United States Patent Office 3,567,359
Patented Mar. 2, 1971

3,567,359

TREATMENT OF CELLULOSIC TEXTILE MATERIALS TO PROVIDE FIRE RESISTANCE THERETO

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No Drawing. Filed Aug. 20, 1965, Ser. No. 481,398
Claims priority, application Great Britain, Aug. 21, 1964, 34,227/64
Int. Cl. D06m 13/34
U.S. Cl. 8—116.2 14 Claims

ABSTRACT OF THE DISCLOSURE

The fire resistance of cellulosic material is improved by impregnating it with a non-volatile inorganic acid, cyanamide, and a halogenated alkyl phosphate and then heating to effect reaction between the cellulose and the impregnants.

The invention relates to a process for the treatment of cellulosic textile materials to improve their properties, particularly the fire-resistance.

In U.S. Pat. No. 2,530,261 a process is described and claimed comprising impregnating cellulosic textile fibres, yarns or fabrics with an aqueous solution containing a non-volatile strong mineral acid and cyanamide and then drying and making the impregnated material to effect reaction between the material, the mineral acid and cyanamide, the reaction conditions being such that the product contains at least 1 percent by weight of combined acid. The acid can be neutralised in part if desired to an extent not exceeding the formation of the monosubstituted salt. Thus, a typical example of the process would be to use an impregnating mixture of orthophosphoric acid, ammonium dihydrogen phosphate and cyanamide.

The above process gives valuable improvements in the flame-resistance of treated fabrics but is not as permanent a treatment as desired.

We have now devised a modification of the above process giving increased and durable fire-resistance to treated materials.

According to the present invention a process for the treatment of cellulosic material comprises impregnating the material with an aqueous solution of a substantially non-volatile inorganic acid, cyanamide and a halogenated alkyl phosphate and heating the impregnated material, whereby effecting reaction between the cellulose and the impregnants.

The cellulosic materials which may be treated by the process of the present invention may take many forms although the process is most useful for the treatment of fabrics and garments. Cellulosic fibres treated may be in staple fibre or in filament form. The cellulosic material may be of natural or man-made origin; thus, for example, regenerated cellulose made by the viscose, cuprammonium or nitrate processes may be treated as may be cotton or linen. The cellulosic materials may be treated on their own, as is preferred, or they may be treated when in combination with non-cellulosic materials.

The degree of fire-resistance imparted by the process to treated materials varies according to the conditions used and the nature of the halogenated alkyl phosphate. As the amount of the impregnants deposited on the material being treated rises, so, within limits, does the degree of flame-proofing.

The impregnants may be applied simultaneously, as for example from a single solution, or they may be applied separately. Preferably they are applied to the material in a single aqueous solution in a padding operation.

The substantially non-volatile inorganic acids which

may be used in the process of the present invention are preferably strong acids, amongst which may be mentioned phosphoric acid, phosphorous acid, pyrophosphoric acid, sulphuric acid and sulphamic acid. The acids may if desired be partly neutralised with bases. Mixtures of acids may be employed. Any acid used should obviously not be so volatile that it vaporises before it can react with the cellulose in the heating operation. Of the acids which may be used, phosphoric acid is preferred.

The amount of acid applied is preferably at least 5 gms. per 100 gms. of material. Thus if the acid is applied to the material in an aqueous solution by a padding operation to 100 percent pick-up, then the solution should preferably contain at least 5 percent by weight of the acid. It is prefererd that the amount of the cyanamide applied to the material should be at least 10 gms. per 100 gms. of material.

The halogenated alkyl phosphate may take several forms. Thus it may be a mono-, di-, or tri-esterified phosphate in which some or all of the substituent alkyl groups are halogen substituted. It is preferred, largely for reasons of availability and cost, that a chlorinated alkyl phosphate should be used. Similarly, the alkyl radical(s) normally contain not more than four carbon atoms. A mixture of phosphates may be used. We have found a commercial mixture of chlorinated ethyl phosphates containing a major proportion of bis-β-chloroethyl phosphate to be satisfactory. The amount of the halogenated alkyl phosphate applied to the material should preferably be at least 10 gms. per 100 gms. of material.

After the material has been impregnated it is heated to effect reaction between the cellulose and the impregnants. The temperature of heating used should preferably be high enough to cause the reaction to proceed at a suitable rate without being so high as to cause degradation or evaporation of the cellulose or impregnants respectively. A temperature in the range of from 100° C. to 150° C. may generally be used satisfactorily.

When cyanamide is heated, some of the dimer dicyanodiamide (cyanoguanidine) is formed. As a modification of the process of the invention, the cyanamide may be replaced wholly or partly by the dimer.

Materials treated by the present process may also be treated with conventional finishing agents as and if desired before or after the impregnation and baking steps. It is also possible to use some additional compounds, for example formaldehyde, in the impregnation of the cellulosic material before heating. Some use of formaldehyde or other cross-linking agents improves the crease-resistance of the treated materials.

The process of the invention is illustrated by the following examples. The mixed chloroethyl phosphates used therein being a commercially available mixture consisting of about 53 percent by weight of bis-β-chloroethyl phosphate, about 35 percent by weight of mono-β-chloroethyl phosphate and about 12 percent by weight of orthophosphoric acid.

EXAMPLE 1

A woven fabric weighing about 5 ozs. per square yard and consisting wholly of viscose rayon staple fibres was padded to 100 percent wet pick-up with an aqueous solution containing:

	Percent w./w.
Phosphoric acid	15
Cyanamide	20
Mixed chloroethyl phosphates	15

The padding solution was prepared immediately before the padding was performed by mixing an aqueous solution containing the phosphoric acid and the chlorinated ethyl phosphates with an aqueous solution of the cyanamide. After padding the fabric was dried and baked at 105° C. for 5 minutes.

The resultant treated fabric was found to contain 3.2 percent by weight of phosphorus and 2.5 percent by weight of nitrogen. When submitted to the Vertical Bunsen Test, as described in British Standard No. 3119 (method of test for flame-proof materials), the fabric charred but did not ignite and exhibited no afterglow.

A sample of the treated fabric was washed in a solution containing 5 gms. per litre of soap and 2 gms. per litre of soda ash for 5 minutes at 40° C. then dried. After a total of 5 successive washes the fabric was again tested for fire-resistance and found only to char, any slight ignition being extinguished on removal of the flame.

After a further five washes as above the fabric could be made to burn very slowly in the Vertical Bunsen Test to leave a strong charred fabric skeleton. The fabric was, however, self-extinguishing on removal of the igniting flame.

EXAMPLE 2

The procedure of Example 1 was repeated except that the concentration of cyanamide was increased to 30 percent by weight.

The resultant fabric contained 3.6 percent phosphorus and 4.2 percent nitrogen. When tested according to British Standard No. 3119 the fabric extinguished immediately after removal of the igniting flame and exhibited no afterglow. A sample of the treated fabric was washed 15 times as described in Example 1. When retested the fabric extinguished within 3 seconds of removing the igniting flame and exhibited no afterglow.

EXAMPLE 3

A sample of the same fabric as used in Example 1 was padded to 100 percent pick-up through a solution containing:

	Percent w./w.
Pyrophosphoric acid	15
Mixed chloroethyl phosphates	15
Cyanamide	20

and was subsequently dried at 60° baked for 5 minutes at 105° C., and then rinsed in hot water.

When tested according to British Standard No. 3119 before and after 5 of the washes, as described in Example 1, the fabric extinguished immediately after removal of the igniting flame and exhibited no afterglow.

EXAMPLE 4

The procedure of Example 3 was followed with one exception, namely the pyrophosphoric acid was replaced by sulphuric acid. When tested prior to washing, the fabric extinguished immediately after removal of the igniting flame and exhibited no afterglow. When tested after five washes (as in Example 1) the fabric still extinguished on removal of the flame, but there was some afterglow in the charred region which ceased within ten seconds.

EXAMPLE 5

A sample of the same fabric as used in Example 1 was padded to 100 percent pick-up through a solution containing:

	Percent w./w.
Phosphoric acid	15
Mixed chloroethyl phosphates	15
Cyanamide	10
Dicyanodiamide	8

Subsequently, the fabric was dried at 60° C., baked for 30 minutes at 105° C., and then rinsed in hot water. When tested before and after two of the washes (as in Example 1), the fabric extinguished on removal of the flame and exhibited no afterglow.

EXAMPLE 6

A fabric weighing about 20 ozs. per square yard of the type normally used for the manufacture of electric blankets and consisting of a "Sarille" (registered trademark) regenerated cellulose yarn weft and a cotton warp was padded to 100 percent pick-up through a solution containing:

	Percent w./w.
Phosphoric acid	7.5
Mixed chloroethyl phosphates	7.5
Cyanamide	15

The fabric was subsequently dried at 60° C., baked for 5 minutes at 105° C., and then rinsed in hot water.

The resultant fabric was found to meet the requirements of British Standard No. 3121 (Performance Requirements of Materials Described As of Low Flammability). This involves testing the fabric according to British Standard No. 2693 (Tests for the Flammability of Fabrics) after washing the fabric twelve times for 30 minutes at 80° C. to 85° C. in a specified detergent. Both before and after these washes the treated fabric came within the "flame not propagated" classification and there was no afterglow.

EXAMPLE 7

A pile fabric weighing about 10 ozs. per square yard and consisting of a cotton backing fabric and a continuous filament viscose rayon pile, the proportions by weight of cotton and rayon being about equal, was padded to 100 percent pick-up through a solution containing:

	Percent w./w.
Phosphoric acid	15
Mixed chloroethyl phosphates	15
Cyanamide	20

and was subsequently dried at 60° C., baked for 5 minutes at 105° C., and then rinsed in hot water.

When tested according to British Standard No. 2963 after 6 of the washes specified in British Standard No. 3121, the fabric was classified as "flame not propagated" and there was no afterglow.

EXAMPLE 8

A woven fabric weighing about 3.6 ozs. per square yard and consisting of "Vincel" (registered trademark) regenerated cellulose staple fibres, was padded to 100 percent pick-up through a solution containing:

	Percent w./w.
Phosphoric acid	15
Mixed chloroethyl phosphates	15
Cyanamide	20

and was subsequently dried at 60° C., baked for 5 minutes at 105° C., and then rinsed in hot water.

When tested according to British Standard No. 3119 after 3 of the washes specified in British Standard No. 3121, the flame extinguished immediately on removal of the igniting flame and exhibited no afterglow.

What we claim is:

1. A process for improving the fire-resistance of cellulosic material comprising impregnating the material with an aqueous solution of a substantially non-volatile inorganic acid, cyanamide and a halogenated alkyl phosphate and heating the impregnated material, thereby effecting reaction between the cellulose and the impregnants.

2. A process according to claim **1**, wherein a mixture of non-volatile inorganic acids is used in the impregnating solution.

3. A process according to claim **1** wherein the acid in the impregnating solution is in part neutralised by a base to give a water-soluble salt.

4. A process according to claim **1** wherein the acid is phosphoric acid, phosphorous acid, pyrophosphoric acid, sulphuric acid or sulphamic acid.

5. A process according to claim **1** wherein the cyanamide is replaced at least in part by dicyanodiamide.

6. A process according to claim **1**, wherein the alkyl radical in the halogenated alkyl phosphate contains not more than four carbon atoms.

7. A process according to claim 6 wherein the halogenated alkyl phosphate is a chlorinated alkyl phosphate.

8. A process for improving the fire-resistance of cellulosic material comprising impregnating the material with at least 5 gms. of a substantially non-volatile inorganic acid, at least 10 gms. of cyanamide and at least 10 gms. of a halogenated alkyl phosphate per 100 gms. of material from an aqueous solution of the inorganic acid, cyanamide and the halogenated alkyl phosphate and heating the impregnated material, thereby effecting reaction between the cellulose and the impregnants.

9. A process according to claim 8 wherein the acid is phosphoric acid, phosphorous acid, pyrophosphoric acid, sulphuric acid or sulphamic acid.

10. A process according to claim 8 wherein the alkyl radical of the halogenated alkyl phosphate contains not more than four carbon atoms.

11. A process according to claim 10 wherein the halogenated alkyl phosphate is a chlorinated alkyl phosphate.

12. A process according to claim 8 wherein the impregnated material is heated to a temperature within the range of from 100° C. to 150° C.

13. A process for improving the fire-resistance of cellulosic material comprising impregnating the material with at least 5 gms. of phosphoric acid, phosphorous acid, pyrophosphoric acid, sulphuric acid or sulphamic acid, at least 10 gms. of cyanamide and at least 10 gms. of a halogenated alkyl phosphate, wherein the alkyl radical contains not more than four carbon atoms, per 100 gms. of material from an aqueous solution containing the inorganic acid, cyanamide and the halogenated alkyl phosphate, and heating the impregnated material to a temperature within the range of from 100° C. to 150° C., thereby effecting reaction between the cellulose and the impregnants.

14. A process for improving the fire-resistance of cellulosic material comprising impregnating the material with at least 5 gms. of phosphoric acid, at least 10 gms. of cyanamide and at least 10 gms. of a chlorinated alkyl phosphate, wherein the alkyl radical contains not more than four carbon atoms, per 100 gms. of material from an aqueous solution containing the phosphoric acid, cyanamide and the chlorinated alkyl phosphate and heating the impregnated material to a temperature within the range of from 100° C. to 150° C., thereby effecting reaction between the cellulose and the impregnants.

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U.S. Cl. X.R.

8—116.3, 120