature increases due to exothermic reaction to a maximum of 73° C. and then reduces to 43° C. at the end of the period of addition of Item D. The temperature of the reaction mixture is then raised to 95° C. and heated at 95–100° C. over a period of 40 minutes.

Example VI

Pad baths were prepared as in Example I, except that the reaction products were not evaporated and an amount of the aqueous solution was taken so as to give 35% of the amino-phosphite condensate in the pad bath. The results are shown in Table 3.

TABLE 3

Example	Additive	Catalyst	Add-on, percent	Flame retardant	WRA, degree	
					Dry	Wet
I-----	None-----	1% H_3PO_4	13	4	160	192
III-----	10% TMG-----	0.5% H_3PO_4	15	25	260	216
	5% TMM-----	0.5% H_3PO_4	18	30	224	255
IV-----	10% TMG-----	0.5% H_3PO_4	17	20	254	230
	10% Aerotex 73-----	0.5% H_3PO_4	11	1-3	245	216
	10% Dextraset UN-----	0.5% H_3PO_4	12	3	274	239

Example VII

This example illustrates reaction of two polyamines, formaldehyde and dimethyl phosphite in the absence of solvent.

Cyanoguanidine -----	4.2 g. (.05 mole).
Guanidinium chloride -----	9.6 g. (.10 mole).
Paraformaldehyde -----	9.0 g. (.30 mole).
Dimethylphosphite -----	33.0 g. (.30 mole).

Reactants mixed and stirred under nitrogen in an oil bath at 120° C. When the reaction temperature reached 100° C. an exotherm developed and the flask was removed from the oil bath. When the exotherm subsided, the flask was returned to the oil bath and heated at 100° C. for 30 minutes. Then paraformaldehyde (9.0 g.; 0.30 mole) and methanol (15 ml.) were added and the solution heated under reflux for 2 hours. The solution was cooled, diluted with 50 ml. H₂O and its pH adjusted from 1.4 to 3.5 with 7 ml. of 50% NaOH. Tetramethylol glycoluril (16.0 g.), NH₄Cl (0.8 g.), Triton X-100 (0.4 g.) were then added and the solution diluted to 160 g. with water to form a bath.

The bath was padded onto twill, dried for 15 minutes at 88° C. and cured for 15 minutes at 160° C. The resultant fabric was flame-retardant for over 20 washes.

Example VIII

Six equivalents of formaldehyde (18 g.) and one equivalent of melamine (12.6 g.) were dissolved in hot water (70–80° C., 100 ml.) at pH 10, three equivalents of dimethyl phosphite (33 g.) were added as soon as a colorless homogeneous solution was obtained, and the resultant solution was rapidly cooled in ice water. Treatment of cotton twill or printcloth with a 40% solids bath of this reaction product, using no added catalyst, afforded fabric which was fire resistant for more than twenty home-type launderings. The fabric had durable press properties, with dry and wet crease recovery angles of 250°–275°.

Example IX

Six equivalents of formaldehyde (18 g.) and one equivalent of melamine (12.6) were dissolved in water at 70–80° (100 ml.) at pH 10, and 3 equivalents (85.8 g.) of tris-(2-chloroethyl) phosphite were added as soon as a homogeneous solution was obtained, and the resultant solution was rapidly cooled in ice water. Fabrics were padded with a solution containing 60% by weight of these reactants to a wet pick-up of 70% for twill and 100% for printcloth. The resultant fabrics were dried and cured in the manner previously described and had add-ons of 22% and 33% respectively. These fabrics were flame retardant for over 15 home launderings and had dry crease recoveries of 269° and 205° respectively.

Example X

Cyanoguanidine (16.8 g.), dimethyl phosphite (44 g.) and formaldehyde (24 g.) were combined in water and heated at 80°–100° C. for one hour. The resulting solution was cooled, adjusted to pH 3.5, 0.5% phosphoric acid was added as catalyst, as well as 0.25% Triton X-100 wetting agent, 3% Mykon SF polyethylene emulsion, and 5% Resloom HP crosslinking additive to form a material treating bath. Total solids concentration was 40%. Cotton twill was padded to 80% wet pickup, dried and cured, after which it was flame retardant for greater than 12 washes.

Example XI

Guanidinium carbonate, dimethyl phosphite and formaldehyde in mol ratios at 1:2:4 were dissolved in water and heated at 80–100° for one hour. Baths were made up as described in Example XIII with the exception that the final pH of the solution was 5.0. Fabrics treated with this bath had 15.1% ad-on after 1 wash, had a soft hand, dry crease recovery of 300° and wet crease recovery of 259°, and flame retardance durable for at least 14 washes.

Example XII

Biguanidine (10.1 g.) was methylolated with two equivalents of paraformaldehyde (66 g.) by refluxing in solvent methanol (150 ml.) for 40 minutes. Two equivalents of dimethyl phosphite (22 g.) were then added, and the mixture refluxed for one hour. Two additional equivalents of paraformaldehyde (6.6 g.) were then added, and re-

fluxed until homogeneous. The solvent was removed, and a 35% solids aqueous pad bath was made up containing 0.5% ammonium chloride as catalyst and 10% tetramethylol glycoluril as additive. When treated as described in Example XIII, the resultant fabric had a crisp hand, dry and wet crease recovery angles of 292° and 267° C. respectively, and was flame retardant for over 15 washes.

Example XIII

Guanyurea (31 g.) in methanol (50 ml.) was stirred for 30 minutes with paraformaldehyde (18.8 g.). Dimethyl phosphite (69 g.) was then added causing an exothermic reaction. The solution was refluxed for 30 minutes, then the pH was adjusted to 8–9 with sodium hydroxide and the solution stirred for 1 hour with Formalin (formaldehyde content 28.2 g.). This solution was used to prepare a pad bath in the usual way using 10% of tetramethylolglycoluril as additive. The finish applied to twill gave a very soft hand at 16.4% add-on and the char length after 1 wash was 3½”.

Example XIV

Guanidinium chloride (9.6 g.; 0.1 mole), dimethyl phosphite (22 g.; 0.2 mole) and methylal (100 g.; large excess) were refluxed for one hour without apparent change. Methanol (50 ml.) and concentrated hydrochloric acid (2 ml.) were added and the mixture refluxed for 30 minutes, after which time the reaction mixture was clear and homogeneous. The methanol and methylal were removed under reduced pressure and cotton twill was treated with a pad bath containing 35% by weight of this product, 10% tetramethylol glycoluril, and 0.5% ammonium chloride catalyst. The fabric had soft hand, good wrinkle resistance, and was flame retardant for more than 15 washes.

Example XV

Guanidine (15.8 g.; 0.27 mole) in ethanol (40 g.) was mixed with dimethyl phosphite (58.5 g.; 0.54 mole). Paraformaldehyde (33.7 g.; 1.07 mole) and methanol (400 ml.) were added and the mixture refluxed for 2 hours. The methanolic solution was evaporated under reduced pressure and cotton twill was treated with a pad bath containing 35% by weight of this product, 10% tetramethylolglycoluril, 0.5% ammonium chloride, 0.25% Triton X-100, and 3% of Mykon SF. The resultant fabric was flame retardant for at least seven washes.

Example XVI

Reactants:

Cyanoguanidine	16.4 g. (0.2 mole).
Paraformaldehyde	12.0 g. (0.4 mole).
Trimethyl phosphite	49.6 g. (0.4 mole).
Dimethyl phosphite	4.4 g. (0.04 mole).

The reactants were mixed and stirred under nitrogen in an oil bath at 125° C. A vigorous exotherm developed as the reaction mixture reached 95° C., and the flask was removed from the oil bath. When the reaction had subsided, the reaction mixture was heated at 90° C. for 2 hours. Then paraformaldehyde (12.0 g.; 0.4 mole) and methanol (30 ml.) were added, and the solution heated under reflux for 1½ hours. The methanol was removed on a rotary evaporator and the resultant viscous liquid dissolved in water (50 ml.) and its pH adjusted from 4.6 to 3.5 with a few drops of phosphoric acid. A pad bath was prepared containing 32% of this material, 9% tetramethylol glycoluril, 0.5% NH₄Cl and 0.25% Triton X-100. The fabric was dipped in this material and then dried for 15 minutes at 85° C. and cured for 15 minutes at 160° C. The fabric had an add-on of 13.5% after 1 wash and in the flame test burned 4”. The flame retardance had gone after 10 washes.

Example XVII

Cyanamide (21 g. of 50% solution; 0.25 mole) and dimethyl phosphite (27.5 g.; 0.25 mole) were mixed, para-

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formaldehyde (15 g.; 0.5 mole) was added, and the mixture was stirred and heated at 80° C. until clear (1 hour). Water was added to bring the solution to 40% solids, the pH was adjusted to 3.5, and 0.5% Triton X-100 and 10% tetramethylol glycoluril were added. Cotton twill was padded, dried, and cured in the usual way and had an add-on of 19.7% after 1 wash, and was flame resistant for 4 washes.

Example XVIII

A mixture of guanidinium chloride (38.2 g.), cyanoguanidine (16.8 g.), dimethyl phosphite (132 g.) and formaldehyde (195 g.; 37%) were dissolved in water and heated 2 hours at 80–100° C.

Pad baths were made up from this reaction product as in Example XXIII, and a number of cross-linking additives compared, as illustrated in the following table:

Cross-linking additive	Durability of flame retardance	Dry crease recovery, degree
None	10 washes	191
10% permafresh	1-5 washes	240
10% tetramethylol glycoluril	10 washes	209
10% dimethylolurea	15 washes	215
10% dimethylol ethylene urea	1-5 washes	257
Dimethylol propylene urea commercially available as Fixapret P.H.	do.	205

Example XIX

A pad bath was prepared as in Example XVIII using 10% tetramethylol glycoluril as additive. A sample of rayon jaquard drapery was treated with this bath in the manner described previously and was found to be flame resistant for at least 15 home-type launderings.

Example XX

Thiourea (7.6 g.) and 37% aqueous Formalin (32.4 g.) were mixed, dimethyl phosphite (22 g.) was added, and the resulting solution was heated at 85–90° C. for 45 minutes and allowed to stand at room temperature for 16 hours. The pH was adjusted to 3.5 with 50% sodium hydroxide, tetramethylol glycoluril (10 g.) was added, as was 0.25% Triton X-100. The mixture was diluted to a total of 100 g. with water, whereupon a small amount of solid separated from the solution. A sample of cotton twill was padded to 80% wet pickup, dried 15 minutes at 90° C., cured 15 minutes at 160° C., and washed in a home type washing machine on the normal cycle using concentrated detergent. The resulting fabric gave a 4 inch char when tested in the standard flame test.

Example XXI

Urea was methylolated with two equivalents of formaldehyde and the resultant dimethylolurea was suspended in one equivalent each of dimethyl phosphite and trimethyl phosphite. The mixture was heated slowly to 85° C. whereupon solution occurred. The solution was heated at 85° C. for 24 hours, cooled, and one equivalent of 37% aqueous Formalin was added and the solution stirred for one hour. A pad bath was made up from this product as described in Example XXVI, and a sample of treated fabric, after washing, was flame resistant for two washes.

Example XXII

This example illustrates the maximum durability of flame-retardancy when the reactants are present in the preferred molar ratios.

Pad baths were prepared as described in Example I except that the proportions of the reactants were varied as indicated.

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TABLE

(1) Mol ratio of gua.:
DMP:HCHO:

(2) No. of washes before loss of flame retardance

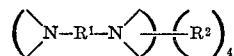
1:1:4	0
1:1:5	0
1:2:0	0
1:2:2	10
1:2:3	15
1:2:4	25
1:2:6	10
1:3:6	2
1:3:2	0
1:4:4	<10

Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described above and as defined in the appended claims.

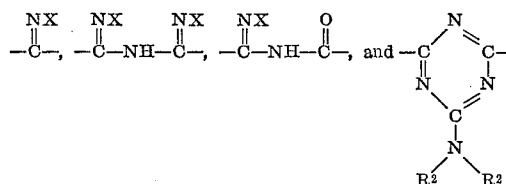
What is claimed is:

1. A method of rendering cellulosic fiber-containing materials flame-retardant comprising in sequence the steps of:

(I) contacting the material with a compound of the formula:



wherein R¹ is a member selected from the group consisting of



wherein the R²'s are selected from the group consisting of hydrogen, radicals of the formula:



and those of the formula:



with the proviso that at least one R² is a radical of the Formula A and at least one R² is hydrogen or a radical of the Formula B; wherein X is hydrogen or cyano; R³ and R⁴ are independently selected from the group consisting of hydrogen and lower alkyl and R⁵ is lower alkyl;

(II) heating the material to fix the compound on the material.

2. The method of claim 1 wherein R₁ is



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3. The method of claim 2 wherein R_3 and R_4 are hydrogen.

4. The method of claim 1 further comprising:

(III) drying the material at 20 to 100° C.; and

(IV) heating the material to 120 to 180° C.

5. The method of claim 4 wherein the cellulosic fiber-containing textile material prior to heating to 120 to 180° C. is contacted with an aqueous solution of at least one crosslinking and crease-proofing agent selected from the group consisting of methylolated ureas, methylolated melamines, dimethylol dihydroxy ethylene urea and tetramethylol glycoluril.

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8—116 P, 120, 185 MP, 190 MP, 192 MP