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[54] **PROCESS FOR RENDERING CELLULOSE-CONTAINING FABRICS DURABLY FLAME-RETARDANT BY WET-CURING A MELAMINE RESIN AND A PHOSPHORIC ACID AMIDE ON THE FABRIC**
14 Claims, No Drawings

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[50] **Field of Search** 8/116.2, 116.3; 117/136

[56] **References Cited**

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ABSTRACT: Cellulose-containing fabrics are rendered durably flame-retardant by coreacting on said fabric

a. a melamine derivative prepared by reacting a melamine with formaldehyde or formaldehyde and an alkanol, and

b. a phosphoric amide.

During said coreaction the moisture content of said fabric is maintained at a minimum of 10 percent by weight based on the weight of the fabric. By this procedure durable flame-retardancy is obtained without undue deterioration of the mechanical strength and hand of the fabric.

PROCESS FOR RENDERING CELLULOSE-CONTAINING FABRICS DURABLY FLAME-RETARDANT BY WET-CURING A MELAMINE RESIN AND A PHOSPHORIC ACID AMIDE ON THE FABRIC

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a process for rendering cellulose-containing fabrics flame-retardant by forming on said fabrics an insoluble product containing nitrogen and phosphorus.

Description of the Prior Art

Heretofore cellulose-containing fabrics have been rendered flame-retardant by procedures which deposit on the fabric compounds containing nitrogen and phosphorus. However, it is difficult to obtain satisfactory flame-retardancy without deteriorating other properties to the extent that the product is commercially unacceptable.

In an article by Frick et al. entitled "Development of Durable Flame-Retardant Finishes for Cotton," published Nov. 1958, Wright Air Development Center Technical Report WADC TR 58-130, there is disclosed treating cellulosic fabric with a mixture of methylolmelamine and the reaction product of formaldehyde and N,N',N''-trimethylphosphoric triamide, using an acid yielding fixation catalyst (either alkanolamine hydrochloride or magnesium chloride). Fixation was carried out by dry-curing at 160° C. for 5 minutes. The flame retardant fixation thus produced had poor durability and there was a large reduction in the tear strength of the treated fabric. When the reaction product of formaldehyde and N,N',N''-trimethylphosphoric triamide was applied without the methylolmelamine there was little or no reaction and the durability of the fixation was very poor.

SUMMARY OF THE INVENTION

In accordance with the present invention durable flame-retardancy of cellulose-containing fabrics is obtained without unduly deteriorating the fabric's physical properties and hand. The fabric is impregnated with a melamine derivative, prepared by reacting melamine with either formaldehyde or formaldehyde and an alkanol, and an amide of phosphoric acid and an insoluble coreaction product is formed in the presence of moisture such as by steaming.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a method of rendering cellulose-containing fabrics durably flame-retardant by forming on said fabrics insoluble reaction products containing phosphorus and nitrogen. The fabric is impregnated with a melamine derivative and an amide of phosphoric acid and then an insoluble reaction product is formed in the presence of moisture. Preferably the amount of reaction product formed on the fabric is such that the phosphorus content is equal to about 0.5 to 4 percent by weight of the finished fabric and the amount of nitrogen is equal to about 1.0 to 15 percent of the weight of the finished fabric.

The melamine derivative is an N-methylol derivative of melamine having from 2 to 6 methylol groups or a lower alkyl ether derived from such an N-methylol compound wherein the sum of $-CH_2OH$ groups and $-CH_2OR$ groups is from 2 to 6 with R being a lower alkyl group of 1 to 3 carbon atoms and preferably being methyl. The N-methylol compounds can be prepared by reacting melamine with 2 or more moles of formaldehyde according to known procedures. The methyl ethers can be prepared by known procedures such as by reacting the N-methylol compounds with an alkanol or coreacting melamine, formaldehyde and alkanol, said alkanol containing 1 to 3 carbon atoms and preferably being methanol. If desired, mixtures of the above-described melamine derivatives can be used.

The amides of phosphoric acid which can be used in the present invention have the formula

$$OP(NRR')_a(OH)_{3-a}$$

wherein *a* is an integer of from 1 to 3, R and R' at each occurrence are independently selected from the group consisting of hydrogen, methyl, ethyl, hydroxymethyl and methoxymethyl provided that at least one of hydrogen, hydroxymethyl or methoxymethyl must be attached to each nitrogen atom. Illustrative phosphoric amides suitable for use in the present invention are listed on the following table:

Name	Formula
Phosphoric triamide	$OP(-NH_2)_3$
N,N',N''-triethylphosphoric triamide	$OP(-NHC_2H_5)_3$
N,N',N''-trimethylphosphoric triamide	$OP(-NHCH_3)_3$
Phosphoramidic acid	$OP(-OH)_2NH_2$
Phosphorodiamidic acid	$OP(-NH_2)_2OH$
Methylphosphoramidic acid	$OP(-OH)_2NHCH_3$
N,N'-diethylphosphorodiamidic acid	$OP(-NHC_2H_5)_2OH$
N-ethyl-N'-methylphosphorodiamidic acid	HNC_2H_5 | $OP-NHCH_3$ | OH
(Hydroxymethyl)phosphoric triamide	$OP(-NH_2)_2NHCH_2OH$
N,N'-bis(hydroxymethyl)phosphoric triamide	$OP(-NHCH_2OH)_2NH_2$
N,N',N''-tris(hydroxymethyl)phosphoric triamide	$OP(-NHCH_2OH)_3$
N,N,N',N''-tetrakis(hydroxymethyl)phosphoric triamide	$OP(-NHCH_2OH)_2$ | $N(-CH_2OH)_2$
Pentakis(hydroxymethyl)phosphoric triamide	$OP[-N(-CH_2OH)_2]_2$ | $HNCH_2OH$
Hexakis(hydroxymethyl)phosphoric triamide	$OP[-N(-CH_2OH)_2]_3$
N-(hydroxymethyl)-N,N',N''-trimethylphosphoric triamide	$OP(-NHCH_3)_2$ | CH_3NCH_2OH
N,N'-bis(hydroxymethyl)-N,N',N''-trimethylphosphoric triamide	$OP[-N(CH_3)CH_2OH]_2$ | $HNCH_3$
N,N',N''-tris(hydroxymethyl)-N,N'N''-trimethylphosphoric triamide	$OP[-N(CH_3)CH_2OH]_3$
N,N',N''-tris(methoxymethyl)-N,N',N''-trimethylphosphoric triamide	$OP[-N(CH_3)CH_2OCH_3]_3$
N,N',N''-triethyl-N-(hydroxymethyl)phosphoric triamide	$OP(-NHC_2H_5)_2$ | $C_2H_5NCH_2OH$
N,N',N''-triethyl-N,N'-bis(hydroxymethyl)phosphoric triamide	$OP[-N(C_2H_5)CH_2OH]_2$ | HNC_2H_5
N,N',N''-triethyl-N,N',N''-tris(methoxymethyl)phosphoric triamide	$OP[-N(C_2H_5)CH_2OCH_3]_3$

Particularly outstanding results are obtained when the phosphoric amide is phosphoric triamide, N,N',N''-trimethylphosphoric triamide, phosphorodiamidic acid, N,N'-tris(hydroxymethyl)phosphoric -tris(hydroxymethyl)-N,N',N''trimethylphosphoric triamide and N,N',N''-triethyl-N,N'N''(hydroxymethyl)phosphoric triamide.

The phosphoric amide and melamine derivatives can be applied from an aqueous solution or dispersion by padding, brushing, spraying or other impregnation technique. Preferably the phosphoric amide and melamine derivative are applied from the same aqueous medium. The mole ratios of the two coreactants can be varied considerably. Generally, about 0.1 to 3 moles of phosphoric amide are applied for each mole of melamine derivative with the use of 0.3 to 1.2 moles of phosphoric amide per mole of melamine derivative being preferred. It is preferred that after the formation of the insoluble coreactant, the add-on of bound phosphorus be about 0.5 to 4 percent by weight and the add-on of bound nitrogen be about 1 to 15 percent by weight, said weights being based on the weight of the finished fabric, i.e., fabric plus the flame-retardant coreaction product. The concentration of individual coreactants in the impregnation bath and the wet pickup are adjusted to give the desired add-ons of phosphorus and nitrogen.

To avoid unduly deteriorating the physical strength of the fabrics, and to obtain fabrics having good hand, the coreactants cannot be insolubilized by dry heat, but rather wet-fixation procedures must be used. In such wet-fixation, the coreactants are formed into an insoluble product, generally at a temperature of about 20° to 110° C. while the moisture content of said fabric is maintained at a level of at least 10 percent based on the weight of the fabric. Wet-fixation is preferably accomplished by contacting the impregnated fabric with saturated steam. Alternatively, wet-fixation can be carried out at lower temperatures by maintaining the fabric in a moist environment at a temperature and for a period of time sufficient to form an insoluble product. For instance, the fabric can be impregnated with an aqueous solution of the coreactants, the fabric wrapped in polyethylene while a substantial amount of water remains in the fabric, and the wrapped fabric stored at a temperature of at least 20° C. until the desired degree of insolubilization is reached.

Use of wet-fixation, rather than dry-curing, greatly reduces the amount of cross-linking of the coreactants with cellulose, thus eliminating undue loss of fabric strength. It appears from the minimal crease-recovery properties of wet-fixed fabric, that wet-fixation induces co-condensation reactions between the melamine derivatives and the phosphoric amide instead of cross-linking The resulting copolymers are insoluble and are fixed (i.e., attached) to the cellulose by mainly noncovalent forces. That is, it appears that cellulose, under the conditions of wet fixation, is not involved to an appreciable extent in condensation reactions leading to cross-linking or other reactions resulting in chemical attachment. Nevertheless, after wet-fixation, the fabric is dimensionably stable.

The foregoing theory that co-condensation dominates while cross-linking is minimized is one of the several possible mechanisms occurring in wet fixation. Without wishing to be bound by any particular theory, another situation to consider in wet-fixation is that the wet swollen state of the fibers not only minimizes cross-linking of the cellulose, but makes less confining or less effective those few cross-links which are formed. What cross-links result are formed when fibers are distended, and hence the treated structure retains a high degree of unrestrained flexibility even later on in the dry state.

It is advantageous to catalyze the wet-fixation by the addition of a catalyst. The amount of catalyst generally useful is from about 0.5 to 12 percent of the total amount of coreactant. Suitable catalysts include acids, acid-forming salts, i.e., salts of strong acids and weak bases, and oxidizing agents. Illustrative of such catalyzing compounds are formic acid, citric acid, tartaric acid, oxalic acid, glycolic acid, lactic acid, malonic acid, succinic acid, hydrochloric acid, sulfuric acid, zinc tetrafluoroborate, zinc nitrate, zinc chloride, magnesium chloride, magnesium nitrate, amine hydrochlorides such as 2-amino-2-methyl-1-propanol hydrochloride or N,N',N''-nitrilotriethanol hydrochloride; ammonium salts such as ammonium tartrate, citrate, oxalate, formate, nitrate, or ammonium dihydrogen phosphate; and peroxy compounds such as hydrogen peroxide, peroxymonosulfates of alkali metals or of ammonium such as potassium peroxydisulfate and ammonium peroxydisulfate.

The aqueous dispersion containing the coreactants and catalyst also may contain adjuncts for other purposes, such as wetting agents and antimicrobial agents. For instance, it is on occasion advisable to add a wetting agent if it is necessary to improve penetration and evenness.

After the coreactants (phosphoric amide and melamine derivative) have been wet-fixed on the fibrous cellulosic material and thereby made insoluble, the material is preferably washed to rinse out any residual chemicals, such as catalysts, and dried, as on a tenter frame in a forced-draft oven. (The washing step may be carried out in boiling water, if desired.) The flame-retardant finish which results is durable through repeated cycles of laundering and drying.

If the fabric is subjected to acid-catalyzed dry aftercuring subsequent to the wet-fixation treatment, such as by heating at 150° to 170° C. in the presence of acid or acid-forming salt, cross-linking of the fabric takes place and durable press properties are imparted. However, such dry aftercuring results in deterioration of the physical properties of the fabric. While this deterioration of physical properties is not as great as when no wet-fixation is employed, dry-aftercuring should generally be avoided.

The present invention can be used with cellulose-containing fabrics which are knitted, woven and nonwoven. The cellulose can be from any source, including such natural sources as seed hairs such as cotton, bast fibers such as flax (linen), ramie, jute, and hemp, as well as regenerated cellulose such as rayon, where wood may serve as the source. The benefits obtainable through this invention are most noticeable with fabrics whose fibers are wholly cellulosic, but blended fabrics such as cotton-polyester blends can be used wherein up to 50 percent of the fibers are noncellulosic.

The following examples are given to further illustrate the invention, but it is understood that the invention is not to be limited in any way by the details described therein. In the examples percents and parts are by weights unless otherwise specified.

ANALTICAL AND TEST METHODS EMPLOYED IN THE EXAMPLES

Bound Nitrogen, N in percent: Determined by Kjeldahl digestion, followed by titration of the distilled ammonia.

Bound Phosphorus, P in percent: Determined by Kjeldahl digestion, followed by colorimetric analysis employing acetone-water to intensify the phosphomolybdate color: Bernhart et al. *Anal. Chem.*, Vol. 27, 440 (1955).

Flame Retardancy (Vertical Test), char length in inches: AATCC 34-1966. A char length of about 6 inches or shorter is passable.

Flame Retardancy (Limiting Oxygen Index), the minimum value of the volume fraction (expressed in decimal form) of oxygen in a metered oxygen-nitrogen mixture, using a flammability index tester (Type FL-101, General Electric Co.): C. P. Fenimore and F. J. Martin, *Combustion and Flame*, Vol. 10, No. 2, 135 (June 1966), and *Modern Plastics*, Vol. 43, No. 11, 141 (Nov. 1966). Generally a limiting oxygen index of about 0.260 or greater is passable. Dry Crease Recovery, total of angular degrees in warp (W) and filling (F) directions: ASTM D 1295-60T.

Wet Crease Recovery: The fabric was first soaked for 5 minutes at approximately 21° C. in an aqueous 0.1 percent solution of a nonionic detergent composed of a mixture of compounds of the formula $(CH_3)_3CCH_2C(CH_3)_2$-p-C_6H_4(-

$OCH_2CH_2)_xOH$ wherein x is close to and averages 10, then the excess solution was removed by blotting, and promptly the recovery angle was measured in the same manner as for dry crease recovery.

Flex Abrasion Resistance, in cycles: ASTM D 1175-44T (0.5-pound head weight and 2-pound toggle tension on a Stoll Flex Abrader).

Laundering: AATCC 88A-1964T, Test III, home-type washer, 5-pound load, full cycle, 60° C., synthetic detergent; tumble drying.

Shrinkage: Markings were placed 10 inches apart in both the warp and filling directions of the fabric before laundering. After 10 cycles of laundering and tumble drying, the distance between markers was measured in both directions, and shrinkage was expressed in percent for each direction.

Stiffness (Cantilever), in mg.—cm.: ASTM ASTM D 1388-64.

Tear Strength (Elmendorf), in pounds: ASTM D 1424-59.

Tensile (Breaking) Strength (1-inch ravelled strip), in pounds: ASTM D 1682-63.

ABBREVIATIONS

OWB: On the weight of the bath used for padding, in percent.
OWF: On the weight of the fabric, in percent.
Wet Pickup (in percent) multiplied by OWB/100 percent equals OWF (in percent).
TMM: Trimethylolmelamine, (s-triazine-2,4,6-triyltriimino)-trimethanol.

EXAMPLE 1

This example illustrates wet-fixation at approximately 40° C. The substrate fabric was all-cotton sheeting in a plain weave (bleached, desized, and weighing 4.3 ounces per square yard). The fabric was impregnated on a laboratory padder with a neutral aqueous solution containing N,N',N''-tris(hydroxymethyl)-N,N',N''-trimethylphosphoric triamide and trimethylolmelamine in the ratio of 0.8:1 by moles, and 0.35 percent hydrogen peroxide. The pressure of the squeeze rolls was adjusted to give a wet pickup of 80 percent. On the weight of the fabric, add-ons were 10 percent for the tris(hydroxymethyl)trimethylphosphoric triamide and 12 percent for the trimethylolmelamine. The padded fabric was dried at room temperature (approximately 21° C.) to a moisture content of 10 percent. Then the fabric was wrapped in polyethylene foil and kept at approximately 40° C. (a technique called "batching") for 48 hours to effect wet-fixation by coreaction of the triamide and trimethylolmelamine. Next, the fabric was washed for 10 minutes at approximately 80° C. in an aqueous solution containing 0.1 percent of sodium carbonate and 0.1 percent of a nonionic detergent [Triton X-100, a mixture of closely related compounds having the formula $(CH_3)_3CCH_2C(CH_3)_2$-p-$C_6H_4(-OCH_2CH_2)_xOH$, with the average value of x being about 10]. Finally, the fabric was neutralized in dilute acetic acid, rinsed in water, dried on a frame in a forced-draft oven, and evaluated. The results were as follows: a weight gain of 19.5 percent; 6.0 percent bound nitrogen; 0.8 percent bound phosphorus corresponding to a 69 percent yield of insolubilized N,N',N''-tris(hydroxymethyl)-N,N',N''-trimethylphosphoric triamide; and in the vertical flame test, char lengths of 4.3 inches before laundering and of 5.5 inches after 50 launderings, proving that the flame-retardant finish was durable.

EXAMPLE 2

This is an illustration of the use of saturated steam for effecting wet-fixation. The procedure resembled that of Example 1, except that the "batching" technique at approximately 40° C. was replaced by exposing the fabric to steam at 101° - 1° C. for 3 minutes in a laboratory steamer. Then the fabric was washed, neutralized, rinsed, and dried as in Example 1, and evaluated. The results are in the accompanying table:

TABLE FOR EXAMPLE 2

	Control data on untreated fabric	
OP[—$N(CH_3)CH_2OH]_3$ add-on OWF, percent	10.4	....
Trimethylolmelamine add-on OWF, percent	12.5	....
Temperature of drying, approx., ° C	21	....
Weight gain, percent	16.1	....
Yield of insolubilized OP[—$N(CH_3)CH_2OH]_3$, percent	75	....
Bound P (as weight percent of treated fabric):		
After rinsing and drying but before laundering, percent	0.9	....
After 25 launderings, percent	0.8	....
After 50 launderings, percent	0.75	....
Char length (vertical flame test):		
After rinsing and drying but before laundering, inches	2.4	....
After 25 launderings, inches	3.1	....
After 50 launderings, inches	3.5	....
Flex abrasion resistance (warp), cycles	510	500
Dry crease recovery (warp+filling), degrees	224	154
Elmendorf tear strength, pounds	1.1	2.2
Stiffness, mg.-cm	500	93

EXAMPLE 3

This example is a variation of Example 2 with respect to catalyst. Instead of 0.35 percent of the pad bath being hydrogen peroxide (as in EXAMPLES 1 and 2), potassium peroxydisulfate was used so it was 0.75 percent on the weight of the fabric. The padded samples were dried for 1.5 minutes at approximately 82° C. in a forced-draft oven and steamed for 3 minutes in a laboratory steamer. Then the fabric was washed, neutralized, rinsed, and dried as in Example 1, and evaluated. The results are in the accompanying table:

TABLE FOR EXAMPLE 3

	Control data on Untreated Fabric	
OP[—$N(CH_3)CH_2OH]_3$ add-on OWF, percent	11.5	....
Trimethylomelamine add-on OWF, percent	15.6	....
Weight gain, percent	19.2	....
Bound P, weight percent of treated fabric:		
After rinsing and drying but before laundering, percent	1.06	....
After 50 launderings, percent	0.9	....
Char length (vertical flame test) after 50 launderings, inches	3.3	....
Limiting oxygen index:		
After rinsing and drying but before laundering	0.275	....
After 25 launderings	0.269	....
After 50 launderings	0.263	....
Elmendorf tear strength (filling):		
After rinsing and drying but before laundering, pound	1.0	1.9
After 10 launderings, pound	0.9	....
Flex abrasion resistance (warp):		
After rinsing and drying but before laundering, cycles	425	500
After 10 launderings, cycles	575	....
Shrinkage after 10 launderings:		
Along Warp, percent	1.0	....
Along Filling, percent	1.0	....

EXAMPLE 4

In this example, latent acid catalysts were used instead of the peroxy compounds of Examples 1, 2 and 3. Pad baths were used which contained either zinc nitrate or magnesium chloride as the catalytic component, in accordance with the accompanying table. Otherwise, the procedure followed that of Example 3. All samples of fabric were washed, neutralized, rinsed, and dried as in Example 1, and evaluated. The results are in the accompanying table:

TABLE FOR EXAMPLE 4

Catalyst formula	$Zn(NO_3)_2$	$MgCl_2$
Amount of catalyst add-on OWF, percent	1	1
OP[—$N(CH_3)CH_2OH]_3$ add-on, OWF percent	10	10
Trimethylolmelamine add-on OWF, percent	12	12
Yield of insolubilized OP[—$N(CH_3)CH_2OH]_3$, percent	90	75
Bound P, weight percent of treated fabric:		
After rinsing and drying but before laundering	1.26	1.07
After 25 launderings	1.25	0.87
After 50 launderings	1.07	0.76
Char length (vertical test), inches, after rinsing and drying but before laundering	3.6	4.0

EXAMPLE 5

In this example, the pad bath had as its catalytic component 1.1 percent of the compound $HOCH_2C(CH_3)_2NH_3Cl$, the

hydrochloride of 2-amino-2-methyl-1-propanol. Otherwise, the procedure followed that of Example 4 with the exception that, directly after the 3-minute steaming period, half of the samples or portions of the fabric were exposed to a 5-minute dry-curing treatment at approximately 150° C. in a forced-draft oven. The results are in the following table:

TABLE FOR EXAMPLE 5

					Control data on untreated fabric
OP[—N(CH_3(CH_2OH)$_3$ add-on OWF, percent	11.4	10.0	11.4	10.0	
Trimethylolmelamine add-on OWF, percent	13.8	12.0	13.8	12.0	
Steamed 3 minutes	(1)	(1)	(1)	(2)	
Dry cured (5 minutes at 150° C.)	(2)	(1)	(1)	(1)	
Weight gain, percent	19.6	17.6	20.3	18.9	
Bound N, weight percent of treated fabric:					
After rinsing and drying but before laundering	5.44	5.37	Undetermined		
Bound P, weight percent of treated fabric:					
After rinsing and drying but before laundering	1.00	0.93	1.00	(3)	
After 50 launderings	0.94	0.87	0.95	(3)	
Char length (vertical test), inches:					
After rinsing and drying but before laundering	4.0	3.3	3.0	4.1	
Limiting oxygen index:					
After rinsing and drying but before laundering	0.281	0.258	0.275	0.263	
After 25 launderings	0.273	0.261	0.270	(3)	
After 50 launderings	0.269	0.265	0.269	(3)	
Tensile strength (filling), pounds:					
After rinsing and drying but before laundering	40	30	29	Undetermined	
After 10 launderings	39	33	28	Undetermined	
Tear strength (filling), pounds:					
After rinsing and drying but before laundering	1.1	0.9	0.7	0.5	1.9
After 10 launderings	1.0	0.9	0.7	0.7	(3)
Flex abrasion resistance (warp), cycles:					
After rinsing and drying but before laundering	550	525	650	175	500
After 10 launderings	615	400	420	125	(3)
Stiffness (warp), mg.-cm.:					
After rinsing and drying but before laundering	697	376	1,450	(3)	93
After 10 launderings	178	142	160	Undetermined	
Dry crease recovery (warp plus filling), degrees:					
After rinsing and drying but before laundering	230	268	253	281	154
After 10 launderings	220	258	247	280	(3)
Shrinkage after 10 launderings, percent:					
Warp	1.0	1.0	1.0	Undetermined	
Filling	0.5	1.0	0.5	Undetermined	

[1] Yes.
[2] No.
[3] Undet.

EXAMPLE 6

This example provides a comparison of results form (1) various types of catalysts, and (2) steaming without and with dry curing, all on a medium-heavy fabric.

Portions of a fabric woven from twisted all-cotton yarn in a twill-weave, weighing 8 ounces per square yard, were padded from baths containing (*a*) N,N',N''-triethyl-N,N',N''-tris(hydroxymethyl)phosphoric triamide and trimethylolmelamine in the ratio of 0.8 to 1 by moles and (*b*) one of the following catalysts as indicated in the accompanying table: potassium peroxydisulfate, the hydrochloride of 2-amino-2-methyl-1-propanol, or magnesium chloride. The pressure of the squeeze rolls was adjusted to give a wet pickup of (75±5) percent. The padded samples were dried in a forced-draft oven at approximately 82° C., then exposed for 3 minutes to steam at 101°±1° C. in a laboratory steamer. The steamed samples were either directly washed, or, as indicated in the table, were heated for 5 minutes at approximately 163° C. in a forced-draft oven to effect dry-curing, and then washed. The washing procedure was that described in Example 1. The results are in the accompanying table. (Control data on the untreated twill fabric woven from twisted all-cotton yarn is given in the table of Example 9).

TABLE FOR EXAMPLE 6

Catalyst, Percent OWB:						
$K_2S_2O_8$	1.0					
$HOCH_2C(CH_3)_2NH_3Cl$		2.2	2.2	2.2	2.2	
$MgCl_2$						1.0
OP[—N(C_2H_5)CH_2OH]$_3$ OWF, percent	14.7	14.1	14.1	11.1	11.1	14.1
Trimethylolmelamine OWF, percent	14.8	14.2	14.2	11.2	11.2	14.2
Steamed 3 minutes	(1)	(1)	(1)	(1)	(1)	(1)
Dry cured (5 minutes near 163° C.)	(2)	(2)	(1)	(2)	(1)	(1)
Weight gain, percent	20.7	20.8	23.3	16.3	17.7	20.8
Bound P, found weight percent	0.95	1.02	1.20	Undetermined		1.10
Bound N, found weight percent	6.2	6.09	5.90	Undetermined		5.48
Tensile strength (warp), pounds	181	181	167	174	162	165
Tear strength (filling), pounds	3.0	2.6	1.5	3.1	2.0	1.5
Dry crease recovery (warp plus filling), degrees	185	183	233	192	235	240
Flex abrasion resistance, cycles:						
After rinsing and drying but before laundering	800	700	1,600	1,026	1,200	570
After 10 launderings	925	900	750	850	775	425
Char length (vertical test), inches:						
After rinsing and drying but before laundering	3.6	3.2	3.8	3.5	4.3	4.5
After 10 launderings	4.5	3.9	4.0	4.5	4.0	4.3
After 50 launderings	5.1	4.2	4.6	7.3	6.0	(3)
Limiting oxygen index:						
After rinsing and drying but before laundering	0.28	0.28	0.28	0.26	0.27	0.28
After 10 launderings	0.27	0.28	0.28	0.26	0.27	0.27
After 25 launderings	0.26	0.26	0.28	0.25	0.26	0.26

[1] Yes.
[2] No.
[3] Undet.

EXAMPLE 7

The procedure was similar to that of Example 6, but instead of triethyltris(hydroxymethyl)phosphoric triamide, the com-

pound that was used in conjunction with trimethylolmelamine was N,N',N''-trimethylphosphoric triamide, $OP(—NHCH_3)_3$. Results are given in the accompanying table:

TABLE FOR EXAMPLE 7

Catalyst, percent OWB:								
$K_2S_2O_8$	1.0							
$HOCH_2C(CH_3)_2NH_3Cl$		2.2	2.4	2.2	2.4			
$MgCl_2$						1.0	1.0	1.0
$OP(—NHCH_3)_3$ percent OWF	8.0	8.4	8.4	6.6	6.6	8.3	8.3	6.3
Trimethylolmelamine, percent OWF	16.0	16.6	16.6	12.9	12.9	16.4	16.4	12.4
Steamed 3 minutes	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)
Dry cured (5 minutes at 163° C.)	(2)	(2)	(1)	(2)	(2)	(2)	(1)	(1)
Weight gain, percent	17.5	18.4	19.0	13.9	15.1	15.6	18.5	14.7
Bound P, weight percent	1.00	1.07	1.13	Undetermined		0.87	1.12	(3)
Bound N, weight percent	6.25	6.74	7.19	Undetermined		5.13	6.18	(3)
Char length (vertical test), inches: After 50 laundering	3.7	3.5	3.2	5.8	3.3	4.2	2.9	4.9
Limiting oxygen index:								
After rinsing and drying but before laundering	0.32	0.32	0.32	0.29	0.29	0.30	0.30	0 30
After 10 laundering	0.28	0.30	0.31	0.27	0.28	0.28	0.30	0.27
After 25 launderings	0.28	0.29	0.29	0.26	0.27	0.27	0.29	0.27
After 50 launderings	0.28	0.29	0.29	0.26	0.27	0.26	0.29	0.26
Tensile strength (warp), pounds	185	185	183	182	180	182	182	177
Tear strength (filling), pounds	3.6	3.6	3.5	4.3	3.8	4.0	2.8	3.6
Dry crease recovery (warp plus filling), degrees	209	194	201	217	233	184	211	213
Flex abrasion resistance, cycles	195	1,100	1,150	1,200	1,950	1,100	1,050	1,200

[1] Yes.
[2] No.
[3] Undet.

EXAMPLE 8

This example is similar to Example 6 except that instead of triethyltris(hydroxymethyl)phosphoric triamide, the compound that was used in conjunction with trimethylolmelamine was phosphoric triamide, $OP(—NH_2)_3$. Results are given in the accompanying table:

TABLE FOR EXAMPLE 8

Catalyst, percent OWB:		
$K_2S_2O_8$	1.0	
$MgCl_2$		1.0
$OP(—NH_2)_3$ percent OWF	5.2	5.9
Trimethylolmelamine percent OWF	14.8	16.6
Steamed 3 minutes	(1)	(1)
Dry cured (5 minutes near 163° C.)	(2)	(2)
Weight gain, percent	11.0	16.9
Bound P, weight percent	0.59	0.99
Bound N, weight percent	4.55	5.91
Char length (vertical test), inches	4.9	3.2
Limiting oxygen index	0.27	0.33

[1] Yes.
[2] No.

EXAMPLE 9

This example provides a comparison of results produced by various fixation conditions. The substrate was a medium heavy fabric woven from twisted all-cotton yarn in a twill-weave, weighing 8 ounces per square yard. Processes of padding and rinsing resembled those described in EXAMPLES 5 and 1, respectively. The source of bound phosphorus was N,N',N''-tris(hydroxymethyl)-N,N',N''-trimethylphosphoric triamide and the fixation catalyst was the hydrochloride of 2-amino-2-methyl-1-propanol (1.1 percent on the weight of the pad bath). Results are given in the accompanying table.

The evaluation data show that fixation only by steaming preserved the mechanical strength properties of the fabric to a higher degree than did dry-curing. Note that fixation by steam alone resulted in high resistance to abrasion, tensile strength, and tear strength (particularly as measured in the direction of the filling).

TABLE FOR EXAMPLE 9

							Control data on untreated fabric
$OP[—N(CH_3)CH_2OH]_3$ percent OWF	22	22	22	11	11	11	
Trimethylolmelamine percent OWF	11	11	11	13	13	13	
Fixation conditions:							
Steamed 3 minutes	(1)		(2)	(1)		(2)	
Steamed and dry cured		(1)			(1)		
Dry cured (5 minutes near 163° C.)	(2)		(1)	(2)		(1)	
Weight gain, percent	21.7	26.0	30.4	18.3	19.1	20.9	
Bound P, weight percent	1.8	2.3	(3)	1.1	(3)	1.1	
Bound N, weight percent	5.5	5.1	(3)	6.1	(3)	6.1	
Char length (vertical test), inches:							
After 10 launderings	3.5	3.5	4.5	3.5	3.5	4.5	
After 25 launderings	4.5	4.0	4.5	3.7	4.1	4.5	
After 50 launderings	5.0	4.0	4.6	5.3	5.1	6.0	
Tensile strength, pounds:							
Warp	189	176	184	169	149	133	187
Filling	66	55	57	64	49	42	78
Tear strength, pounds:							
Warp	3.6	2.3	1.2	4.6	3.2		7.2
Filling	2.5	1.3	0.7	2.5	1.4	1.1	5.1
Crease recovery, degrees:							
Dry	156	219	240	202	242	261	141
Wet	254	253	235	207	231	226	160
Flex abrasion resistance (warp), cycles	500	225	60	450	125	65	550
Shrinkage after 10 launderings, percent:							
Warp	2.0	1.5	1.0	2.0	1.5	1.5	10
Filling	0.0	0.5	0.5	0.0	0.0	0.0	+1.0

[1] Yes.
[2] No.
[3] Undet.

The higher dry-crease recovery-angles resulting from dry-curing indicate that dry-curing brings about much more cross-linking than steam-fixation does.

EXAMPLE 10

The procedure resembled that of Example 9, except that the substrate fabric was all-cotton sheeting, as described in Example 1. Results are given in the accompanying table.

TABLE FOR EXAMPLE 10

							Control data on untreated fabric
$OP[-N(CH_3)CH_2OH]_3$ percent OWF	26.0	26.0	26.0	10.0	10.0	10.0	
Trimethylolmelamine percent OWF	12.5	12.5	12.5	12.0	12.0	12.0	
Fixation conditions:							
Steamed 3 minutes	(1)		(2)	(1)		(2)	
Steamed and dry cured		(1)			(1)		
Dry cured (5 minutes at 163° C.)	(2)		(1)	(2)		(1)	
Weight gain, percent	24.6	28.3	33.4	17.1	17.1	20.3	
Bound P, weight percent	2.2	(3)	2.5	1.0	(3)	1.1	
Bound N, weight percent	6.6	(3)	7.7	6.0	(3)	6.0	
Char length (vertical test), inches:							
After 10 launderings	3.7	3.5	4.1	4.5	5.0	5.0	
After 25 launderings	3.8	3.7	5.0	4.0	5.0	5.5	
After 50 launderings	4.9	4.6	4.9	6.3	5.0	6.0	
Tensile strength, pounds:							
Warp	54	57	54	62	51	46	68
Filling	39	33	28	40	31	23	51
Tear strength, pounds:							
Warp	1.6	0.5	0.2	1.9	1.5	1.0	2.4
Filling	1.0	0.4	0.2	1.2	0.9	0.6	1.6
Crease recovery, degrees:							
Dry	166	215	243	232	250	282	177
Wet	261	263	261	213	233	234	148
Flex abrasion resistance (warp), cycles	500	125	95	450	350	175	675
Shrinkage after 10 launderings, percent:							
Warp	1.5	2.0	(3)	1.5	1.0	0.5	8.5
Filling	2.0	1.2	(3)	1.0	0.5	0.0	5.5

[1] Yes.
[2] No.
[3] Undet.

It will be apparent that many modifications and variations may be effected without departing from the scope of the novel concepts of the present invention, and the illustrative details disclosed are not to be construed as imposing undue limitations on the invention.

I claim:

1. A process for treating cellulose-containing fabric to render said fabric flame-retardant, said process comprising impregnating said fabric with

a. a melamine derivative prepared by reacting melamine with either formaldehyde or formaldehyde and an alkanol of 1 to 3 carbon atoms, said melamine derivative having attached to its nitrogen atoms from 2 to 6 substituents of the formula $-CH_2OZ$ wherein Z is hydrogen or alkyl of 1 to 3 carbon atoms,

b. a phosphoric amide of the formula

$$OP(NRR')_a(OH)_{3-a}$$

wherein *a* is an integer of from 1 to 3 and R and R' at each occurrence are independently selected from the group consisting of hydrogen, methyl, ethyl, hydroxymethyl and methoxymethyl provided that at least one of hydrogen, hydroxymethyl or methoxymethyl must be attached to each nitrogen atom, and

c. a catalyst which is an acid, acid-forming salt or oxidizing agent

and coreacting said melamine derivative and said phosphoric amide to form an insoluble product while maintaining the moisture content of said fabric at a minimum of 10 percent by weight based on the weight of said fabric.

2. A process as claimed in claim 1 wherein said catalyst is selected from the group consisting of ammonium peroxydisulfate, potassium peroxydisulfate, hydrogen peroxide, magnesium chloride, zinc nitrate, and the hydrochloride of 2-amino-2-methyl-1-propanol.

3. A process as claimed in claim 1 wherein the amount of catalyst is equal to about 0.5 to 12 percent by weight of the total weight of coreactants.

4. A process as claimed in claim 1 wherein about 0.1 to 3 moles of phosphoric amide are employed for each mole of melamine derivative.

5. A process as claimed in claim 1 wherein said insoluble product contains an amount of phosphorus equal to about 0.5 to 4 percent by weight of the total weight of the treated fabric and an amount of nitrogen equal to about 1.0 to 15 percent by weight of the total weight of treated fabric.

6. A process as claimed in claim 1 wherein said melamine derivative is trimethylolmelamine.

7. A process as claimed in claim 1 wherein the phosphoric amide is selected from the group consisting of phosphoric triamide, N,N',N''-trimethylphosphoric triamide, phosphorodiamidic acid, N,N',N''-tris(hydroxymethyl)-N,N',N''-trimethylphosphoric triamide and N,N',N''-triethyl-N,N',N''-tris(hydroxymethyl)phosphoric triamide.

8. A process as claimed in claim 1 wherein said coreaction is carried out in the presence of steam.

9. A process for treating cellulose-containing fabric to render said fabric flame-retardant, said process comprising impregnating said fabric with

a. a melamine derivative prepared by reacting melamine with either formaldehyde or formaldehyde and methanol, said melamine derivative having attached to its nitrogen atoms from 2 to 6 substituents of the formula $-CH_2OZ$ wherein Z is hydrogen or $-CH_3$

b. a phosphoric amide of the formula $OP(NRR')_a(OH)_{3-a}$ wherein *a* is an integer of from 1 to 3 and R and R' at each occurrence are independently selected from the group consisting of hydrogen, methyl, ethyl, hydroxymethyl and methoxymethyl provided that at least one of hydrogen, hydroxymethyl or methoxymethyl must be attached to each nitrogen atom and,

c. a catalyst which is an acid, acid forming salt or oxidizing agent

and coreacting said melamine derivative and said phosphoric amide to form an insoluble product while maintaining the moisture content of said fabric at a minimum of 10 percent by weight based on the weight of said fabric, said insoluble product containing an amount of phosphorus equal to about 0.5 to 4 percent by weight of the total weight of the treated fabric and an amount of nitrogen equal to about 1.0 to 15 percent by weight of the total weight of the treated fabric.

10. A process as claimed in claim 9 wherein the amount of catalyst is equal to about 0.5 to 12 percent by weight of the total weight of coreactants.

11. A process as claimed in claim 9 wherein about 0.1 to 3 moles of phosphoric amide are employed for each mole of melamine derivative.

12. A process as claimed in claim 9 wherein about 0.3 to 1.2 moles of phosphoric amide are employed for each mole of melamine derivative.

13. A process as claimed in claim 9 wherein said melamine derivative is trimethylolmelamine.

14. A process as claimed in claim 9 wherein said coreaction is carried out in the presence of steam.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,632,297 Dated January 4, 1972

Inventor(s) Stephen B. Sello

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

Column 3, line 3, "N,N'- " should read -- N,N',N" -- ;
Column 3, line 4, "tris(hydroxymethyl)phosphoric" should be deleted;
Column 3, line 6, "(hydroxymethyl)" should read -- -tris(hydroxymethyl) --.
Column 4, line 8, after "ammonium"(first instance) insert -- and peroxydisulfates of alkali metals or of ammonium --;
Columns 7-8, In Table for Example 6, Flex Abrasion resistance cycles: After rinsing and drying, but before laundering "1,026" should read -- 1,025 --;
Columns 9-10, In Table for Example 7, Dry Cured (5 minutes at 163°C), the fifth item "(2)" should read -- (1) --.
Columns 9-10, In Table for Example 7, Flex Abrasion resistance cycles, the first item "195" should read -- 915 --.

Signed and sealed this 2nd day of July 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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