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3,681,060

PREPARATION OF FLAME-RETARDANT FABRICS

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14 Claims

ABSTRACT OF THE DISCLOSURE

Cellulose-containing fabrics are rendered durably flame retardant without undue physical strength deterioration or excessive stiffening by applying to said fabric

- (a) a melamine derivative prepared by reacting melamine with formaldehyde or formaldehyde and an alkanol,
- (b) a phosphoric amide of the formula



where R is alkyl of 1 to 4 carbon atoms, and

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

The fabric is then heated to cause said melamine derivative and said phosphoric amide to coreact and form an insoluble product on the fabric. It is essential that more than 1.0 mole of melamine derivative be used for each mole of phosphoric amide, that the amount of insoluble reaction product formed on the fabric be such that the weight gain is at least 14% after removal of any soluble product by a hot process wash (e.g. 15 minutes at 90° C.) and that the nitrogen to phosphorus weight ratio of the insoluble product be at least 5.0 to 1.

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 forming thereon insoluble reaction products of a methylolmelamine and a phosphoric triamide. In the prior art procedures this reaction was carried out with either no catalyst at all, which gives relatively poor yields of insoluble reaction product, or with an acidic catalyst under such conditions that the fabric was unduly physically weakened and was made excessively stiff.

British Pat. 790,663 discloses flame proofing cellulosic fabrics by treating them with an aqueous solution containing a derivative of phosphoric acid such as N,N',N''-trimethylphosphoric triamide and a methylolmelamine as a fixing agent and heating the treated fabric. No catalyst is employed and we have found that when using such a procedure the amount of flame-proofing agent fixed on the fabric is insufficient to impart satisfactory flame retardance.

In an article by Frick et al., entitled "Development of Durable Flame-Retardant Finishes for Cotton," published November 1958, Wright Air Development Center Technical Report WADC TR 58-130, there is disclosed treating cellulosic fabric with a mixture of methylolmelamine and N,N',N''-trimethylphosphoric triamide, using an acid yielding fixation catalyst (either alkanolamine hydrochloride or magnesium chloride). From 1 to 4 moles of N,N',N''-trimethylphosphoric triamide were employed for each mole of trimethylolmelamine and fixation was carried out by dry curing at 160° C. for 5 minutes. The

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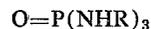
flame-retardant finish thus produced had poor durability. Further, on repeating the procedure of Frick et al., we found that the fabric was frequently excessively stiffened.

To improve the durability of the finish, Frick et al., pretreated the N,N',N''-trimethylphosphoric triamide with formaldehyde, thereby forming N,N',N''-tris(hydroxymethyl) - N,N',N''-trimethylphosphoric triamide. While this pretreatment improved the durability of the flame-retardant finish, the durability was still not satisfactory and even the best samples had lost their flame resistance after 15 laundry cycles. In addition, when the formaldehyde pretreatment was employed, there was a large loss in the tear strength of the fabric.

In my copending application Ser. No. 19,116, filed Mar. 12, 1970, now U.S. Pat. No. 3,632,297, it is disclosed that the large loss of tear strength can be avoided by replacing the dry curing of Frick et al. with wet fixation. While this procedure gives a very satisfactory flame-retardant finish, many of the plants in which finishes are applied to fabrics do not have the necessary equipment for wet fixation.

SUMMARY OF THE INVENTION

In accordance with the present invention, durable flame retardancy is imparted to fabrics without unduly damaging or stiffening the fabric by applying to the fabric a melamine derivative prepared by reacting melamine with either formaldehyde or formaldehyde and an alkanol, a phosphoric amide of the formula



where R is alkyl of 1 to 4 carbon atoms and a catalyst which is an acid, an acid forming salt, an oxidizing agent or a neutral salt. The fabric is then heated to cause said melamine derivative and said phosphoric amide to coreact and form an insoluble product. It is important that more than 1 mole of melamine derivative be used for each mole of phosphoric amide, that the insoluble reaction product have a nitrogen to phosphorus weight ratio of at least 5.0 to 1, and that the amount of insoluble reaction product formed on the fabric be such that the weight gain is at least 14% after removal of any soluble chemicals by a hot process wash. When an acid, yielding salt or oxidizing agent is used as the catalyst, the amount applied to the fabric should not be greater than about 1.5% by weight based on the weight of the fabric and when a neutral salt is used, the amount applied to the fabric should not be greater than 6% by weight based on the weight of the fabric. Using the above reactants and catalysts in the defined amounts, a durable flame retardant finish can be obtained by dry heating without excessively stiffening the fabric or damaging the physical strength of the fabric.

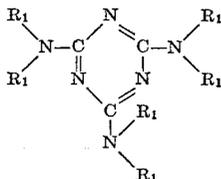
DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a method of rendering cellulose-containing fabric durably flame retardant by forming on said fabric insoluble reaction products containing phosphorus and nitrogen employing certain reactants in critical ratios and amounts and certain catalysts in specific amounts. The fabric is impregnated with an aqueous solution containing a melamine derivative, a phosphoric amide and catalyst, and then an insoluble product is formed by heating. More than 1.0 mole of melamine derivative must be present for each mole of phosphoric amide, the insoluble reaction product formed must have a nitrogen to phosphorus weight ratio at least 5.0 to 1 and the weight gain cannot be less than 14% after the removal of the soluble products from the fabric by a severe hot process wash (e.g., 90° C. for 15 minutes in an aqueous bath containing 0.1% by weight Na₂CO₃ and 0.1% by weight of nonionic detergent). The fabric

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must have a phosphorus content equal to at least 0.6% by weight of the finished fabric, i.e., total weight of fabric plus flame-retardant finish.

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 $-\text{CH}_2\text{OH}$ groups and $-\text{CH}_2\text{OX}$ groups is from 2 to 6 with X being a lower alkyl group of 1 to 4 carbon atoms and preferably being methyl. The melamine derivative is thus defined by the formula



where R_1 at each occurrence is independently hydrogen or $-\text{CH}_2\text{OZ}$ with Z being hydrogen or alkyl of 1 to 4 carbon atoms and with at least two of said R_1 groups being $-\text{CH}_2\text{OZ}$. The N-methylol compounds (wherein Z is always hydrogen) can be prepared by reacting melamine with 2 or more moles of formaldehyde according to known procedures. The lower alkyl 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 4 carbon atoms and preferably being methanol. If desired, mixtures of the above-described melamine derivatives can be used.

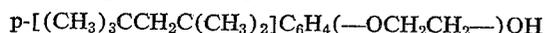
The phosphoric amide is a compound of the formula



where R is an alkyl group of 1 to 4 carbon atoms. Illustrative of suitable phosphoric amides are N,N',N''-trimethylphosphoric triamide and N,N',N''-triethylphosphoric triamide.

The mole ratio of melamine derivative to phosphoric amide greatly affects the stiffness of the treated fabric when sufficient amounts of these reactants are used to give durable flame retardancy and curing is effected by dry heating. As the mole ratio of melamine derivative to phosphoric amide is increased, the stiffness of the treated fabric drops sharply when the mole ratio approaches 1 to 1. The fabric is made excessively stiff when less than one mole of melamine derivative is employed per mole of phosphoric amide while at a mole ratio of 1:1 results are marginal with acceptable stiffness being obtained only some of the time. In order to consistently obtain treated fabrics having acceptable stiffness, more than 1 mole, preferably at least 1.07 moles of melamine derivative should be employed per mole of phosphoric amide. Particularly outstanding results are obtained when from 1.75 to 5.0 moles of melamine derivative are used per mole of phosphoric amide. This preferred range gives a very high yield of insoluble reaction product and excellent durability.

To obtain self-extinguishing properties after laundering, it is also necessary that the insoluble reaction product be present in an amount equal to at least 14% by weight based on the weight of the fabric after washing the treated fabric for 15 minutes at 90° C. in an aqueous solution containing 0.1% of sodium carbonate and 0.1% of nonionic detergent (Triton® X-100, a mixture of closely related compounds having the formula



where x has an average value of about 10). If the add-on of insoluble reaction product is less than the amount defined above, even a slight decrease of phosphorus and nitrogen content in the laundering cycles impairs the level of flame resistance and the self-extinguishing properties cannot be maintained for the required period of

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usage, i.e., through 50 laundry cycles. Another requirement for obtaining acceptable flame retardancy is that the amount of phosphorus in the insoluble reaction product must be at least 0.6% by weight of the finished product, i.e., total weight of the fabric plus reaction product.

The catalyst used can be an acid, an acid forming salt, an oxidizing agent or a neutral salt which is alkali metal chloride, bromide, iodide or nitrate. Illustrative of such catalytic compounds are: hydrochloric acid; zinc nitrate; zinc chloride; magnesium chloride; magnesium nitrate; amine hydrochlorides, including alkylamine hydrochlorides where the alkyl group is preferably 1 to 8 carbon atoms such as methylamine hydrochloride, and alkanolamine hydrochlorides, preferably of 1 to 8 carbon atoms such as 2-amino-2-methyl-1-propanol hydrochloride and N,N',N''-nitrilotriethanol hydrochloride; ammonium salts such as ammonium tartrate, citrate, oxalate, formate, nitrate, or ammonium dihydrogen phosphate; peroxy compounds such as hydrogen peroxide, peroxymonosulfates of alkali metals or of ammonium and peroxydisulfates of alkali metals or of ammonium such as potassium peroxydisulfate and ammonium peroxydisulfate; LiNO_3 ; NaNO_3 ; KNO_3 ; LiCl ; LiBr ; LiI ; NaCl , NaBr , NaI , KCl , KBr , KI , RbCl , RbBr and CsI . Particularly outstanding results are obtained with alkylamine hydrochlorides, alkanolamine hydrochlorides and the above defined neutral salts.

The stiffness of the flame retardant fabric increases as the concentration of catalyst increases. To avoid an excessively stiff product, i.e., one having a warp stiffness of over 5,000 mg.-cm., the concentration of catalyst on the fabric during the coreaction of melamine derivatives and phosphoric amide should not be greater than about 1.5% by weight of the weight of the fabric when an acid, acid forming salt or oxidizing agent is used as the catalyst and 6% by weight when a neutral salt is used as catalyst. Preferably, the minimum amount of catalyst used should be about 0.05% by weight based on the weight of the fabric for acids, acid yielding salts and oxidizing agents and about 1.0% for neutral salts.

The phosphoric amide, melamine derivative and catalyst are applied from an aqueous solution by padding, brushing, spraying or other impregnation technique. The critical concentration of reactants and catalyst and the required add-on of reaction product are obtained by controlling the concentrations of compounds in the aqueous solutions and the wet pick-up of solution of the fabric.

The phosphoric amide and melamine derivatives are coreacted by heating at a temperature of about 90 to 210° C. One of the important aspects of the present invention is that this coreaction can be effected by dry heating, such as in an oven, without either unduly deteriorating the physical strength of the fabric or giving an excessively stiff product. The fact that dry heat can be used is very advantageous, since many plants where fabrics are finished do not have wet fixation (e.g., steaming) equipment. If desired, the coreaction can be effected by wet fixation, i.e., heating the fabric while maintaining the moisture content at a level of at least 10% based on the weight of the fabric.

The aqueous dispersion containing the coreactants and catalyst also may contain additives for other purposes, such as wetting 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 reacted to form an insoluble product on the cellulose-containing fabric, the fabric is preferably washed to rinse out any soluble chemicals, such as catalyst, and unreacted starting material, and then dried, as on a tenter frame or 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.

The present invention can be used with cellulose-containing fabrics which are knitted, woven or non-woven. The cellulose can be from any source, including such natural sources as seed fibers 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 of cellulose. 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 about 50% or more of the fibers are non-cellulosic.

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 weight unless otherwise specified. The trimethylolmelamine used in the examples was a commercial product (Resloom HP) containing about 2.7 methylol groups per molecule of melamine.

Analytical and test methods employed in the examples

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 (November 1966). Generally, a limiting oxygen index of about 0.260 or greater is passable.

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

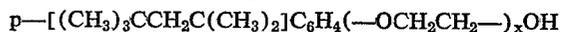
Laundrying: AATCC 88A-1964T, Test III, home-type washer, 5-pound load, full cycle, 60° C., synthetic deter-

TPMA: N,N',N''-tris(hydroxymethyl) - N,N',N''-trimethylphosphoric triamide.

EXAMPLE 1

A series of aqueous baths were prepared containing 0.5% by weight of methyl amine hydrochloride and varying relative amounts of N,N',N''-trimethylphosphoric triamide and trimethylolmelamine. The baths were adjusted to pH 7 with HCl.

Samples of fabric woven from twisted, all-cotton yarn in a twill weave, weighing 8 ounces per square yard, were padded in the aqueous baths with the pressure of the squeeze rolls adjusted to give a wet pick-up of about 80%, i.e., to each ounce of fabric there was added about 0.8 ounce of aqueous dispersion. The padded samples of fabric were dried in a forced-draft oven at approximately 66° C., then dry cured by heating at 182° C. for 5 minutes. The specimens of fabric were washed for 15 minutes at approximately 90° C. in an aqueous solution, of which 0.1% was sodium carbonate and 0.1% was a non-ionic detergent (Triton® X-100, a mixture of closely related compounds having the formula



where x has an average value of 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. Results are shown in Table 1.

The results show that the use of less than 1.0 mole of trimethylolmelamine per mole of phosphoric amide results in low efficiency of the phosphorus chemical and in an extremely stiff product having unsatisfactory durability on being subjected to repeated launderings. The stiffness decreased but was still unacceptable at 1:1 mole ratio while samples obtained with compositions containing more than 1 mole trimethylolmelamine per mole of phosphoric amide possessed acceptable stiffness and very good durability to launderings.

TABLE 1

| Percent TPA OWF ¹ | Percent TMM OWF ¹ | Moles TMM per mole TPA | Percent weight gain | Phos- phorus content ¹ | Nitrogen content ² | N/P weight ratio | Warp stiffness, mg.-cm. | LOI | | Char length (in.) | |
|---------------------------------|------------------------------------|------------------------------|---------------------------|---|----------------------------------|------------------------|-------------------------------|-------|-----|----------------------|-----|
| | | | | | | | | Orig. | 50L | Orig. | 50L |
| 7.0 | 16.4 | 1.50 | 18.5 | 1.24 | 7.35 | 5.9 | 4,603 | .30 | .29 | 3.5 | 4.3 |
| 15.0 | 15.0 | 1.25 | 16.7 | 1.27 | 6.89 | 5.4 | 2,080 | .30 | .28 | 3.4 | 4.5 |
| 10.4 | 16.7 | 1.00 | 18.2 | 1.44 | 7.09 | 4.9 | 9,800 | .30 | .28 | 3.5 | 4.3 |
| 14.5 | 17.3 | 0.75 | 15.6 | 1.49 | 6.76 | 4.5 | >12,000 | .31 | .26 | 6.4 | 5.7 |

¹ Compound on the fabric after padding.

² Percent by weight based on total weight of fabric plus insoluble reaction product.

gent; tumble drying.

Stiffness (Cantilever), in mg.-cm.: ASTM D 1388-64. Generally a warp stiffness of 5,000 or less is acceptable.

Tear Strength (Elmendorf), in pounds: ASTM D 4124-59.

Abbreviations

OWB: On the weight of the bath used for padding, in percent.

OWF: On the weight of the fabric, in percent.

Wet pick-up (in percent) multiplied by OWB/100% equals OWF (in percent)

TMM: trimethylolmelamine, (s - triazine - 2,4,6 - trilyl-imino) trimethanol.

TPA: N,N',N''-trimethylphosphoric triamide.

EXAMPLE 2

The procedure of Example 1 was repeated using as the catalyst 1.0% by weight based on the weight of the bath of 2-amino-2-methyl-1-propanol hydrochloride. The results are given in Table 2.

The data indicate that at comparable weight gains (ranging from 17.6% to 18.9%), only those samples have acceptable stiffness which were treated with a composition containing more than 1 mole of trimethylolmelamine per mole of phosphoric amide. These samples (TMM/TPA mole ratio is >1.0) exhibit excellent durability. The utilization of the chemicals and especially of the phosphoric amide increases as the TMM/TPA mole ratio increases.

TABLE 2

| Percent TPA OWF ¹ | Percent TMM OWF ¹ | Moles TMM per mole TPA | Percent weight gain | Percent phosphorus content ¹ | | Percent nitrogen content ² (orig.) | N/P weight ratio (orig.) | Warp stiffness, mg.-cm. | LOI | | Char length (in.) | |
|---------------------------------|------------------------------------|------------------------------|---------------------------|---|-----|--|-----------------------------------|-------------------------------|-------|-----|----------------------|-----|
| | | | | Orig. | 50L | | | | Orig. | 50L | Orig. | 50L |
| 5.1 | 15.9 | 2.0 | 17.6 | 1.1 | 7.3 | 6.4 | 3,000 | .30 | .30 | 3.8 | 3.7 | |
| 7.5 | 17.4 | 1.5 | 18.9 | 1.2 | 1.0 | 7.7 | 3,800 | .31 | .31 | 3.5 | 3.1 | |
| 7.6 | 17.1 | 1.25 | 18.1 | 1.2 | 0.9 | 7.0 | 4,800 | .31 | .29 | 3.9 | 3.5 | |
| 10.6 | 16.7 | 1.0 | 17.9 | 1.5 | 1.1 | 7.3 | 4,900 | .32 | .30 | 3.0 | 3.3 | |
| 14.9 | 17.7 | 0.75 | 17.8 | 1.6 | 0.9 | 6.9 | >12,000 | .32 | .26 | 3.3 | 5.4 | |

¹ Compound on the fabric after padding.

² Percent by weight based on total weight of fabric plus insoluble reaction product.

7 EXAMPLE 3

The procedure of Example 2 was repeated, but the chemicals were used in such a concentration as to get about 20% weight gain.

The results (Table 3) indicate that excellent durable flame resistance can be attained even at 0.7% phosphorus content when 5.0 moles trimethylolmelamine was used per mole of phosphoric amide. At such a TMM/TPA mole ratio the utilization of the phosphorus chemical is 100%, while at 0.75 mole ratio it is significantly lower.

TABLE 3

| Percent TRA OWF ¹ | Percent TMM OWF ¹ | Moles TMM per mole TPA | Percent weight gain | Percent phosphorus content ¹ original | Percent nitrogen content ² (orig.) | N/P weight ratio (orig.) | Warp stiffness mg.-cm. | LOI | | Char length (in.) | |
|------------------------------|------------------------------|------------------------|---------------------|--|---|--------------------------|------------------------|-------|-----|-------------------|-----|
| | | | | | | | | Orig. | 50L | Orig. | 50L |
| 2.5 | 20.1 | 5.0 | 19.7 | 0.7 | 8.4 | 12.0 | 5,700 | .28 | .28 | 4.8 | 3.8 |
| 18.2 | 21.6 | 0.75 | 20.6 | 1.9 | 7.2 | 3.7 | >12,000 | .32 | .29 | 3.4 | 4.0 |

¹ Compound on the fabric after padding.

² Percent by weight based on total weight of fabric plus insoluble reaction product.

8 EXAMPLE 6

The general procedure of Example 1 was repeated using aqueous pad baths containing 9.5% by weight N,N',N''-trimethylphosphoric triamide and 19.0% by weight trimethylolmelamine. The catalyst and catalyst concentrations of each bath, along with the results obtained, are specified in Table 6.

The results (Table 6) show that the samples having less than 14.0% weight gain exhibit marginal flame resistance, especially after repeated launderings.

TABLE 6

| Catalyst | Percent catalyst OWB | Percent weight gain | Limiting oxygen index | | | | Char length (inches) | | | |
|------------------|----------------------|---------------------|-----------------------|-----|-----|-----|----------------------|-----|-----|-----|
| | | | Orig. | 10L | 25L | 50L | Orig. | 10L | 25L | 50L |
| NaCl | 1.0 | 10.6 | .27 | .24 | .22 | .22 | 4.4 | BEL | | |
| NaCl | 2.0 | 12.9 | .28 | .26 | .24 | .24 | 3.7 | 4.5 | BEL | |
| NaCl | 4.0 | 13.1 | .27 | .26 | .25 | .25 | 4.3 | 4.5 | 4.6 | BEL |
| Alkanolamine HCl | 0.3 | 14.6 | .30 | .27 | .27 | .26 | 4.0 | 4.2 | 4.9 | 6.8 |
| Do. | 1.0 | 16.6 | .30 | .30 | .29 | 2.9 | 4.3 | 3.4 | 3.2 | 3.4 |

EXAMPLE 4

The procedure of Example 2 was repeated, but the chemicals were used in such a concentration as to get about 16% weight gain.

The results (Table 4) indicate that at 16% weight gain 1.07 TMM/TPA mole ratio imparts excellent flame resistance with acceptable stiffness.

TABLE 4

| Percent TPA OWF ¹ | Percent TMM OWF ¹ | Moles TMM per mole TPA | Percent weight gain | Percent phosphorus content ¹ original | Percent nitrogen content ² (orig.) | N/P weight ratio (orig.) | Warp stiffness, mg.-cm. | LOI | | Char length (in.) | |
|------------------------------|------------------------------|------------------------|---------------------|--|---|--------------------------|-------------------------|-------|-----|-------------------|-----|
| | | | | | | | | Orig. | 50L | Orig. | 50L |
| 6.8 | 13.3 | 1.25 | 16.5 | 1.3 | 6.5 | 5.0 | 1,500 | .31 | .29 | 3.4 | 2.9 |
| 7.2 | 13.0 | 1.15 | 15.5 | 1.3 | 6.3 | 4.8 | 1,300 | .30 | .28 | 4.5 | 4.7 |
| 7.6 | 12.9 | 1.07 | 16.0 | 1.3 | 6.3 | 4.8 | 2,275 | .31 | .27 | 3.6 | 4.6 |

¹ Compound on the fabric after padding.

² Percent by weight based on total weight of fabric plus insoluble reaction product.

EXAMPLE 7

The general procedure of Example 1 was repeated using an aqueous pad bath containing 9.2% by weight of N,N',N''-triethylphosphoric triamide, i.e., (C₂H₅NH)₃P=O, 14% by weight of trimethylolmelamine and 10% by weight of 2-amino-2-methyl-1-propanol hydrochloride.

The results are given in Table 7.

TABLE 7

| Percent weight gain | Phosphorus content | Nitrogen content | N/P weight ratio | Warp stiffness, mg.-cm. | Char length, inches | | LOI ¹ | |
|---------------------|--------------------|------------------|------------------|-------------------------|---------------------|-----|------------------|------|
| | | | | | Orig. | 25L | Orig. | 25L |
| 16.8 | 1.06 | 6.07 | 6.0 | 1,570 | 5.6 | 4.5 | .273 | .273 |

¹ Limiting oxygen index.

EXAMPLE 5

The general procedure of Example 1 was repeated using aqueous pad baths containing 9.5% by weight of N,N',N''-trimethylphosphoric triamide and 19.0% by weight trimethylolmelamine. The catalyst and catalyst concentration of each bath, along with the results obtained are given in Table 5.

The results show that the use of the respective catalysts in concentrations which are higher than required to attain maximum yield of insolubilization of the melamine derivative and phosphoric amide give an extremely stiff product.

TABLE 5

| Catalyst | Percent catalyst OWB | Percent weight gain | Percent phosphorus content | Percent nitrogen content | N/P weight ratio | Warp stiffness, mg.-cm. | Limiting oxygen index | | | Char length (in.) | |
|------------------------------------|----------------------|---------------------|----------------------------|--------------------------|------------------|-------------------------|-----------------------|-----|-----|-------------------|-----|
| | | | | | | | Orig. | 10L | 25L | Orig. | 25L |
| None | 0 | 7.3 | 0.78 | 3.20 | 4.1 | 830 | .21 | .21 | | BEL | BEL |
| CH ₃ NH ₂ Cl | 0.3 | 17.2 | 1.31 | 6.75 | 5.2 | 2,785 | .30 | .28 | .29 | 3.0 | 3.9 |
| CH ₃ NH ₂ Cl | 3.0 | 16.4 | 1.12 | 6.59 | 5.9 | 7,615 | .30 | .29 | .29 | 3.8 | 4.0 |
| Alkanolamine HCl | 0.3 | 15.2 | 1.23 | 6.55 | 5.3 | 2,043 | .28 | .30 | .29 | 3.3 | 4.2 |
| Do. | 1.0 | 17.6 | 1.37 | 6.95 | 5.1 | 3,616 | .29 | .31 | .32 | 3.4 | 3.0 |
| Do. | 3.0 | 18.2 | 1.26 | 6.98 | 5.5 | 7,225 | .32 | .31 | .31 | 3.9 | 3.4 |
| NaCl | 4.0 | 14.9 | 1.22 | 6.38 | 5.2 | 4,120 | .24 | .27 | .28 | 3.8 | 4.3 |

EXAMPLE 8

An aqueous bath was prepared containing 20% by weight of trimethylolmelamine, 10% by weight of N,N',N''-trimethylphosphoric triamide and 1.5% by weight of NaCl. The pH of the bath was adjusted to pH 7 with HCl and then lightweight rayon fabric was padded therein. The wet pick-up was 119%. The padded sample was dried at 66° C. and then dry cured at 182° C. for 5 minutes. The sample was washed, neutralized, rinsed and dried as described in Example 1. A weight gain of 26.5% was obtained. Flame retardance is given in Table 8.

TABLE 8

| Vertical flame | | Limiting oxygen index | | |
|----------------|----------------------|-----------------------|---------------------|---------------------|
| Original | 10 laund- derings | Original | 10 laun- derings | 25 laun- derings |
| 4.8 | 4.0 | .287 | .287 | .270 |

EXAMPLE 9

This example provides a comparison of the results obtained when N,N',N''-tris(hydroxymethyl)-N,N',N''-trimethylphosphoric triamide is used in place of N,N',N''-trimethylphosphoric triamide.

Two aqueous pad baths were prepared, one containing N,N',N''-tris(hydroxymethyl)-N,N',N''-trimethylphosphoric triamide and the other containing N,N',N''-trimethylphosphoric triamide and trimethylolmelamine. The catalyst in both baths was the hydrochloride of 2-amino-2-methyl-1-propanol (1.1% on the weight of the bath).

Samples of the same fabrics as used in Example 1 were padded in the aqueous baths so as to give a wet pick-up of about 80%. The padded samples were dried for 1½ minutes in a forced draft oven at approximately 82° C. and then dry-cured for 5 minutes at 163° C. The padded samples were then washed, neutralized, rinsed and dried as in Example 1 and evaluated. Results are shown in Table 9, with the amounts of reactants given in terms of compound on the fabric after padding, i.e., OWB times percent weight pick-up or OWF. The results show that the losses in flex abrasion resistance and tear strength are much greater with N,N',N''-tris(hydroxymethyl)-N,N',N''-trimethylphosphoric triamide.

TABLE 9

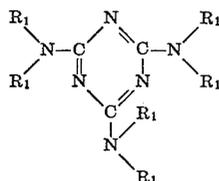
| Percent solids OWF | | | Percent weight gain | Vertical flame test (inches) | | | Flex abrasion (W), cycles | Tear (F), lbs. |
|--------------------|-------|------|---------------------|------------------------------|-----|-----|---------------------------|----------------|
| TMPA | TPA | TMM | | Orig. | 25L | 50L | | |
| 10.9 | ----- | 13.1 | 20.9 | 4.8 | 4.5 | 6.0 | 65 | 1.1 |
| | 7.2 | 14.4 | 16.6 | 3.9 | 3.6 | 6.0 | 225 | 2.8 |
| Untreated control | | | ----- | B.E.L.----- | | | 825 | 6.4 |

It will be apparent that many modifications and variations can 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 unnecessary limitations on the invention.

What is claimed is:

1. A process for treating cellulose-containing fabric to render said fabric flame retardant, said process comprising applying to said fabric an aqueous solution of

(a) a melamine derivative of the formula



where R₁ at each occurrence is independently selected from the group consisting of hydrogen and —CH₂OZ with Z being hydrogen or alkyl of 1 to 4 carbon atoms, provided that at least two of said R₁ groups are —CH₂OZ,

(b) a phosphoric amide of the formula



wherein R is alkyl of 1 to 4 carbon atoms, at least 1.25 moles of melamine derivative being employed for each mole of phosphoric amide, and,

(c) a catalyst which is an acid, an acid forming salt,

an oxidizing agent, or a neutral salt of an alkali metal and an anion selected from the group consisting of chloride, bromide, iodide and nitrate,

and heating said impregnated fabric to a temperature of about 60 to 210° C. to coreact said melamine derivative and said phosphoric amide to form on said fabric an insoluble product having a nitrogen to phosphorus weight ratio of at least 5.0 to 1 and containing an amount of phosphorus equal to at least 0.6% by weight of the combined weight of the fabric and the insoluble product, the amount of catalyst present on said fabric during said coreaction being about 0.05 to 1.5% by weight of the weight of the fabric when the catalyst is an acid, an acid forming salt, or an oxidizing agent and 1.0 to 6.0% when the catalyst is a neutral salt and the amount of the insoluble product formed on said fabric being equal to at least 14% by weight of the fabric as measured after the treated fabric has been subjected to a hot process wash to remove any soluble chemicals.

2. A process as claimed in claim 1 wherein said phosphoric amide is N,N',N''-trimethylphosphoric triamide.

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

4. A process as claimed in claim 1 wherein about 1.75 to 5.0 moles of melamine derivative are used per mole of phosphoric amide.

5. A process as claimed in claim 1 wherein said catalyst is an alkylamine hydrochloride or an alkanolamine hydrochloride.

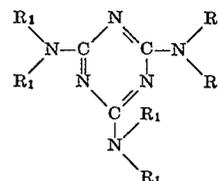
6. A process as claimed in claim 1 wherein said fabric is composed of cotton.

7. A process as claimed in claim 1 wherein said fabric is composed of rayon.

8. A process as claimed in claim 1 wherein the heating of said impregnated fabric is carried out by dry heating.

9. A process for treating cellulose-containing fabric to render said fabric flame retardant, said process comprising applying to said fabric an aqueous solution of

(a) a melamine derivative of the formula



where R₁ at each occurrence is independently selected from the group consisting of hydrogen and —CH₂OZ with Z being hydrogen or alkyl of 1 to 4 carbon atoms, provided that at least two of said R₁ groups are —CH₂OZ,

(b) a phosphoric amide of the formula



wherein R is alkyl of 1 to 4 carbon atoms, about 1.75 to 5.0 moles of melamine derivative being employed for each mole of phosphoric amide, and,

(c) a catalyst which is an acid, an acid forming salt, an oxidizing agent, or a neutral salt of an alkali metal and an anion selected from the group consisting of chloride, bromide, iodide and nitrate,

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and heating said impregnated fabric to a temperature of about 60 to 210° C. to coreact said melamine derivative and said phosphoric amide to form on said fabric an insoluble product having a nitrogen to phosphorus weight ratio of at least 5.0 to 1 and containing an amount of phosphorus equal to at least 0.6% by weight of the combined weight of the fabric and the insoluble product, the amount of catalyst present on said fabric during said coreaction being about 0.05 to 1.5% by weight of the weight of the fabric when the catalyst is an acid, an acid forming salt, or an oxidizing agent and 1.0 to 6.0% when the catalyst is a neutral salt.

10. A process as claimed in claim 8 wherein said phosphoric amide is N,N',N''-trimethylphosphoric triamide.

11. A process as claimed in claim 8 wherein said melamine derivative is trimethylolmelamine.

12. A process as claimed in claim 8 wherein the amount of the insoluble product formed on said fabric is equal to at least 14% by weight of the weight of the fabric as measured after the treated fabric has been subjected to a hot process wash to remove any soluble chemicals.

13. A process as claimed in claim 9 wherein said phosphoric amide is N,N',N''-trimethylphosphoric triamide, said melamine derivative is trimethylolmelamine and said catalyst is an alkylamine hydrochloride or an alkanolamine hydrochloride.

14. A process as claimed in claim 9 wherein the heating of said impregnated fabric is carried out by dry heating.

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8—116.2; 117—136, 143 A, 145; 252—8.1

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,681,060 Dated August 1, 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 2, line 43, "yielding" should read -- acid yielding -- .

Column 3, line 44, "malamine" should read -- melamine -- .

Column 3, line 51, "obtaine" should read -- obtain -- .

Column 4, line 49, "derivatives" should read -- derivative --

Column 7, Table 3, first column "percent TRA" should read -- Percent TPA --.

Column 8, Table 6, under Limiting Oxygen Index, 50L, bottom line "2.9" should read -- .29 -- .

Signed and sealed this 3rd day of July 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

Rene Tegtmeyer
Acting Commissioner of Patents

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