

UNITED STATES PATENT OFFICE

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TREATMENT OF FLAMMABLE MATERIALS
TO IMPART FLAME RESISTANCE THERE-
TO, COMPOSITIONS THEREFOR, AND
PRODUCTS THEREOFMaurice Robert Burnell, Noroton Heights, and
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This invention relates broadly to the treat-
ment of flammable materials to impart flame
resistance thereto, compositions therefor and
products thereof. The invention is concerned
more particularly with certain new and useful
improvements in the art of imparting durable
flame resistance to normally flammable mate-
rials, more particularly organic textile materials,
including natural cellulose-containing textiles,
regenerated cellulose-containing textiles, and
wool- and other protein-containing textiles.

For a description of the various compounds and
compositions which have been used or suggested
for use as agents for treating fibrous cellulosic
and other normally flammable organic materials
in order to render them resistant to flame, see
the book entitled "Flameproofing Textile Fab-
rics," edited by Robert W. Little and published
in 1947 by Reinhold Publishing Corporation, New
York, N. Y., and the references cited therein.

Agents or treatments for imparting flame re-
sistance to normally flammable organic mate-
rials properly may be classified as (1) tempo-
rary, (2) semi-durable and (3) permanent or
durable, based on their durability in providing
continued resistance of the treated textile or
other material to flame during use. See page 6
of the aforementioned book by Little for a more
complete description of these classes. The pres-
ent invention is concerned primarily with cer-
tain new and useful improvements in the perma-
nent or durable agents or treatments of the kind
aforementioned.

The durable treatments heretofore used or sug-
gested have been of three general kinds or types:

1. Urea-phosphate type.
2. Double-bath precipitation type.
3. Metallic oxide-chlorinated body type.

See Little's book, supra, pages 179-284, for a com-
plete description and discussion of each of these
types. One of the main objections to the urea-
phosphate type of treatment is the tendering ef-
fect of the treatment on the organic material
whereby its tensile strength is reduced consid-
erably. The double-bath precipitation and the
metallic oxide-chlorinated body types of treat-
ments generally yield textiles having a harsh or
stiff hand, so that the treated textile has a lim-
ited field of utility.

The present invention is based on our dis-
covery that various textile materials including
natural cellulose-containing textiles, regenerated
cellulose-containing textiles, and wool- and other
protein-containing textiles can be rendered sub-
stantially permanently resistant to flame by suit-
ably treating them with compositions of the kind
hereinafter described. Our treated textiles in
thread, yarn, fabric or other form are unique
in that they are characterized not only by their

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substantially permanent flame resistance but also
by their crease resistance and shrinkage resistance. Fur-
thermore, these properties are obtained without
excessive tendering of the textile, the treated
textile in general having a total tensile strength
(average of the sum of the tensile strength of
the warp and filling) of at least 80% of that of
the untreated textile when similarly tested for
tensile strength, and in some cases a tensile
strength which is even higher than that of the
untreated textile. Another novel feature of our
invention resides in the fact that the desirable
properties of flame resistance (flame retardance),
crease resistance and shrinkage control of the
textile are obtained in a single, one-bath treat-
ment. Furthermore, the preferred impregnating
or treating solution is aqueous and clear, and
therefore has obvious practical advantages from
an application standpoint.

The foregoing and other valuable and unobvi-
ous results are obtained by practicing the method
of our invention. Briefly described, this method
comprises impregnating the textile material to be
rendered flame-resistant with an aqueous liquid
composition containing the following initial or
starting ingredients (that is, in the form in which
they exist prior to incorporation in the aqueous
liquid composition) in the specified, critical pro-
portions by weight: (1) from 2 to 20 parts, more
particularly from about 5 to 10 parts, of a heat-
curable (thermosetting) reaction product of in-
gredients comprising formaldehyde and a mem-
ber of the class consisting of urea, melamine and
mixtures of urea and melamine, more particular-
ly a heat-curable member of the class consisting
of methylol melamines, methylated methylol
melamines, methylol ureas, methylated methylol
ureas, mixtures thereof, and water-soluble reac-
tion products and phosphoric acid-soluble reac-
tion products of the said methylol compounds
and of mixtures of the said methylol compounds;
(2) from 10 to 35 parts, more particularly from
about 20 to 30 parts and specifically about 25
parts, of a methylol dicyandiamide, e. g., mono-
methylol dicyandiamide, dimethylol dicyandi-
amide, trimethylol dicyandiamide, etc., or a mix-
ture in any proportions of the various methylol
dicyandiamides; and (3) an oxygen-containing
acid of phosphorus in an amount which is equiv-
alent, based on phosphorus content, to from 5 to
30 parts of 85% H_3PO_4 . The oxygen-containing
acid of phosphorus initially can be in the form
(as desired or as conditions may require) of phos-
phoric acid (also known as orthophosphoric acid
and available either as H_3PO_4 or as $2H_3PO_4 \cdot H_2O$),
pyrophosphoric acid ($H_4P_2O_7$), metaphosphoric
acid (HPO_3), hypophosphoric acid ($H_4P_2O_6$), the
various phosphorous acids, or in the form of mix-
tures of any or all of the various phosphorous
and phosphoric acids in any proportions, or in

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the form of solutions (e. g., aqueous solutions, alcoholic solutions, etc.) of any one or more or all of the various phosphorous and phosphoric acids in any proportions. For example, we can use a mixture of ortho-, meta- and pyrophosphoric acids, such mixed acids being sometimes collectively designated as "polyphosphoric" acid. The oxygen-containing acids of phosphorus are particularly advantageous over other acids in practicing our invention because of their excellent afterglow-retarding properties. Orthophosphoric acid is preferred.

The treating compositions of our invention are prepared, for example, by mixing together the heat-curable reaction product, e. g., trimethylol melamine, and the methylol dicyandiamide, followed by the addition of a suitable amount of water. The mixture is stirred until the ingredients are thoroughly mixed together and the mixture is smooth. The phosphoric acid or other oxygen-containing acid of phosphorus, for instance in the form of an aqueous solution containing about 85% by weight of H_3PO_4 , or in any other desired concentration or form, is now stirred into the smooth mixture of the other ingredients. The resulting slurry is heated, with rapid stirring, to a temperature sufficiently high, e. g., about 120° F., to cause all of the soluble ingredients to dissolve. A clear, aqueous solution usually results, especially when the preferred ingredients are employed. The mixture should be well stirred in order to prevent local polymerization of the heat-curable reaction product. Ordinarily, the mixture becomes exothermic when heated to a temperature of about 115° F. A typical formulation (I) is as follows:

	Parts by weight
Trimethylol melamine -----	5
Monomethylol dicyandiamide -----	25
Aqueous phosphoric acid (about 85% H_3PO_4) -	15
Water -----	55

After preparing our liquid, textile-treating composition, for instance as described above by way of example, it is preferably cooled, e. g., to about 80°-90° F., and is now ready for application to the textile to be treated. Or, if desired, it may be applied hot to the textile. Lower concentrations of solids in the solution can be produced by diluting a more highly concentrated solution (e. g., a solution containing about 40 to 45% by weight of the aforementioned ingredients) with a suitable solvent, e. g., water. The bath stability of an aqueous solution containing about 40-45% by weight of the ingredients specified in Formulation I is at least 8 hours.

In some cases it may be desirable to generate the phosphoric acid or other oxygen-containing acid of phosphorus while in contact with, as in the form of a solution or admixture of, any or all of the other initial components of the treating composition. This can be done, for instance, by using (instead of the oxygen-containing acid of phosphorus per se) an equivalent amount of a suitable salt, e. g., an ammonium salt, of such an acid, and generating the free acid in situ, for example by heating or by treating the composition containing the salt with formaldehyde or a strong acid (e. g., HCl) whereby the salt is decomposed and the oxygen-containing acid of phosphorus is released. If the salt is an ammonium salt, the evolved ammonia can be fixed or bound in any suitable manner, for example by adding formaldehyde in the form of paraformaldehyde or other suitable form to the composition.

Illustrative examples of textile materials that

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can be treated with the compositions herein described to impart flame resistance thereto are those formed of or containing fibers of natural cellulose or regenerated cellulose, e. g., cotton, linen, hemp, jute, ramie, sisal, viscose rayons, cuprammonium rayons, etc.; textiles formed of mixtures or blends of such fibrous cellulosic materials; protein-containing textiles, for instance those formed of or containing wool, silk, mohair, leather, fur, regenerated protein fibers, e. g., those produced from casein, soyabean, peanut, corn (zein), egg albumin, feathers (keratin, collagen, etc.); textiles formed of mixtures of such fibrous protein-containing materials; and textiles formed of mixtures of such fibrous protein-containing and cellulose-containing materials.

Any suitable apparatus can be employed in applying the treating composition to the textile material. For example, a dry or substantially dry textile or, if desired, a wet textile to be treated can be immersed in the aqueous composition and then passed through pressure rolls, mangles or centrifugal extractors to secure uniform impregnation and a controlled removal of the excess material. The textile in fabric or other form also can be impregnated by other methods, e. g., by spraying, brushing, etc. The wet pick-up of the composition by the textile may range, for example, between about 15% and about 300% by weight of the textile undergoing treatment. The wet pick-up of the treating agent by the textile material is adjusted so that the finished textile contains from about 10% to about 100%, usually from 15 or 20% to about 40 or 45% by weight, based on the dry weight of the untreated textile, of wash-fast impregnant.

The amount of solids in the aqueous treating agent as applied to the textile can be varied as desired or as conditions may require, e. g., within the range of from about 5 or 10% to about 70 or 75% by weight thereof, more particularly from about 25 or 30% to about 60 or 65% by weight of the composition.

After impregnating the textile material with an aqueous liquid composition, more particularly an aqueous solution, of the kind aforescribed, the wet impregnated textile is heated to insolubilize or cure the impregnant. Heating can be carried out in one or two steps to secure the same ultimate result. For instance, the impregnated textile can be dried at room temperature or by heating it at an elevated temperature up to 212° F. or higher. If drying is effected by heating, then as a part of the same general operation or as a separate step, the dried impregnated textile is heated at a temperature within the range of about 250° F. to about 400° F. The higher the temperature, the shorter is the period of heat treatment. Thus, drying the impregnated textile for 3 minutes in an oven maintained at a temperature of about 250° F. followed by heating at a higher temperature, e. g., for 10 minutes at 320° F. or for 5 minutes at 340° F., is generally effective in obtaining the desired results. These specific time and temperature periods are merely illustrative of those that can be employed.

During the drying and subsequent heat-treatment of the impregnated textile, the reactive ingredients of (1), (2) and (3) described in the sixth paragraph of this specification co-react with each other (and apparently also with the textile) to form a product of heat reaction in situ, whereby the heat-treated textile is rendered resistant to flame, creasing (wrinkling) and shrinkage.

The dried, heat-treated or cured textile usually

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is somewhat stiff initially, but this stiffness decreases markedly on rinsing and washing. If a flame-resistant textile having a softer hand (softer feeling to the touch) is wanted, this can be attained advantageously by calendering the textile after it has been dried and before it has been cured. If the textile is calendered after it has been cured, a loss in tensile strength generally results.

After the heat treatment at the higher temperature, that is, above the drying temperature, the cured textile is rinsed, e. g., with water, to remove free acid and any other water-soluble substances that may be present therein. A rinse of from 5 to 10 minutes in running water at about 100° F. for rayon and woolen fabrics and at about 160° F. for cotton fabrics is usually satisfactory, and this was the practice employed in the examples which follow. The finished, rinsed and dried textile is substantially permanently resistant to flame, that is, it is resistant to flame even after numerous laundering (washing in detergent solutions) or dry-cleaning operations. Hence the flame-resistant textiles of our invention properly may be designated as being of the "durable" type or kind.

In order that those skilled in the art better may understand how the present invention can be

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sistance was determined by a vertical flame test, using the same procedure and apparatus in all tests. The "char" length (charred length) was ascertained by measuring the tear length produced with a tearing weight equal to approximately 10% of the tearing strength of the unburned fabric. The tensile strength tests were made on the rinsed samples. The flame tests were usually made on washed samples (after the stated periods) but in some cases also were made on the rinsed samples. Washings were carried out in a small agitator-type washer using, unless otherwise stated, a 0.1% neutral soap solution, followed by thorough rinsing to remove any traces of soap and then drying before testing, usually (unless otherwise stated) by pressing until dry on a Hoffman steam press. The temperature of the wash water was about 160° F. in the case of the cotton fabrics and about 100° F. in the case of woolen and rayon fabrics. All percentages are by weight, as also are the parts, including those of the various formulations.

EXAMPLE 1

This example illustrates the results obtained when the flame-proofing composition described as Formulation I is used to treat various cotton, rayon and woolen fabrics.

Table of Example 1

Kind of Textile	Vertical Flame Test (Height of Burned Area in Inches) After Washing in Soap Solution for—			Total Tensile Strength in Lbs. (Warp plus Filling)
	1 Hr.	3 Hrs.	5 Hrs.	
Tricot netting, untreated	Burned completely			39
Tricott netting, treated	3.7	3.8	3.8	27
136 x 60 broadcloth, untreated	Burned completely			125
136 x 60 broadcloth, treated ¹	3.1	3.0	3.4	112
80 x 80 cotton sheeting, untreated	Burned completely			100
80 x 80 cotton sheeting, treated	3.0	3.3	3.6	99
8 oz. woolen flannel, untreated	Burned completely			68
8 oz. woolen flannel, treated ²	3.8			75
Viscose rayon, untreated	Burned completely			121
Viscose rayon, treated	2.7	3.1		100

¹ In this case, the treating composition (Formulation I) was diluted with water to give a solution containing about 35% by weight of solids.

² After 5 washing cycles of 10 minutes each, the treated wool showed a shrinkage of 13% whereas the untreated wool, when similarly washed, showed a shrinkage of about 20%. Woolen flannel which has been treated with a composition like Formulation VI given under Example 6 shows a shrinkage of only 8.6% after 5 washing cycles of 10 minutes each.

carried into effect, the following examples are given by way of illustration and not by way of limitation. Unless otherwise stated, the wet impregnated textiles were dried for 3 minutes in an oven maintained at a temperature of about 250° F. and then were heated at a higher temperature, viz., either for 10 minutes at 320° F. or for 5 minutes at 340° F., to convert the impregnant to

EXAMPLE 2

This example illustrates the results obtained when the flameproofing composition contains various concentrations of solids (trimethylol melamine, monomethylol dicyandiamide and phosphoric acid), and when additional quantities of monomethylol dicyandiamide have been added to the diluted solutions.

Table of Example 2

80 x 80 Cotton Sheeting	Vertical Flame Test (Height of Burned Area in Inches) After Washing in Soap Solution for—			Approx. Per Cent by Wt. of "Add-on" Based on the Dry Wt. of the Cloth	Total Tensile Strength in Lbs. (Warp plus Filling)
	10 Min.	1 Hr.	3 Hrs.		
Untreated	(²)			0	100
Treated, about 40% solids in composition (A)	3.2	3.9	3.9	34	97
Treated, about 35% solids in composition (B)	3.3	3.9	4.4	30	90
Treated, about 30% solids in composition (C)	3.9	3.8	4.7	25.5	90
Treated, (A)+5% MMD ¹	2.8	3.7	4.6	40	105
Treated, (B)+10% MMD	2.7	3.3	4.1	40	104
Treated, (C)+15% MMD	3.0	3.6	4.1	40	96

¹ "MMD" represents monomethylol dicyandiamide.

² Burned completely.

a cured or substantially water-insoluble state. The wet pick-up was approximately 85% in the case of cotton textiles and approximately 100% with rayon and woolen textiles. The flame re-

EXAMPLE 3

This example illustrates the results obtained when dicyandiamide and formaldehyde in the

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approximate proportions to form monomethylol dicyandiamide and dimethylol dicyandiamide are used in place of corresponding amounts of the said methylol compounds.

	Formulation II	Formulation III
Trimethylol melamine.....	5.0	5.0
Dicyandiamide.....	21.2	18.4
HCHO (in the form of an aqueous soln.).....	7.6	13.2
Aqueous phosphoric acid (about 85% H ₃ PO ₄).....	15.0	15.0
Water.....	55.0	55.0

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with other variations in the proportions of the heat-curable reaction product, specifically trimethylol melamine, the oxygen-containing acid of phosphorus, specifically phosphoric acid, and the methylol dicyandiamide, specifically monomethylol dicyandiamide. For the purpose of comparison test results also are included wherein the phosphoric acid or the methylol dicyandiamide was omitted from the formulation. The various compositions were used in treating 80 x 80 cotton sheeting. The per cent given for each ingredient refers to the weight percentage thereof in the aqueous flameproofing composition, the re-

Table of Example 3

80 x 80 Cotton Sheeting	Vertical Flame Test (Height of Burned Area in Inches) After Washing in Soap Solution for—				Total Tensile Strength in Lbs. (Warp plus Filling)
	10 Min.	1 Hr.	3 Hrs.	5 Hrs.	
Untreated.....	(¹)				100
Treated with Formulation II.....	3.0	3.8	4.5	4.7	110
Treated with Formulation III.....	2.8	4.7			79

¹ Burned completely.

From the foregoing results it will be seen that it is not essential that preformed monomethylol

mainder (bringing the total to 100%) being water.

Table of Example 4

Per Cent Trimethylol melamine	Per Cent Monomethylol Dicyandiamide	Per Cent Phosphoric Acid (85% H ₃ PO ₄)	Vertical Flame Test (Height of Burned Area in Inches)			Remarks
			After Rinsing	After Washing in Soap Soln. for—		
				1 Hr.	5 Hrs.	
2	25	10	3.3	4.7	-----	No loss in t. s. ¹
10	25	10	2.7	3.0	3.4	About 15% gain in t. s.
20	25	10	2.9	3.7	-----	Treated cotton was very stiff.
2½	25	15	3.6	3.9	-----	No loss in t. s.
5	25	15	2.9	3.1	3.6	About 5% gain in t. s.
15	25	15	3.0	3.0	2.5	About 30% gain in t. s.
5	10	10	4.0	7.1	-----	About 25% loss in t. s.
5	25	5	4.0	6.4	-----	About 5% loss in t. s.
5	25	15	2.9	3.1	3.4	About 5% gain in t. s.
5	25	20	2.8	3.1	3.5	About 10% gain in t. s.
5	25	25	2.9	3.1	3.7	About 1% loss in t. s.
5	25	30	2.8	2.9	4.2	About 35% loss in t. s.
5	35	15	3.4	3.1	3.6	About 10% gain in t. s.
10	25	5	3.7	4.1	-----	
10	25	10	2.7	3.0	3.4	About 15% gain in t. s.
10	25	20	2.7	2.9	-----	
5	25	0	(2)	-----	-----	
2	0	10	(2)	-----	-----	
5	0	10	(2)	-----	-----	

¹ "t. s." means "tensile strength."

² Burned completely.

dicyandiamide or dimethylol dicyandiamide be employed, but that the ingredients and proportions thereof used in preparing said compounds likewise can be employed. However, we prefer to use monomethylol dicyandiamide (or monomethylol dicyandiamide plus added formaldehyde) or dimethylol dicyandiamide instead of dicyandiamide and formaldehyde as described in the foregoing example, because of the better solubility characteristics of the methylol derivatives.

EXAMPLE 4

This example illustrates the results obtained

EXAMPLE 5

This example illustrates the use of various modifiers in the primary flameproofing compositions of our invention, which ordinarily and advantageously contain a heat-curable (preferably a water-soluble, heat-curable) melamine-formaldehyde or an alkylated, specifically methylated, melamine-formaldehyde reaction product, a methylol dicyandiamide and a water-stable phosphoric acid, e. g., H₃PO₄. More particularly the modifiers used in this example were phosphates, specifically guanylurea phosphate and methylguanylurea phosphate. The various com-

positions were used in treating 5.5 oz. white poplin. After impregnating the test pieces, they were dried for 3 minutes at 250° F. followed by heating for 5 minutes at 340° F. to insolubilize (cure) the impregnant. All washings were carried out at 160° F., using water containing 0.1% soap and 0.1% sodium carbonate. The rinsed and washed samples were dried for 10 minutes at 200° F. before testing. As in the preceding example and heading of the tabulated data, the percent given for each ingredient refers to the weight percentage thereof in the aqueous flameproofing composition, the remainder (bringing the total to 100%) being water. For purpose of comparison, the results obtained with an unmodified flameproofing composition also are given. The total tensile strength of the untreated poplin (warp plus filling) was 132 pounds.

Table of Example 5

5% Trimethylol Melamine Plus—				Vertical Flame Test (Height of Burned Area in Inches)		Total Tensile Strength in Lbs. (Warp plus Filling)
Monomethylol Dicyandiamide, Per Cent	Guanylurea Phosphate, Per Cent	Methyl-guanylurea Phosphate Per Cent	Phosphoric Acid (85% H ₃ PO ₄), Per Cent	After Rinsing	After Washing for 1 Hr.	
25	0	0	15	2.9	3.9	144
22.5	5	0	12.5	2.8	4.2	143
20	10	0	10	2.9	4.8	135
17.5	15	0	7.5	2.8	—	148
22.5	0	5	12.5	2.7	4.1	148
20.0	0	10	10	2.7	3.9	154
17.5	0	15	7.5	2.7	3.9	149

¹ Also 4.1 after washing for 3 hours.

² 4.5 after washing for 3 hours.

EXAMPLE 6

This example illustrates the results obtained when dimethylol dicyandiamide or a mixture of monomethylol and dimethylol dicyandiamides is used in place of monomethylol dicyandiamide alone in our flameproofing compositions. For comparative purposes the results obtained with monomethylol dicyandiamide alone are also given. The textile treated was 80 x 80 cotton sheeting. The compositions were as follows:

	Formulation				
	I	IV	V	VI	VII
Trimethylol melamine	5	5	5	10	10
Monomethylol dicyandiamide	25	—	12.5	25	—
Dimethylol dicyandiamide	—	25	12.5	—	25
Aqueous phosphoric acid (about 85% H ₃ PO ₄)	15	15	15	10	10
Water	55	55	55	55	55

The test data are given in the table which follows:

Table of Example 6

80 x 80 Cotton Sheeting	Vertical Flame Test (Height of Burned Area in Inches)				Total Tensile Strength in Lbs. (Warp plus Filling)
	After Rinsing	After Washing in Soap Sol'n. for—			
		1 Hr.	3 Hrs.	5 Hrs.	
Untreated	(¹)				144
Treated with Formulation I	2.6	3.0	3.4	3.8	157
Treated with Formulation IV	2.8	2.8	3.1	3.6	142
Treated with Formulation V	2.5	2.9	3.2	3.9	149
Treated with Formulation VI		2.7	2.9	3.5	143
Treated with Formulation VII		3.0	3.3	3.7	149

¹ Burned completely.

Instead of a 50-50 mixture of monomethylol and dimethylol dicyandiamides as used in Formulation V, a mixture of these methylol derivatives in any proportions can be used, e. g., from 1 to 99% of the one to from 99 to 1% of the other.

EXAMPLE 7

The same procedures and formulations are followed as described under Examples 1 to 6, inclusive, with the exception that instead of trimethylol melamine there is used in each case an identical amount of one or another of the following:

- Dimethylol melamine,
- Tetramethylol melamine,
- Pentamethylol melamine,
- Hexamethylol melamine,

or a mixture of any or all of the aforementioned methylol melamines in any proportions with each other, or a mixture of any or all of them in any proportions with trimethylol melamine. Similar results are obtained. For purposes of illustration specific formulations using dimethylol melamine and the results of tests on 80 x 80 cotton sheeting treated with the compositions are given below:

	Formulation	
	VIII	IX
Dimethylol melamine	5	10
Monomethylol dicyandiamide	25	25
Aqueous phosphoric acid (about 85% H ₃ PO ₄)	15	10
Water	55	55

80 x 80 Cotton Sheeting	Vertical Flame Test (Height of Burned Area in Inches)			
	After Rinsing	After Washing in Soap Solution for—		
		1 Hr.	3 Hrs.	5 Hrs.
Untreated.....	(¹)	-----	-----	-----
Treated with Formulation VIII.....	3.1	3.0	4.7	-----
Treated with Formulation IX.....	3.1	3.0	3.1	3.8

¹ Burned completely.

EXAMPLE 8

The same procedures and formulations are followed as described under Examples 1 to 6, inclusive, with the exception that instead of trimethylol melamine there is used in each case an identical amount of dimethylol urea. Similar flame-resisting products are obtained but greater difficulty is encountered in applying the material because of the poorer stability of the aqueous compositions containing dimethylol urea. Hence the melamine-formaldehyde reaction products are preferred.

EXAMPLE 9

The same procedures and formulations are followed as described under Examples 1 to 6, inclusive, with the exception that instead of trimethylol melamine there is used in each case an identical amount of a mixture of mono- and dimethylol ureas, more particularly a mixture of from 1 to 25% of monomethylol urea and from 99 to 75% of dimethylol urea, specifically a 50-50 mixture of each. Results similar to those described under Example 8 are obtained.

EXAMPLE 10

The same procedures and formulations are followed as described under Examples 1 to 6, inclusive, with the exception that instead of trimethylol melamine there is used in each case a mixture of (1) a polymethylol melamine (di-, tri-, tetra-, penta- or hexamethylol melamine, or a mixture of any or all of them) and (2) dimethylol urea, in any proportions, more particularly from 1 to 99% of the ingredient of (1) to from 99 to 1% of the ingredient of (2). Similar results are obtained.

EXAMPLE 11

The same procedures and formulations are followed as described under Examples 1 to 6, inclusive, with the exception that instead of trimethylol melamine there is used in each case an identical amount of one or another of the following alkyl (specifically methyl) ethers of polymethylol melamines:

Methyl ether of dimethylol melamine,
Methyl ether of trimethylol melamine,
Methyl ether of tetramethylol melamine,
Methyl ether of pentamethylol melamine,
Methyl ether of hexamethylol melamine,

or a mixture of any or all of the aforementioned ethers in any proportions with each other. These ethers also properly may be described as being methylated (methyl alcohol-reacted) di-, tri-, tetra-, penta- and hexamethylol melamines. The preparation of methylated and other alkylated methylol melamines which can be used in practicing our invention is described, for instance, in Johnstone, Jr., et al. Reissue Patent No. 22,566.

For purpose of illustration specific formulations using a methylated trimethylol melamine and a methylated hexamethylol melamine, as well as the results of tests on 80 x 80 cotton sheeting treated with the compositions, are given below.

	Formulation			
	X	XI	XII	XIII
Methylated trimethylol melamine.....	5	10	-----	-----
Methylated hexamethylol melamine.....	-----	-----	5	10
Monomethylol dicyandiamide.....	25	25	25	25
Aqueous phosphoric acid (about 85% H ₃ PO ₄).....	15	10	15	10
Water.....	55	55	55	55

80 x 80 Cotton Sheeting	Vertical Flame Test (Height of Burned Area in Inches)			
	After Rinsing	After Washing in Soap Solution for—		
		1 Hr.	3 Hrs.	5 Hrs.
Untreated.....	(¹)	-----	-----	-----
Treated with Formulation X.....	3.0	3.3	3.4	3.7
Treated with Formulation XI.....	3.2	3.4	3.4	3.7
Treated with Formulation XII.....	2.8	3.1	3.3	4.5
Treated with Formulation XIII.....	2.9	3.1	3.6	3.5

¹ Burned completely.

Instead of the ethers of methylol melamines mentioned under this example, we can use a mixture of any or all of the said ethers in any proportions with any one or more, or all, of the following:

Dimethylol urea,
Dimethyl ether of dimethylol urea,
Dimethylol melamine,
Trimethylol melamine,
Tetramethylol melamine,
Pentamethylol melamine, or
Hexamethylol melamine.

Similar results are obtained.

It will be understood, of course, by those skilled in the art that in the foregoing and other examples herein where reference is made to a urea or melamine derivative, more particularly to a methylol urea or a methylol melamine, it is not necessary to use a pure compound or mixture of pure compounds. Instead we can use such compounds or mixtures thereof as commercially produced or reaction products of formaldehyde and urea and/or melamine wherein the reaction has proceeded somewhat beyond the methylol stage so that resinification to some extent has occurred. However, it is usually desirable to employ such reaction products while they are still in essentially a water-soluble (or readily water-dispersible) or a phosphoric acid-soluble stage.

EXAMPLE 12

The same procedures and formulations are followed as described under Examples 1 to 6, inclusive, with the exception that instead of trimethylol melamine there is used in each case an identical amount of a dialkyl (specifically dimethyl) ether of dimethylol urea. Similar results are obtained.

EXAMPLE 13

The same procedures and formulations are followed as described under Examples 1 to 6, inclusive, with the exception that instead of trimethylol melamine there is used in each case an identical amount of a mixture of (1) the monomethyl ether of monomethylol urea and (2) the dimethyl ether of dimethylol urea, more particularly a mixture of from 1 to 25% of the monomethyl ether of (1) and from 99 to 75% of the dimethyl ether of (2), specifically a 50-50 mixture of each. Similar results are obtained.

EXAMPLE 14

This example illustrates the properties of mercerized voile before and after treatment with flameproofing compositions of our invention. The treated voile possessed good resistance to flame.

Table A of Example 14

Mercerized Voile	Gurley Stiffness in Mg.		
	After Rinsing	After Washing in Soap Solution for— ¹	
		5 Hrs.	10 Hrs.
Untreated.....	5.9	2.9	2.8
Treated with Formulation I (see Ex. 6), about 35% solids ²	127.8	32.6	20.8
Treated with Formulation I, about 10% solids ³	15.9	6.5	4.6
Treated with Formulation VI (see Ex. 6), about 35% solids.....	147.0	78.5	55.9
Treated with Formulation VI, about 10% solids.....	21.2	8.5	6.8

¹ The apparatus and method employed in making this test are described, for example, in Bulletin No. 1600 published by W. & L. E. Gurley, Troy, N. Y.

² The composition was diluted with water before use to give a solution containing about 35% by weight of solids.

³ The composition was diluted with water before use to give a solution containing about 10% by weight of solids.

Table B of Example 14

Mercerized Voile	Total Tensile Strength in Lbs. (Warp plus Filling)		
	After Rinsing	After Washing in Soap Solution for—	
		5 Hrs.	10 Hrs.
Untreated.....	48	47	43
Treated with Formulation I, about 35% solids.....	52	35	41
Treated with Formulation I, about 10% solids.....	41	42	39
Treated with Formulation VI, about 35% solids.....	40	41	37
Treated with Formulation VI, about 10% solids.....	44	42	38

Table C of Example 14

Mercerized Voile	Warp Shrinkage in Per Cent After Washing in Soap Solution for—		
	1 Hr.	2 Hrs.	3 Hrs.
Untreated.....	2.8	3.6	3.9
Treated with Formulation I, about 35% solids.....	0.8	1.1	1.1
Treated with Formulation I, about 10% solids.....	0.8	1.1	1.4
Treated with Formulation VI, about 35% solids.....	0.6	0.8	0.8
Treated with Formulation VI, about 10% solids.....	0.8	0.8	1.1

EXAMPLE 15

This example illustrates the results of treating mercerized voile with Formulations I and VI (see Example 6) without diluting it with water to a lower concentration of solids.

Table of Example 15

After Rinsing or Washing in Soap Solution for Stated Period.	Vertical Flame Test (Height of Burned Area in Inches)	Total Tensile Strength in Lbs. (Warp plus Filling)	Gurley Stiffness in Mg.	Total T. B. L. Crease Resistance in Cm. (Warp plus Filling)	Taber Abrasion Resistance (Number of Cycles)
MERCERIZED VOILE, UNTREATED					
Rinsed.....	Burned completely.	49	2.7	4.2	632
Washed 1 hr.....	do.....	40	2.8	4.4	588
Washed 3 hrs.....	do.....	46	2.7	4.3	643
Washed 5 hrs.....	do.....	47	2.8	4.2	692
TREATED WITH FORMULATION I					
Rinsed.....	3.0	60	54	4.9	492
Washed 1 hr.....	3.2	51	17	4.8	582
Washed 3 hrs.....	3.5	47	12	4.8	386
Washed 5 hrs.....	4.7	44	8	5.0	630
TREATED WITH FORMULATION VI					
Rinsed.....	3.4	59	115	4.5	1072
Washed 1 hr.....	3.3	56	81	3.9	1115
Washed 3 hrs.....	3.4	53	46	4.6	591
Washed 5 hrs.....	3.8	43	34	4.2	640

EXAMPLE 16

This example illustrates the results of treating mercerized poplin with Formulations I and VI, and both with and without calendering the treated poplin after it has been dried and before it has been cured.

Table of Example 16

After Rinsing or Washing in Soap Solution for Stated Period.	Vertical Flame Test (Height of Burned Area in Inches)	Total Tensile Strength in Lbs. (Warp plus Filling)	Gurley Stiffness in Mg.	Total T. B. L. Crease Resistance in Cm. (Warp plus Filling)	Taber Abrasion Resistance (Number of Cycles)
MERCERIZED POPLIN, UNTREATED					
Rinsed.....	Burned completely.	144	15	3.9	1522
Washed 1 hr.....	do.....	144	16	4.2	1692
Washed 3 hrs.....	do.....	137	17	3.8	1639
Washed 5 hrs.....	do.....	139	18	4.0	1654
TREATED WITH FORMULATION I, UNCALENDERED					
Rinsed.....	2.7	139	256	5.8	2839
Washed 1 hr.....	3.2	137	57	5.2	1752
Washed 3 hrs.....	3.1	129	43	5.3	1918
Washed 5 hrs.....	4.1	128	31	5.1	1331
TREATED WITH FORMULATION I, COLD CALENDERED					
Rinsed.....	2.9	126	66	5.4	1637
Washed 1 hr.....	3.1	98	56	5.3	1308
Washed 3 hrs.....	3.4	91	32	5.5	1538
Washed 5 hrs.....	4.5	90	29	5.2	1387
TREATED WITH FORMULATION VI, UNCALENDERED					
Rinsed.....	2.9	145	345	5.4	3672
Washed 1 hr.....	3.3	132	194	5.4	3090
Washed 3 hrs.....	3.2	135	93	5.6	2954
Washed 5 hrs.....	3.7	124	72	5.6	2217
TREATED WITH FORMULATION VI, COLD CALENDERED					
Rinsed.....	2.9	127	115	5.6	1964
Washed 1 hr.....	3.4	99	60	5.9	1379
Washed 3 hrs.....	3.4	107	47	6.0	2562
Washed 5 hrs.....	4.0	102	44	5.5	2052

In the table of Example 16, it will be noted from the results of Gurley stiffness tests on the

The phosphorous acid was used in the form of a 30% aqueous solution, and the amount of water specified in Formulation XV includes that which is present in the phosphorous acid.

The above compositions were used in treating

80 x 80 cotton sheeting. The results were as follows:

Table of Example 17

80 x 80 Cotton Sheeting	Vertical Flame Test (Height of Burned Area in Inches)				Total Tensile Strength in Lbs. (Warp plus filling)
	After Rinsing	After Washing in Soap Solution for—			
		1 Hr.	3 Hrs.	5 Hrs.	
Untreated.....	(1)	-----	-----	-----	99
Treated with Formulation XIV.....	3.2	3.0	2.9	3.3	104
Treated with Formulation XV.....	-----	3.4	3.7	3.4	73

¹ Burned completely.

rinsed, calendered and uncalendered samples that calendering causes a marked reduction in the stiffness of the treated, rinsed samples.

EXAMPLE 17

This example illustrates the use of flameproofing compositions of our invention in which oxygen-containing acids of phosphorus other than phosphoric (orthophosphoric) acid are employed. The formulations were as follows:

Formulation.....	XIV	XV
Trimethylol melamine.....	5	5
Monomethylol dicyandiamide.....	25	25
Pyrophosphoric acid (100%).....	15	-----
Phosphorous (orthophosphorous) acid.....	-----	15
Water.....	55	55

The proportions of heat-curable reaction product (numerous illustrations of which are given in the various examples), methylol dicyandiamide and oxygen-containing acid of phosphorus, more particularly a phosphoric acid (e. g., H_3PO_4), are critical in producing a durable flame-resistant textile that will satisfy the requirements of the trade. The specified minimum amount of the acid of phosphorus is required in order to obtain adequate flame resistance and retardance of afterglow. On the other hand, if H_3PO_4 or other oxygen-containing acid of phosphorus is used much in excess of the maximum amount specified, then excessive tendering (loss in tensile strength) of the textile occurs. The methylol dicyandiamide and heat-curable melamine-formaldehyde, urea-formaldehyde or melamine-urea-

formaldehyde reaction product should be used within the stated weight proportions in order to obtain optimum flame resistance, durability, tensile strength, crease resistance and shrinkage control. In general, when the proportions of other ingredients and the conditions are the same, an increase in the content of heat-curable (thermosetting or potentially thermosetting) nitrogenous reaction product increases the durability, stiffness and tensile strength of the treated textile. (The heat-curable nitrogenous reaction product initially may be either resinous or potentially resinous, and initially may be normally crystalline but convertible, e. g., under heat, to a resin.) Ordinarily, too (when proportions of other ingredients and conditions are the same), increasing the content of methylol dicyandiamide increases the durability and tensile strength of the treated textile as well as the effectiveness of the treatment. The nitrogen contents of the heat-curable nitrogenous reaction product and of the methylol dicyandiamide also add to the flame resistance of the treated textile, especially in view of the proportions thereof to the oxygen-containing acid of phosphorus, specifically phosphoric acid. An optimum nitrogen-to-phosphorus ratio in the additives generally provides optimum flame resistance when other conditions are the same, but in some cases it may be desirable to sacrifice maximum flame resistance in order to improve other useful properties of the treated textile, e. g., crease resistance, shrinkage resistance, durability, tensile strength, etc.

The fundamental treating compositions of this invention can be modified by incorporating therein various soluble or dispersible modifying agents which aid in further improving the flame-resistant characteristics of the treated material or which facilitate the technique of application. For instance, the compositions can also contain minor amounts (e. g., from 1 to 30% by weight of the total solids content) of such glow retardants as the glow-retarding borates, phosphates, pyrophosphates, etc., e. g., zinc borate, zinc phosphate, zinc ammonium phosphate, stannic phosphate, phenyl diamido phosphate, melamine pyrophosphate, etc. Agents which have a buffering effect on the composition after being applied to the fabric or other textile, e. g., calcium carbonate, magnesium oxide, hexamethylene tetramine and other polyalkylene polyamines, etc., can be incorporated into the treating compositions as desired or as conditions may require. Examples of other dispersible additives are metallic oxides, e. g., zirconium, tin, titanium, antimony and bismuth oxides; and thermally unstable, halogen-containing thermoplastic substances, more particularly such substances containing at least 20% of combined halogen and capable of rupturing under heat at carbon-halogen bonds, including halogen-containing vinyl resins in which not less than 20% by weight of combined halogen is present, for instance polymeric and copolymeric vinyl chloride and others such as are mentioned in Loukowsky et al. co-pending application Serial No. 64,416, filed December 9, 1948, now Patent No. 2,519,388, issued August 22, 1950. The amounts of such oxides and halogen-containing thermoplastic substances in the compositions and their ratio to each other can be the same as are given in the said Loukowsky et al. application.

The present invention is applicable to the production of a wide variety of flame-resistant ma-

terials, e. g., wearing apparel of all kinds, especially children's clothes and clothing used by the armed forces, curtains, draperies, sheeting, furniture coverings, linings for electric blankets, net fabrics, non-woven fabrics, chenilles, etc., and which are made of materials such as are described in the first paragraph of this specification and elsewhere herein. Other applications of the flame-resistant products of our invention include those described in chapters VII and VIII of the aforementioned book, edited by Little, entitled "Flameproofing Textile Fabrics." The compositions of this invention also are useful in the treatment of wood (in veneer or other form) as well as in rendering flame resistant other cellulosic and other normally flammable materials which are not in textile form.

The terms "flame resistance" and "flame-resistant" as used herein and in the appended claims with reference to textile materials are used generically to include within their meanings treated materials (e. g., treated fabrics) which, after ignition, will continue to burn at a relatively slow rate as well as those which, after ignition, will burn over only a limited area beyond that directly exposed to the source of ignition and which may be specifically designated as "fire-resistant" materials. It will be apparent from the examples herein given that most of the products of our invention properly fall within the specific classification of fire-resistant materials.

The terms "textile" and "textile material" as used generically herein and in the appended claims include within their meanings filaments, fibers, rovings, slivers, threads, yarns, twisted yarns, etc., as such or in woven, felted or otherwise formed fabrics, sheets, cloths and the like.

We claim:

1. A composition adapted for use in the treatment of natural cellulosic and other textile materials to impart flame resistance thereto, said composition comprising an aqueous treating agent containing the following initial ingredients in the specified proportions by weight: (1) from 2 to 20 parts of a heat-curable member of the class consisting of methylol melamines, methylated methylol melamines, methylol ureas, methylated methylol ureas, mixtures thereof, and water-soluble reaction products and phosphoric acid-soluble reaction products of the said methylol compounds and of mixtures of the said methylol compounds; (2) from 10 to 35 parts of a methylol dicyandiamide; and (3) an oxygen-containing acid of phosphorus in an amount which is equivalent, based on phosphorus content, to from 5 to 30 parts of 85% H_3PO_4 .

2. A composition as in claim 1 wherein the heat-curable substance of (1) is a polymethylol melamine, and the oxygen-containing acid of phosphorus of (3) is phosphoric acid in the stated amount.

3. A composition as in claim 1 wherein the methylol dicyandiamide of (2) is monomethylol dicyandiamide, and the oxygen-containing acid of phosphorus of (3) is phosphoric acid in the stated amount.

4. A composition adapted for use in the treatment of natural cellulosic and other textile materials to impart flame resistance thereto, said composition comprising an aqueous solution containing the following initial ingredients in the specified proportions by weight: (1) from about 5 to 10 parts of a polymethylol melamine; (2) about 20 to 30 parts of monomethylol dicyandi-

amide; and (3) phosphoric acid in an amount corresponding to from about 10 to 15 parts of 85% H_3PO_4 .

5. A composition as in claim 4 wherein the reaction product of (1) is trimethylol melamine.

6. The method which comprises impregnating a textile material to be rendered flame-resistant with an aqueous composition containing the following initial ingredients in the specified proportions by weight: (1) from 2 to 20 parts of a heat-curable member of the class consisting of methylol melamines, methylated methylol melamines, methylol ureas, methylated methylol ureas, mixtures thereof, and water-soluble reaction products of the said methylol compounds and of mixtures of the said methylol compounds; (2) from 10 to 35 parts of a methylol dicyandiamide; and (3) an oxygen-containing acid of phosphorus in an amount which is equivalent, based on phosphorus content, to from 5 to 30 parts of 85% H_3PO_4 ; drying the impregnated textile followed by heating the dried textile at a temperature within the range of about 250° F. to about 400° F.; and removing any residual water-soluble substances from the resulting textile.

7. A method as in claim 6 wherein the aqueous composition contains the following initial ingredients in the specified proportions by weight: (1) from about 5 to 10 parts of a polymethylol melamine; (2) about 20 to 30 parts of monomethylol dicyandiamide; and (3) phosphoric acid in an amount corresponding to from about 10 to 15 parts of 85% H_3PO_4 .

8. A method as in claim 6 wherein the textile material which is rendered flame-resistant is a natural cellulose-containing textile.

9. A method as in claim 6 wherein the textile material which is rendered flame-resistant is a wool-containing textile.

10. Flame-resistant textile materials which are normally flammable textile materials impregnated and rendered flame-resistant with the product of heat reaction in situ of a mixture including the following initial ingredients in the specified proportions by weight: (1) from 2 to 20 parts of a heat-curable member of the class consisting of methylol melamines, methylated methylol melamines, methylol ureas, methylated methylol ureas, mixtures thereof, and water-soluble reaction products and phosphoric acid-soluble reaction products of the said methylol compounds and of mixtures of the said methylol compounds; (2) from 10 to 35 parts of a methylol

dicyandiamide; and (3) an oxygen-containing acid of phosphorus in an amount which is equivalent, based on phosphorus content, to from 5 to 30 parts of 85% H_3PO_4 .

11. Flame-resistant textile materials as in claim 10 wherein the heat-curable substance of (1) is a polymethylol melamine, and the oxygen-containing acid of phosphorus of (3) is phosphoric acid in the stated amount.

12. Flame-resistant textile materials as in claim 10 wherein the methylol dicyandiamide of (2) is monomethylol dicyandiamide, and the oxygen-containing acid of phosphorus of (3) is phosphoric acid in the stated amount.

13. Flame-resistant textile materials as in claim 10 wherein the methylol dicyandiamide of (2) is dimethylol dicyandiamide, and the oxygen-containing acid of phosphorus of (3) is phosphoric acid in the stated amount.

14. Flame-resistant cotton cloth which is impregnated with the product of heat reaction in situ of a mixture including the following initial ingredients in the specified proportions by weight: (1) from about 5 to 10 parts of polymethylol melamine; (2) about 25 parts of monomethylol dicyandiamide; and (3) phosphoric acid in an amount corresponding to from about 10 to 15 parts of 85% H_3PO_4 .

15. Flame-resistant wool-containing fabric material which is impregnated with the product of heat reaction in situ of a mixture including the following initial ingredients in the specified proportions by weight: (1) from about 5 to 10 parts of a polymethylol melamine; (2) about 25 parts of monomethylol dicyandiamide; and (3) phosphoric acid in an amount corresponding to from about 10 to 15 parts of 85% H_3PO_4 .

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