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FLAME-PROOFING OF TEXTILES

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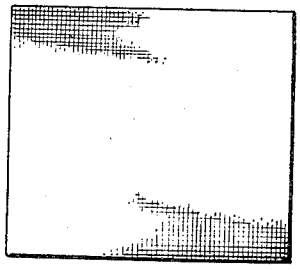

Textile Material Flame-Proofed with the aid of

(1) Reaction product of urea and O-containing compound of phosphorus, and

(2) Methylol-melamine

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FLAME-PROOFING OF TEXTILES

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This is a continuation in part of my U. S. patent application Serial No. 301,377, filed July 28, 1952, now amended. Known processes for rendering textile fabrics flame-proof have the disadvantages that either the impregnating baths are not sufficiently stable and are therefore little suited especially for the treatment of large batches of textile fabrics, or the tensile strength and the feel of the textiles are changed by the treatment in an undesirable way.

The present invention is based on the observation that textile fabrics can be rendered flame-proof while avoiding the above drawbacks to a great extent by impregnating the fabric with an aqueous liquid which contains (1) from about 12 to 48% by weight, and preferably from about 24 to 38% by weight, of a reaction mixture obtained by heating an excess of urea together with an oxygen-containing compound of phosphorus selected from the group consisting of ortho-phosphoric acid, pyrophosphoric acid, meta-phosphoric acid and ammonium salts of these acids, at a high temperature, and (2) from about 2 to 18% by weight, and preferably from about 4 to 12% by weight of a methylol compound of an aminotriazine, the ratio of component (1) to component (2) ranging from 3:1 to 6:1, and drying the impregnated fabric at a raised temperature.

The reaction mixture used as component (1) may be prepared by heating an oxygen-containing compound of phosphorus of the group consisting of ortho-phosphoric acid, pyrophosphoric acid, meta-phosphoric acid and ammonium salts of said acids, together with an excess of urea, preferably in a weight ratio of 3 parts of the former to 5 to 8 parts of the latter, at a temperature of between about 100° C. and 200° C., preferably at 155°–160° C., for a period of time ranging from about some minutes to about two hours. In case the mixture is heated at a temperature in the neighborhood of 100° C., the heating period is advantageously more than 2 hours, e. g. 4, 6, or even 8 hours. Such reaction mixture can easily be dissolved in about their own weight of water to produce concentrated stock solutions.

As methylol compounds of an aminotriazine used as component (2) there may be used the methylol-compounds of 2:4:6-triamino-1:3:5-triazine (melamine), and also methylol compounds of those derivatives of melamine which still contain at least one amino group, and advantageously at least two amino groups, for example, methylol compounds of melam, melem, ammeline, ammelide or a halogen-substituted aminotriazine, such as 2-chloro-4:6-diamino-1:3:5-triazine, and also methylol compounds of guanamines such, for example, as those of benzo-guanamine (2-phenyl-4:6-diamino-1:3:5-triazine), aceto-guanamine (2-methyl-4:6-diamino-1:3:5-triazine), or formo-guanamine (4:6-diamino-1:3:5-triazine), and finally methylol compounds which are partially etherified with aliphatic alcohols of low molecular weight, such as methyl alcohol or butyl alcohol, for example, methyl ethers of methylol-melamines containing 4 to 6 methylol groups, in which 2 to 6 methylol groups are etherified.

Advantageously methylol-melamines are used, and especially those which are of unlimited solubility in water. Very suitable condensation products are those of unlimited solubility in water which are obtainable from one molecular proportion of melamine and about 2 to 3 molecular proportions of formaldehyde. Obviously there may also be used mixtures of such aminotriazine condensation products.

For preparing the aqueous impregnating liquids the individual components may be dissolved or dispersed in water, whereby clear solutions or very finely divided dispersions are obtained.

The textile fabrics may be impregnated with the bath by means of the known methods and apparatus for impregnating fabrics. There are advantageously used concentrated impregnating baths which are rendered slightly alkaline, for example, by adjustment to a pH value of 8. In this manner the impregnation produces a large increase in the weight of the fabric, so that the flame-proof effect is considerably enhanced. Wetting agents may also be added to the bath in order to improve the wetting of the fabric. There are advantageously used baths having a dry content of about 30–50 percent. Such baths are stable for long periods, for example, from 4 hours to several days, that is to say, no water-insoluble compounds are formed when the baths are allowed to stand at ordinary temperature, or if insoluble compounds were formed at the outset the amount thereof increases slowly and the undissolved portions remain in a finely dispersed form. During the drying of the fabric at a raised temperature there are formed from the various components of the impregnating bath and probably also with the assistance of the textile fibers, insoluble compounds which produce the flame-proof effect.

The strength with which the finish is fixed on the fibrous material depends on the drying temperature. If the drying is carried out at a temperature below 100° C., for example, at 70° C., the flame-proof finish is resistant to water and the feel and tensile strength of, for example, a cotton fabric, are not changed. If the drying is carried out at a temperature above 100° C., for example, at 120–160° C., or if the fabric is dried at a temperature below 100° C., and then after hardening is brought about at, for example, 120–160° C., the flame-proof finish is also resistant to washing with neutral washing agents. One or other method of drying is used depending on the purpose for which the treated fabric is to be used. The quality of the flame-proof finish depends not only on the conditions of drying or hardening but, as stated above, also on the amount of the impregnating substances fixed on the fiber. Experiments have shown that it is of advantage to carry out the impregnation in such manner that an increase in weight of not substantially less than about 6 percent occurs. At increases in weight ranging from 10–15 percent there are obtained very good flame-proof effects. The impregnation may also be carried out more strongly so as to produce, for example, an increase in weight of about 20 percent. (The increases in weight are calculated on the material after it has been dried, hardened, rinsed and again dried, the untreated fabric serving as the starting point.) The quantity of the phosphorus fixed on and in the fibers is each time about 1.3–4%, and of nitrogen about 2.8–6%.

As fabrics which can be rendered flame-proof by the present process there come into consideration principally cellulose fibers, for example, linen, jute, viscose and especially cotton. There also come into consideration protein fibers, such as wool. By the process of the invention there is also imparted to the treated fabric certain protection against attack by micro-organisms.

The accompanying sheet of drawing diagrammatically

illustrates textile material flame-proofed according to the present invention.

The following examples illustrate the invention, the parts being by weight unless otherwise stated and the relationship of parts by weight to parts by volume being the same as that of the kilogram to the liter:

Example 1

15 parts of pyrophosphoric acid and 80 parts of urea are slowly heated to 140° C., and at 140–145° C. a further 15 parts of pyrophosphoric acid are added, the temperature is raised to 160° C. and this temperature is maintained for 30 minutes. The mixture is then allowed to cool to about 100° C. and 90 parts of water are added to the reaction mixture, whereby a clear solution is obtained. The whole is then allowed to cool to 10–15° C., whereupon a small amount of biuret crystallizes out. The mixture is filtered to remove this precipitate, and the filtrate is mixed with ammonia until the solution has a pH value of 8. The solution is stable at ordinary temperature and can be used for the preparation of impregnating baths.

An impregnating bath (containing about 36% of the above reaction mixture and 9% of the component (2) described below) is prepared by mixing 80 parts of the above described concentrated solution, with 10 parts of a condensation product of unlimited solubility in water from 1 molecular proportion of melamine and about 2 to 3 molecular proportions of formaldehyde (component (2)), and 20 parts of water, a small amount of a precipitate being formed which remains in a fine state of dispersion.

Cotton is impregnated at ordinary temperature with the above bath, and the cotton is squeezed, then dried at 70° C. and subjected to a heat-treatment at 150° C. for five minutes. It is then thoroughly rinsed with cold water and again dried.

Analysis shows a phosphorus content of 2.85% and a nitrogen content of 5.25% by weight based on the dry weight of the untreated textile fabric. The flame-proof effect is very good. The material does not after flame or after glow. The tensile strength is not affected by the treatment and the feel of the material remains unaltered.

Instead of the above mentioned heat treatment at 150° C., the fabric dried at 70° C. can be impregnated a second time and dried again at 70° C.

The treated material of this and the subsequent examples is tested for its flame-proof quality by means of the vertical Bunsen burner test. This test is described for example, in the book by R. W. Little ("Flame-Proofing of Textile Fabrics," Reinhold Publishing Corporation, New York, 1947, page 111 et seq.).

Example 2

A cotton fabric is impregnated in a bath having the following composition: 20 parts of water, 10 parts of a condensation product of unlimited solubility in water from 1 molecular proportion of melamine and about 2 to 3 molecular proportions of formaldehyde, (component (2)), 80 parts of a solution obtained by dissolving about 30 parts of the reaction mixture (component (1)) described below in 50 parts of water.

The impregnating bath thus contains about 27% of component (1) and 9% of component (2).

After squeezing the fabric, it is dried at 70° C., subjected to a heat-treatment at 160° C. for 3 minutes and then rinsed with water and again dried. Analysis shows a phosphorus content of 2.53% and a nitrogen content of 4.85%.

The flame-proof finish so obtained is resistant to a washing treatment carried out at 70° C. for 30 minutes in a bath containing 1 gram per liter of a sulfonated washing agent having a neutral reaction. Washing can also be carried out at the boil when a washing agent free from ions is used.

The above mentioned reaction mixture (component (1) is made by heating 30 parts of pyrophosphoric acid with 50 parts of urea for 30 minutes at 160° C.

Instead of the above mentioned condensation product of unlimited solubility in water prepared from 1 molecular proportion of melamine and 2 to 3 molecular proportions of formaldehyde, there may be used such a condensation product which is soluble in water only in the ratio of 1:1, or there may be used a condensation product of unlimited solubility in water prepared from 1 molecular proportion of melamine and 4 molecular proportions of formaldehyde.

Example 3

The procedure is the same as that described in Example 2, except that the fabric after being dried at 70° C. is subjected to a heat treatment at 120° C. for 20 minutes. Analysis shows a phosphorus content of 1.30% and a nitrogen content of 3.31%.

Example 4

200 parts of urea are melted at 140° C. 100 parts of diammonium ortho-phosphate are gradually introduced while stirring. The mixture is then heated to 160° C. and maintained at that temperature for 30 minutes. There is obtained a clear melt. After cooling to 110° C., 200 parts of water are added. When the solution is cooled to room temperature a small amount of insoluble matter precipitates and is removed by filtration. The filtrate is then adjusted to a pH value of 8 by means of ammonia.

An impregnating bath is prepared by mixing 80 parts of the above described concentrated solution with 10 parts of a condensation product of unlimited solubility in water from 1 molecular proportion of melamine and about 2 to 3 molecular proportions of formaldehyde, and 20 parts of water.

This impregnating bath contains 38% of the reaction mixture and 9% of the said methylol melamine.

Cotton is impregnated with the above bath at ordinary temperature. Then it is sequeezed, dried at 70° C., subjected to a heat-treatment at 130° C. for 10 minutes, rinsed with water and dried. Analysis shows a phosphorus content of 1.77% and a nitrogen content of 4.13%.

Example 5

250 parts of urea and 100 parts of orthophosphoric acid of 75 percent strength are heated at 140° C. A further 100 parts of ortho-phosphoric acid of 75 percent strength and 50 parts of urea are added to the reaction mixture at that temperature, and the mixture is then heated for 10 minutes at 160° C. After cooling to 110° C., 400 parts of water are added and the solution, after being cooled to room temperature, is adjusted to a pH value of 8 by means of ammonia.

An impregnating bath is prepared by mixing 80 parts of the above described concentrated solution with 10 parts of a condensation product of unlimited solubility in water from 1 molecular proportion of melamine and about 2 to 3 molecular proportions of formaldehyde, and 20 parts of water.

This impregnating liquid contains 32% of the above reaction mixture and 9% of the said methylol melamine.

The procedure is the same as that described in Example 4, except that the heat-treament is carried out at 140° C. for 6 minutes. Analysis shows a phosphorus content of 2.09% and a nitrogen content of 4.9%.

Example 6

400 parts of urea are melted and at 140° C. 150 parts of meta-phosphoric acid are slowly introduced into the melt, the temperature increasing to 160° C. When the addition is complete, the melt is maintained for a further 15 minutes at 160° C. and then cooled to 110° C., whereupon 400 parts of water are added. After cooling to room temperature the undissolved matter is removed by filtra-

tion, and the filtrate is adjusted to a pH value of 8 by means of ammonia.

An impregnating bath is prepared by mixing 80 parts of the above described concentrated solution with 10 parts of a condensation product of unlimited slubility in water from 1 molecular proportion of melamine and about 2 to 3 molecular proportions of formaldehyde, and 20 parts of water.

This impregnating liquid contains about 36% of the above reaction mixture and 9% of the said methylol melamine.

The procedure is the same as that described in Example 4, except that the heat-treatment is carried out at 150° C. for 5 minutes.

Example 7

In order to improve its absorptive capacity wool gabardine is treated for 30 minutes at 45–50° C. in a bath which contains 1 cc. of ammonia solution of 20 percent strength, and 1 gram of a sulfonated washing agent per liter, and the fabric is rinsed and dried. The fabric is then impregnated with the bath described in Example 1, dried at 80° C., again impregnated and dried for 30 minutes at 80° C., and then well rinsed.

The wool so treated has a very good flameproof property. The feel of the fabric is not changed by the treatment.

What is claimed is:

1. A process for rendering textile fabrics flameproof, which comprises impregnating the fabric in an aqueous liquid which contains (1) about 12–48% by weight of a reaction mixture obtained by heating an excess of urea together with an oxygen-containing compound of phosphorus selected from the group consisting of ortho-phosphoric acid, pyrophosphoric acid, meta-phosphoric acid and ammonium salts of these acids, at a high temperature, and (2) about 2–18% by weight of a methylol-melamine, the ratio of component (1) to component (2) ranging from 3:1 to 6:1, and drying the impregnated fabric at a raised temperature.

2. A process for rendering textile fabrics flameproof, which comprises impregnating the fabric in an aqueous liquid which contains (1) about 24–38% by weight of a reaction mixture obtained by heating an excess of urea together with an oxygen-containing compound of phosphorus selected from the group consisting of ortho-phosphoric acid, pyrophosphoric acid, meta-phosphoric acid and ammonium salts of these acids, at a high temperature, and (2) about 4–12% by weight of a methylol-melamine, the ratio of component (1) to component (2) ranging from 3:1 to 6:1, and drying the impregnated fabric at a raised temperature.

3. A process for rendering textile fabrics flameproof, which comprises impregnating the fabric in an aqueous liquid which contains (1) about 24–38% by weight of a reaction mixture obtained by heating an excess of urea together with pyrophosphoric acid at a high temperature, and (2) about 4–12% by weight of a methylol-melamine the ratio of component (1) to component (2) ranging from 3:1 to 6:1, and drying the impregnated fabric at a temperature ranging from 70° C. to 160° C.

4. A process for rendering textile fabrics flameproof, which comprises impregnating the fabric in an aqueous liquid which contains (1) about 27–37% by weight of a reaction mixture obtained by heating 5–8 parts of urea with 3 parts of pyrophosphoric acid at 160° C. for 30 minutes, and (2) 9% by weight of a condensation product of unlimited water-solubility of one mol of melamine with about 2–3 mols of formaldehyde, drying the impregnated fabric at 70° C. and after-hardening the dried fabric at 150–160° C.

5. A process for rendering textile fabrics flameproof, which comprises impregnating the fabric in an aqueous liquid which contains (1) about 24–38% by weight of a reaction mixture obtained by heating an excess of urea together with diammonium ortho-phosphate at a high temperature, and (2) about 4–12% by weight of a methylol-melamine, the ratio of component (1) to component (2) ranging from 3:1 to 6:1, and drying the impregnated fabric at a temperature ranging from 70° C. to 160° C.

6. A process for rendering textile fabrics flameproof, which comprises impregnating the fabric in an aqueous liquid which contains (1) 38% by weight of a reaction mixture obtained by heating 6 parts of urea with 3 parts of diammonium ortho-phosphate at 160° C. for 30 minutes, and (2) 9% by weight of a condensation product of unlimited water-solubility of one mol of melamine with about 2–3 mols of formaldehyde, drying the impregnated fabric at 70° C. and after-hardening the dried fabric at 130° C.

7. A process for rendering textile fabrics flameproof, which comprises impregnating the fabric in an aqueous liquid which contains (1) about 24–38% by weight of a reaction mixture obtained by heating an excess of urea together with ortho-phosphoric acid at a high temperature, and (2) about 4–12% by weight of a methylol-melamine, the ratio of component (1) to component (2) ranging from 3:1 to 6:1, and drying the impregnated fabric at a temperature ranging from 70° C. to 160° C.

8. A process for rendering textile fabrics flameproof, which comprises impregnating the fabric in an aqueous liquid which contains (1) 32% by weight of a reaction mixture obtained by heating 6 parts of urea with 3 parts of ortho-phosphoric acid at 160° C. for 10 minutes, and (2) 9% by weight of a condensation product of unlimited water-solubility of one mol of melamine with about 2–3 mols of formaldehyde, drying the impregnated fabric at 70° C. and after-hardening the dried fabric at 140° C.

9. A process for rendering textile fabrics flameproof, which comprises impregnating the fabric in an aqueous liquid which contains (1) about 24–38% by weight of a reaction mixture obtained by heating an excess of urea together with meta-phosphoric acid at a high temperature, and, (2) about 4–12% by weight of a methylol-melamine, the ratio of component (1) to component (2) ranging from 3:1 to 6:1, and drying the impregnated fabric at a temperature ranging from 70° C. to 160° C.

10. A process for rendering textile fabrics flameproof, which comprises impregnating the fabric in an aqueous liquid which contains (1) 36% by weight of a reaction mixture obtained by heating 8 parts of urea with 3 parts of meta-phosphoric acid at 160° C. for about 15 minutes, and (2) 9% by weight of a condensation product of unlimited water-solubility of one mol of melamine with about 2–3 mols of formaldehyde, drying the impregnated fabric at 70° C. and after-hardening the dried fabric at 150° C.

11. A textile fabric which has a flameproof dressing obtained by impregnating the fabric in an aqueous liquid which contains (1) about 12–48% by weight of a reaction mixture obtained by heating an excess of urea together with an oxygen-containing compound of phosphorus selected from the group consisting of ortho-phosphoric acid, pyrophosphoric acid, meta-phosphoric acid and ammonium salts of these acids, at a high temperature, and (2) about 2–18% by weight of a methylol-melamine, the ratio of component (1) to component (2) ranging from 3:1 to 6:1, and drying the impregnated fabric at a raised temperature, the amounts of phosphorus and nitrogen fixed in and on the fibers being about 1.3–4.0% of the former and about 2.8–6.0% of the latter.

12. A textile fabric which has a flameproof dressing obtained by impregnating the fabric in an aqueous liquid which contains (1) about 24–38% by weight of a reaction mixture obtained by heating an excess of urea together with an oxygen-containing compound of phosphorus selected from the group consisting of ortho-phosphoric acid, pyrophosphoric acid, meta-phosphoric acid

and ammonium salts of these acids, at a high temperature, and (2) about 4–12% by weight of a methylol-melamine, the ratio of component (1) to component (2) ranging from 3:1 to 6:1, and drying the impregnated fabric at a raised temperature, the amounts of phosphorus and nitrogen fixed in and on the fibers being about 1.3–4.0% of the former and about 2.8–6.0% of the latter.

13. A textile fabric which has a flameproof dressing obtained by impregnating the fabric in an aqueous liquid which contains (1) about 24–38% by weight of a reaction mixture obtained by heating an excess of urea together with pyrophosphoric acid at a high temperature, and (2) about 4–12% by weight of a methylol-melamine the ratio of component (1) to component (2) ranging from 3:1 to 6:1, and drying the impregnated fabric at a temperature ranging from 70° C. to 160° C., the amounts of phosphorus and nitrogen fixed in and on the fibers being about 1.3–4.0% of the former and about 2.8–6.0% of the latter.

14. A textile fabric which has a flameproof dressing obtained by impregnating the fabric in an aqueous liquid which contains (1) about 27–37% by weight of a reaction mixture obtained by heating 5–8 parts of urea with 3 parts of pyrophosphoric acid at 160° C. for 30 minutes, and (2) 9% by weight of a condensation product of unlimited water-solubility of one mol of melamine with about 2–3 mols of formaldehyde, drying the impregnated fabric at 70° C. and after-hardening the dried fabric at 150–160° C., the amounts of phosphorus and nitrogen fixed in and on the fibers being 2.5–2.9% of the former and 4.8–5.3% of the latter.

15. A textile fabric which has a flameproof dressing obtained by impregnating the fabric in an aqueous liquid which contains (1) about 24–38% by weight of a reaction mixture obtained by heating an excess of urea together with diammonium ortho-phosphate at a high temperature, and, (2) about 4–12% by weight of a methylol melamine, the ratio of component (1) to component (2) ranging from 3:1 to 6:1, and drying the impregnated fabric at a temperature ranging from 70° C. to 160° C., the amounts of phosphorus and nitrogen fixed in and on the fibers being about 1.3–4.0% of the former and about 2.8–6.0% of the latter.

16. A textile fabric which has a flameproof dressing obtained by impregnating the fabric in an aqueous liquid which contains (1) 38% by weight of a reaction mixture obtained by heating 6 parts of urea with 3 parts of diammonium ortho-phosphate at 160° C. for 30 minutes, and (2) 9% by weight of a condensation product unlimited water-solubility of one mol of melamine with about 2–3 mols of formaldehyde, drying the impregnated fabric at 70° C. and after-hardening the dried fabric at 130° C., the amounts of phosphorus and nitrogen fixed in and on the fibers being about 1.7–1.8% of the former and about 4.1–4.2% of the latter.

17. A textile fabric which has a flameproof dressing obtained by impregnating the fabric in an aqueous liquid which contains (1) about 24–38% by weight of a reaction mixture obtained by heating an excess of urea together with ortho-phosphoric acid at a high temperature, and (2) about 4–12% by weight of a methylol-melamine, the ratio of component (1) to component (2) ranging from 3:1 to 6:1, and drying the impregnated fabric at a temperature ranging from 70° C. to 160° C., the amounts of phosphorus and nitrogen fixed in and on the fibers being about 1.3–4.0% of the former and about 2.8–6.0% of the latter.

18. A textile fabric which has a flameproof dressing obtained by impregnating the fabric in an aqueous liquid which contains (1) 32% by weight of a reaction mixture obtained by heating 6 parts of urea with 3 parts of ortho-phosphoric acid at 160° C. for 10 minutes, and, (2) 9% by weight of a condensation product of unlimited water-solubility of one mol of melamine with about 2–3 mols of formaldehyde, drying the impregnated fabric at 70° C. and after-hardening the dried fabric at 140° C., the amounts of phosphorus and nitrogen fixed in and on the fibers being about 2.1% of the former and about 5.0% of the latter.

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