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METHOD FOR RETAINING FLAME AND SOIL RESISTANCES TO FABRICS

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U.S. Cl. 117—137 10 Claims

ABSTRACT OF THE DISCLOSURE

A method in which flame and soil resistance of fabrics are retained without yellowing or lowering of the strength of the fabrics by treating fabrics containing cellulose or protein fibers with an aqueous solution of a composition consisting of a condensed phosphoric acid and a tertiary amine or quaternary ammonium compound, the relative proportion of the phosphoric acid to the amine or ammonium compound being such that for each atom of phosphorous there is 0.5 to 2 atoms of nitrogen and subjecting the thus treated fabrics to a heat treatment at 110°–170° C. for 30 seconds to 30 minutes.

This invention relates to a commercially advantageous process for retaining flame and soil resistances durable to drycleaning and washing in fabrics comprising cellulose or protein fibers.

Heretofore, methods for retaining flame resistance in fabrics by using various phosphoric acid-nitrogenous compounds have been proposed. However, as there are impermissible disadvantages in these conventional methods, satisfactory results have not been obtained up to now. The method in which fabrics are subjected to treatment with ammonium phosphate, which has been long known as a flame retardant, leads to yellowing or a lowering of the strength of fabrics, even if baking of the fabrics is effected for long periods, and furthermore, it causes low washing durability to flame resistance, which is lost by washing. On the other hand, in the case of the method in which flame resistance is imparted by using urea and ammonium phosphate or urea and phosphoric acid, it is possible that flame resistance durable to washing is tentatively retained in the fabrics when large amounts of the agents are used. However, impermissible decreases in whiteness and strength of the fabrics also occur in this case. Therefore, this method cannot be used commercially.

Those fabrics having a soil resistance are very useful from a practical view point, but it has not been successful to industrially treat fabrics to retain soil resistance. The method in which soil resistance of fabrics is caused by a treatment using a sodium phosphate such as sodium-hexametaphosphate is described in American Dyestuff Reporter vol. 53, page 362 (1964). In practice, the soil resisting effect produced by said method is not sufficient. Thus, it will be recognized that fabrics are not rendered sufficiently soil resistant to be practically useful. Furthermore, since the treatment by means of the sodium salts requires rather severe heat-treating condition, it is unsuitable for treating silk, wool, regenerated cellulosic fibers, and the like, and still more, it causes a remarkable discoloration and lowers handling.

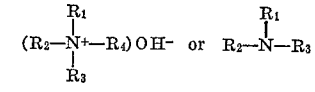
From the results of applicant's investigation in which they have endeavored to overcome various disadvantages produced by conventional methods using phosphoric acid-nitrogenous compounds, and to establish a method for retaining superior flame resistance in fabrics, there

is provided a method in which a lowering of the strength and a decrease of a whiteness are not caused and a superior soil resisting effect is retained.

In conventional methods for retaining a flame resisting effect in fabrics by using phosphoric acid-nitrogenous compounds, the same has been carried out by fixing the retardants to fabrics, then baking the fabrics at a temperature so high that brittleness of the fabrics is caused or for so long a time that it is industrially impossible to obtain durability to washing. The retardants and conditions selected according to this invention make it possible to bake them under normal fabric-treating conditions in which the baking may be carried out at a temperature of 110° to 170° C. for a few seconds to a few minutes.

Treated fabrics are normally washed after the baking, but in the present invention, even if the washing is omitted, problems such as a lowering of the strength, discoloration, and the like do not occur. This is also a remarkable characteristic in this invention.

According to the present invention, there is provided a method for retaining flame and soil resistances in fabrics which method comprises treating the fabrics with an aqueous solution of a composition comprising (1) a condensed phosphoric acid having a degree condensation of more than 3 and (2) a basic compound represented by the following formulae:



wherein R_1, R_2, R_3 and R_4 are hydrogen, alkyl or hydroxyalkyl group having 1 to 3 carbon atoms, the relative proportion of (1) to (2) being such that a ratio as 1 phosphorous atom to 0.5 to less than 2 nitrogen atoms is established, optionally drying the resulting fabrics, and baking same at a temperature of 110° to 170° C. for 30 seconds to 30 minutes.

The cellulosic fibers referred to in the present invention are natural cellulosic fibers such as cotton, hemp, and the like, regenerated cellulosic fibers such as viscose rayon, cupra rayon, Fortison, and the like, derivatives of cellulose such as acetate rayon, and the protein fibers are silk, wool, polyamino fibers and the like. The method of the invention may also be applied to a mixture of the above-mentioned fibers and a mixture of 50:50 of the above-mentioned fibers and synthetic fibers such as nylon, polyester, acryl, and the like.

In the present invention, it is important that the mean degree of condensation of the phosphorus component be more than 3. It has been found that when the degree of condensation is more than 3, excellent results are obtained. The most important advantage among them are the flame and soil resisting effects. For example, it is well known that even if fabrics are treated with a phosphoric acid having a degree of condensation of 1, i.e., ortho phosphoric acid, and the basic substance defined according to the present invention, and then heated strongly, the fabrics are imparted with neither flame resistance nor soil resistances durable to practical washing. It is clear from the instant investigation that when the degree of condensation gradually increases from 1, there is a remarkable tendency to increase the fixation of phosphorus to the fabrics with an increase of the degree of condensation, and when the mean degree of condensation reaches about 3, the fabrics substantially retain flame and soil resistances which are durable to washing. The other important advantage discovered by applicant relates to the coloring of the treated fabrics. Thus, when the present invention is carried out with a lower degree of condensation of

condensed phosphoric acid and a basic compound defined by this invention, coloring or yellowing is caused in the fabrics by the baking step. However, the coloring diminishes with an increase of the degree of condensation, and when the mean degree of condensation reaches about 3, the coloring decreases to a negligible extent. However higher the degree of condensation is, there are no specific obstacles to the washing resistance and coloring. However, since the preparation of more highly condensed compounds is not always advantageous, it is practical to use compounds having a mean degree of condensation of 3 to 3. Only when a mean degree of condensation of more than 3 is employed, are commercially valuable fabrics having flame and soil resistances obtained.

In the present invention, the degree of condensation of the phosphorus component is important as described above. On the other hand, the kind of condensed phosphoric acids used is independent of the method. Thus, as a condensed phosphoric acid all the condensed phosphoric acids having linear, branched or cyclic structure, may be employed. A mixture of two or more of the above-mentioned phosphoric acids or salts thereof may also be used.

The basic materials used in this invention are organic amines such as monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monopropylamine, dipropylamine, tripropylamine, monomethanolamine, dimethanolamine, trimethanolamine, monoethanolamine, diethanolamine, triethanolamine, tetramethylammoniumhydroxide, tetraethylammoniumhydroxide, tetrapropylammoniumhydroxide, and the like, and ammonia and a mixture of said basic materials. These amine or ammonium salts of the condensed phosphoric acid impart higher soil resistance to fabrics than do the corresponding sodium salts. Furthermore, when fabrics are subjected to treatment with sodium salts, flame resistance is scarcely observed, but superior flame resistance durable to washing is simultaneously obtained in fabrics treated according to the present invention.

The relative proportion of the condensed phosphoric acid and the basic compound is also very important in the present method. It is necessary to constitute the proportions of the two such that a ratio of 1 atom of phosphorus to 0.5 to less than 2 atoms of nitrogen exists. When the fabrics are treated with a solution having a ratio of 1 atom of phosphorus to less than 0.5 atom of nitrogen, they will not only be wanting in flame and soil resistances but also quite injured in regard to the strength of the fabrics. On the other hand, when the fabrics are treated with a solution having a ratio of 1 atom of phosphorus to more than 2 atoms of nitrogen, effects durable to washing are not obtained. The reason will perhaps depend upon the fact that the desired reaction does not occur in the fabrics.

The treating solution of this invention is obtained by dissolving in water, salts made of the above-mentioned condensed phosphoric acids and basic materials in the proportion defined above, or by admixing in water the above-mentioned condensed phosphoric acids and basic materials in the proportion defined above. The amounts of the compounds used in the treatment is ordinarily 0.3 to 30% by weight based on the fabrics, and the treatment may be completed by dipping the fabrics in the treating solution for only a few seconds.

Although the flame and soil resisting effects based on the present invention are caused by the phosphorus and nitrogen, required amounts of retardants should be fixed to the fabric in accordance with the degree of flame and soil resistances desired to in the specific fabric. Therefore, the present invention will not be especially limited by the amount of the retardants fixed to the fabrics.

A variety of agents which are employed in the usual fabric treatments can be used together with the retardants of this invention. For example, there may be used a resin-treating agent such as dimethylol urea, dimethylol ethylene urea, or the like, and an acidic catalyst, water-proofing agent, oiling-agent or the like. The nitrogen derived from these substances is naturally excluded from the calculation of the ratio between the phosphorus and the nitrogen.

Example 1

Solution A which is based on the present invention consists of a condensed phosphoric acid having a degree of condensation of 4, contained in a 1 liter aqueous solution of 200 g. of ammonium condensed phosphate in which the ratio of phosphorus to nitrogen is 1:1.

Solution B, which is a different treating solution than that of this invention, contained a sodium salt which is 200 g. of sodiumhexametaphosphate in 1 liter of an aqueous solution.

Solution C contained 200 g. of monobasic ammoniumphosphate in 1 liter of an aqueous solution.

A refined and undyed plain weave fabric consisting of cotton fibers of 60 S warp and filling was treated with each of the A, B and C solutions, respectively, squeezed at 80% wet pick up, dried at 80° C., baked at 150° C. for six minutes, and finally finished by washing with a soap solution.

The soil and flame resistances, whiteness and tensile strength of the fabrics treated with solutions A, B and C are evaluated as shown in following table.

Designation of treating solution	Soil resistance, percent	Flammability char length, cm.	Whiteness, percent	Tensile strength, g.
A	73.1	6.2	80.0	776
B	59.4	(1)	73.3	783
C	52.5	(1)	55.7	622
Untreated fabric	51.4	(1)	81.9	831

[1] Completely burned.

It is apparent from the Table that the fabric treated with solution A was exceedingly superior as to the soil resistance as well as flame resistance, no decreases of the whiteness and strength were observed.

On the other hand, as to the fabric treated with solution B, the soil and flame resistances were so inferior that it may not be used practically. Moreover, a decrease of the whiteness was also observed. When the fabric was treated with solution C, the flame and soil resistances were not retained at all, and remarkable decreases of the whiteness and strength were observed. In the Table, the determination of the soil resistance was carried out as follows: 1.5 g. of carbon black and 1 g. of olive oil were added to 100 ml. of water, and then mixed together thoroughly, 2 g. of a test strip of the fabric were dipped in the solution thus prepared at room temperature for 1 minute, washed twice with 80 ml. of water at room temperature for 5 minutes, and dried. The soil resistance of the strip thus treated was evaluated by measuring the surface reflectance with a spectrophotometer. The spectrophotometer was mounted with a reflected light-measuring apparatus in which the surface reflectance of the fabric to a standard white plate (magnesium oxide) at a wave length of 480 mμ was determined by means of an integrating sphere. The soil resistance was evaluated by means of this surface reflectance. When the numerical value thereof is large, the whiteness of the fabric is superior and the resistance to soils is large.

The flammability was expressed in terms of char length which was measured in accordance with the procedure of AATCC (American Association of Textile Chemists and Colorists) Standard Test Method 34–1952. The lower the char length obtained, the higher is the flame resistance.

The whiteness was expressed in terms of the surface reflectance of the test fabric. The surface reflectance was evaluated by the reflectance which is measured by a spectrophotometer mounted with a reflected light-measuring apparatus in which the surface reflectance of the fabric compared to a standard white plate (magnesium oxide) at a wave length of 480 mμ is determined by means of an

integrating sphere. The tensile strength was measured by the Schopper type tensile tester.

Example 2

A fabric consisting of rayon fibers of 20 S warp and wool yarns of 20 S filling was treated with 10% aqueous solution of ammonium condensed phosphate having a mean degree of condensation of 3.5, in which the ratio of phosphorus to nitrogen was 1 to 1.3, dried and then baked at a temperature of 155° C. for 4 minutes and finally finished by washing with a soap solution. Said fabric was upholstered to chairs and practically used for 10 months without any soil on the fabric. The same fabric which was not treated with the solution according to this invention was practically used under the same conditions, but conspicuous soil appeared on the fabric within 4 months.

The flammability of the treated fabric was measured in accordance with the procedure of AATCC Standard Test Method 34–1952, the after flame and the after glow were both 0, and the char length was 7.4 cm. In the case of the untreated fabric, no flame resistance was observed with this method, and the sample was completely burned.

Example 3

An organdie fabric consisting of ply silk yarns of 15 denier warp and filling was treated with a 6% aqueous solution of ammonium condensed phosphate having a mean degree of condensation of 5.3, in which the ratio of phosphorus atoms to nitrogen atoms was 1 to 0.6, dried and then baked at a temperature of 130° C. for 2 minutes, and finished.

Slight soils such as dust and stains were observed in the treated fabric after two weeks wearing usage, but conspicuous soils such as dust, stains and grime were observed in the untreated fabric after wearing under the same condition for five days. After drycleaning and washing in accordance with the procedure AATCC–33–1962, the measured flammability was 6.8 seconds. The value indicates higher flammability as compared with the flammability of 2.5 seconds observed for the untreated fabric.

Example 4

Plain weave fabric consisting of cupra rayon yarns of 50 denier warp and filling was treated with an 8% aqueous solution of ammonium condensed phosphate having a mean degree of condensation of 6.2, in which the ratio of phosphorus atoms to nitrogen atoms was 1 to 0.8, dried and baked at a temperature of 160° C. for one minute. The data obtained by examining the treated fabric were as follows:

	Untreated fabric	Treated fabric
Whiteness, percent	83.9	82.6
Flammability:		
Before drycleaning and washing (sec.)	2.7	5.7
After drycleaning and washing (sec.)	2.9	5.4
Soil resistance, percent	53	75

The whiteness and soil resistances were measured in the same manner as in Example 1, and flammability was measured as in Example 3.

Example 5

A cotton fabric of 60 S warp and filling was dipped in an aqueous treating solution containing 15% ammonium condensed phosphate having a mean degree of condensation of 13.2 in which the ratio of phosphorus to nitrogen in said solution is 1 to 1, 10% dimethylol ethylene urea and a small amount of ammonia, dried, baked at 130° C. for 10 minutes and finally washed. The data obtained by examining the treated fabric were as follows:

	Untreated fabric	Treated fabric
Whiteness, percent	88.2	87.3
Flammability:		
Char length (cm.)	(1)	7.3
After flame (sec.)	25	0
After glow (sec.)		2
Soil resistance, percent	55.1	69.3
Crease recovery, percent	34.0	72.4

[1] Completely burned.

In this table, the whiteness, soil resistance and flammability were measured in the same manner as in Example 1, and the crease recovery was measured in accordance with the Monsanto method.

Example 6

A rayon fabric consisting of 120 denier warp and filling was treated with a 15% aqueous solution of ammonium condensed phosphate having a mean degree of condensation of 28, in which the ratio of phosphorus atoms to nitrogen atoms was 1 to 0.7, dried baked at 160° C. for 30 seconds, and finished. The data obtained by examining the treated fabric were as follows:

	Untreated fabric	Treated fabric
Whiteness, percent	91.7	91.5
Flammability:		
Before drycleaning and washing (sec.)	4.2	10.5
After drycleaning and washing (sec.)	4.7	9.2
Soil resistance, percent	62.1	78.9

The whiteness and soil resistance were measured in the same manner as in Example 1, and the flammability was measured as in Example 3.

Example 7

A hemp-polyester union yarn (the union rate was 1:1) of 60 S warp and filling was dipped in a treating solution which was produced by dissolving 10 g. of condensed phosphoric acid having a mean degree of condensation of 14.3 into 1 liter of 10% aqueous ammonia maintained at below 3° C. squeezed, dried and baked at 140° C. for 6 minutes.

When a flame was brought to the treated fabric it burned, but by keeping the flame away from the fabric the combustion thereof ceased. On the other hand, in case of untreated fabric, the combustion did not cease even when the flame was removed.

The whiteness, measured in the same manner as in Example 1 was 87.3% (untreated fabric was 86.6%) and soil resistance was 63.8% (untreated fabric was 47.8%).

Example 8

A rayon fabric of 40 denier warp and filling was treated with an aqueous solution of 5% monoethanolamine salt of condensed phosphoric acid which was produced by dissolving 82.3 parts of condensed phosphoric acid of a mean degree of condensation of 7.7 and 61.0 parts of monoethanolamine, 10% dimethylolethyleneurea and 0.5% octadecylethyleneurea, dried and baked at a temperature of 170° C., for 1 minute.

In the following table, the data for soil and flame resistances as to the treated and untreated fabrics are given.

The soil resistance was measured in the same manner as in Example 1 and the flame resistance was measured as in Example 3.

	Untreated fabric	Treated fabric
Soil resistance, percent	57.6	76.9
Flammability:		
Before drycleaning and washing (sec.)	3.3	6.2
After drycleaning and washing (sec.)	3.7	5.8

Example 9

A fabric consisting of nylon yarn of 50 denier warp and rayon yarn of 40 denier filling was treated with an aqueous solution which was produced by dissolving 100

g. of a condensed phosphoric acid having a mean degree of condensation of 10.3 into 1 liter of an aqueous solution containing 80 g. of diethylamine maintained below 3° C., dried and baked at 130° C. for 4 minutes.

The flammability of the treated fabric was measured in the same manner as in Example 3. The values thereof before and after drycleaning and washing were 5.6 and 6.0 seconds, respectively. The flammability of the untreated fabric before and after drycleaning-and-washing were 2.7 and 2.6 seconds. From these results, it is seen that the flamability of the treated fabric was extremely low.

Example 10

A cotton fabric of 40 S warp and filling was treated with an aqueous solution which was produced by dissolving 100 g. of a condensed phosphoric acid having a mean degree of condensation of 13 into 1 liter of an aqueous solution containing 90 g. of tetramethyl ammonium hydroxide maintained below 4° C., baked at 110° C. for 30 minutes and then washed.

The data obtained by examining the treated fabric were as follows:

	Untreated fabric	Treated fabric
Whiteness, percent	83.7	83.9
Flammability:		
Char length (cm.)	(1)	6.3
After flame (sec.)	18	1
After glow (sec.)		1
Soil resistance, percent	57.8	75.7

[1] Completely burned.

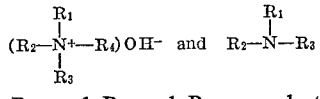
Example 11

Fifty g. of a condensed phosphoric acid which contained 85% by weight of phosphoric acid having a degree of condensation of more than 10, were dissolved dropwise, at below 5° C., into 500 ml. of an aqueous solution containing 50 g. of triethanolamine. The aqueous solution of said condensed phosphate thus obtained was diluted to 1 liter with water to produce the treating solution. A union organdie fabric consisting of ply silk yarns of 21 denier warp and cupra yarns of 40 denier filling was dipped in said treating solution, dried, baked at 130° C. for 2 minutes, and then finished.

The treated fabric was not soiled after 10 days use, but in the untreated fabric, soil was observed after 3 days wearing. The flammability of the treated fabric measured in the same manner as in Example 3 was 5.8 seconds. This value exhibits remarkable flame resistance compared with 2.8 seconds for the untreated fabric.

What is claimed is:

1. A method for retaining flame and soil resistances in fabrics which comprises treating fabrics with an aqueous solution of a composition consisting of a condensed phosphoric acid having a mean degree of condensation of more than 3 and a member selected from the group consisting of basic compounds of the formulae:



wherein R_1, R_2, and R_3 and R_4 are selected from the group consisting of hydrogen and alkyl groups of 1 to 3 carbon atoms, said condensed phosphoric acid and said member being present in amounts such that for each atom of phosphorus, there are 0.5 to less than 2 atoms of nitrogen, and baking the thusly treated fabrics at a temperature of 110° C. to 170° C. for 30 seconds to 30 minutes.

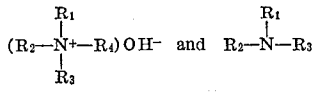
2. A method as claimed in claim 1 wherein the mean degree of condensation is in the range of more than 3 to 30.

3. A method as claimed in claim 2 wherein the basic compound is monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monopropylamine, dipropylamine, tripropylamine, monomethanolamine, dimethanolamine, trimethanolamine, monoethanolamine, diethanolamine, triethanolamine, monopropanolamine, dipropanolamine, tripropanolamine, tetramethylammoniumhydroxide, tetraethylammoniumhydroxide, tetrapropylammoniumhydroxide or ammonia.

4. A method as claimed in claim 1 comprising drying the fabrics after treatment thereof with the aqueous solution.

5. A method as claimed in claim 2 comprising drying the fabrics after treatment thereof with the aqueous solution.

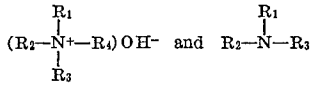
6. A method for imparting flame and soil resistances to fabrics which comprises treating fabrics with an aqueous solution of a composition consisting of at least two condensed phosphoric acids having mean degrees of condensation in the range of more than 3 to 30 and at least two members selected from the group consisting of basic compounds of the formulae



wherein R_1, R_2, R_3 and R_4 are selected from the group consisting of hydrogen and alkyl groups of 1 to 3 carbon atoms, said condensed phosphoric acids and said members being present in amounts such that for each atom of phosphorus, there are 0.5 to less than 2 atoms of nitrogen, and baking the thusly treated fabrics at a temperature of 110° to 170° C. for 30 seconds to 30 minutes.

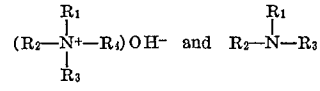
7. A method as claimed in claim 6 comprising drying the fabrics after treatment thereof with the aqueous solution.

8. A method for retaining flame and soil resistances in fabrics which comprises treating fabrics with an aqueous solution of a salt of a condensed phosphoric acid having a mean degree of condensation in the range of more than 3 to 30 and a member selected from the group consisting of basic compounds of the formulae



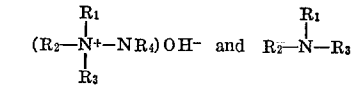
wherein R_1, R_2, R_3 and R_4 are selected from the group consisting of hydrogen and alkyl groups of 1 to 3 carbon atoms, said salt of a condensed phosphoric acid and said member being present in amounts such that for each atom of phosphorous there are 0.5 to less than 2 atoms of nitrogen and baking the thusly treated fabrics at a temperature of 110° to 170° C. for 30 seconds to 30 minutes.

9. A method for imparting flame and soil resistances durable to dry cleaning and washing, to fabrics which comprises dipping, for a few seconds fabrics into an aqueous solution of a composition consisting of a condensed phosphoric acid having a mean degree of condensation in the range of more than 3 to 30 and a member selected from the group consisting of basic compounds of the formulae



wherein R_1, R_2, R_3 and R_4 are selected from the group consisting of hydrogen and alkyl groups of 1 to 3 carbon atoms, said condensed phosphoric acid and said member being present in amounts such that for each atom of phosphorous, there are 0.5 to less than 2 atoms of nitrogen and baking the thusly treated fabrics at a temperature of 110° to 170° C. for 30 seconds to 30 minutes.

10. A method for retaining flame and soil resistances in fabrics which comprises treating fabrics with an aqueous solution containing from 0.3 to 30% by weight based on the fabrics, of a salt of a condensed phosphoric acid having a mean degree of condensation in the range of more than 3 to 30 and a member selected from the group consisting of basic compounds of the formulae



wherein R_1, R_2, R_3 and R_4 are selected from the group consisting of hydrogen and alkyl groups of 1 to 3 carbon atoms, said condensed phosphoric acid and said member being present in amounts such that for each atom of phosphorous, there are 0.5 to less than 2 atoms of nitrogen

and baking the thusly treated fabrics at a temperature of 110° to 170° C. for 30 seconds to 30 minutes.

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