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**EUROPEAN PATENT APPLICATION**

(21) Application number: **89308815.3**

(51) Int. Cl.<sup>5</sup>: **D 06 M 15/277**  
**D 06 M 11/72, D 06 M 13/432**

(22) Date of filing: **31.08.89**

(30) Priority: **31.08.88 GB 8820530**  
**31.08.88 GB 8820529**  
**01.09.88 GB 8820659**  
**01.09.88 GB 8820658**

(43) Date of publication of application:  
**07.03.90 Bulletin 90/10**

(84) Designated Contracting States:  
**AT BE CH DE ES FR GB GR IT LI LU NL SE**

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(54) **Flame retardants and method of use.**

(57) Aqueous compositions imparting semi durable flame retardant properties to cellulosic substrates contain an ammonium or organic quaternary ammonium condensed phosphate and a dispersion of a fluoropolymer and preferably a carbamic acid derivative such as urea. The substrate are impregnated and cured at 120-170°C.

## Description

## FLAME RETARDANTS AND METHOD OF USE

This invention concerns flame retardant compositions and methods of rendering textile substrates flame retardant with them.

5 Cotton fabrics can be rendered flame retardant by incorporation therein of a wide variety of chemicals, some of which provide durable flame retardance and some of which provide non durable retardance. Among the latter chemicals are ammonium phosphate and polyphosphate optionally with added urea. While such compounds are cheap, their effectiveness is short lived as they are removed by washing with water. Attempts to increase the durability with such compounds included high temperature curing at above 150°C (see e.g. BP 1504507). However such high temperature treatments have tended to discolour the fabric. The curing of the polyphosphate can be associated with cocuring with a variety of usual fabric treatments agents e.g. dimethylolethylene urea (see e.g. BP 1069946).

We have discovered flame retardant compositions and processes for applying them to fabrics of cellulosic materials to give fabrics of increased durability of flame retardant.

15 The present invention provides a flame retardant composition comprising an aqueous medium comprising an ammonium or organic quaternary ammonium condensed phosphate in an amount of 7-24% (by weight) and a dispersion of a fluoropolymer. The composition preferably also contains a carbamic acid derivative eg urea. The aqueous solution of polyphosphate and if present the carbamic acid may be in one pack of a 2 pack system, the fluoro dispersion being in the other pack, the contents of the 2 packs being for mixing to form compositions of the invention.

20 The present invention also provides a method of flame retarding a cellulosic substrate e.g. a cellulosic fabric, which comprises impregnation thereof with an aqueous composition comprising an ammonium or organic quaternary ammonium condensed phosphate and a dispersion of a fluoro polymer, preferably a flame retardant composition of this invention, drying and curing at 120-170°C, the aqueous composition also comprising a carbamic acid derivative e.g. urea when the curing is at 147-170°C, said derivative being in weight percentage (expressed as urea) of 50-300% to the weight of condensed phosphate (expressed as ammonium polyphosphate).

25 The polyphosphate salt is made by reaction of a condensed phosphoric acid with ammonia or an organic amine or quaternary ammonium hydroxide to give a water soluble product. The condensed phosphoric acid usually has a mean degree of condensation of more than 3, e.g. 3-30, and usually has a linear branched or cyclic structure. Preferably the salts contain N and P in an atomic ratio of 0.5-2:1 especially about 1:1. The polyphosphate salt is preferably a mixture of the ammonium salts of a plurality of polyphosphoric acids, which mixture has been produced by a process of reacting an aqueous solution of phosphoric acids containing 80-86% by weight of phosphorus pentoxide with ammonia or a basic derivative thereof at a temperature of 15-70°C e.g. 15-40°C and at a pH of 4-12 such as 5-9 e.g. 6.5-7.5, or 5 to 12 especially 6 to 8. Ammonium polyphosphate mixtures which may be used are described in BP 1504507 and may be made as described therein.

35 The flame retardant medium preferably also contains a carbamic acid derivative having 2 amino groups per molecule in a weight percentage (expressed as urea) to the ammonium polyphosphate (expressed by weight as ammonium polyphosphate itself) of 0.5%-300% such as 0.5-50% eg 5-30% such as 7-20% or 10-20% while 50-300% e.g. 50-200% and especially 75-200% or 75-125% are preferred, particularly for higher temperature curing; generally the higher the cure temperature the higher the proportion of carbamic acid derivative. The carbamic acid derivative may be guanidine or dicyandiamide, but is preferably urea; the weights are expressed as urea but equivalent weights of the other carbamic acid derivative can be used. The presence of the carbamic acid derivative reduces any tendency to discoloration of the fabric after heat curing, especially at high temperature, and may increase the wet pick up.

40 The flame retardant medium also contains a dispersion of fluorocarbon polymer which is preferably capable of being heat cured at more than 160°C eg 160-200°C. The fluorocarbon polymer is one which forms in the flame retardant medium a dispersion which is usually stable for at least a few days eg at least 2 days; thus fluoro polymers incompatible with the condensed phosphate solution (with carbamic acid derivative if present) and forming precipitates on mixing therewith are avoided. The medium is usually substantially free of other heat curable water soluble resins or resin precursors such as formaldehyde condensates with NH compounds such as melamine, urea or ethylene urea. Such aqueous dispersible fluorocarbon polymers usually have perfluoro alkyl side chains e.g. in perfluoro-acyl, -sulphonyl or -sulphonamido groups, especially ones with 3-12 carbon atoms in the perfluoroalkyl group; carboxy groups may also be present. The fluorocarbon polymers are preferably derived from acrylic or methacrylic esters of hydroxy compounds containing perfluoro alkyl groups but can be derived from vinyl esters, vinyl ethers, allyl esters or thiomethacrylates with perfluoro-alkyl side chains. Especially preferred polymers are ones containing (N-alkyl N- perfluoroalkylsulphon-amido) alkylene side chains e.g. 2- (N- propyl N- perfluorooctylsulphonamido) -ethylene side chains with an acrylate or methacrylate ester back bone. The polymers may be made only from monomers containing perfluoro alkyl groups but these monomers may have been copolymerized with other copolymerizable monomers, particularly ones fluorine free, e.g. ones containing one or especially two olefinic double bonds e.g. as in halo butadienes such as 2-chloro 1,3- butadiene. Olefinic monomer units containing carboxylic acid groups e.g.

acrylic, methacrylic or maleic acid groups may be present in the polymer. The fluoro polymers are usually sold in the form of aqueous dispersions e.g. for fluoropolymer soil repellent finishes for fabrics. The polymer dispersion may be non ionic but is preferably cationic or especially anionic. The fluoropolymer dispersions may also contain small amounts of water miscible organic solvents e.g. acetone, MIBK or ethylene glycol. A preferred polymer dispersion is that sold by 3M Company under the trademark SCOTCHGARD 270 or by Ciba Geigy Ltd under the trademark SCOTCHGARD FC451. This polymer is believed to be a copolymer of an 2 (N-alkyl N-perfluoro octylsulphonyl amido) ethyl acrylate and a comonomer probably 2-chloro -1, 3,-butadiene. Another preferred fluoropolymer dispersion is that sold by Hoechst AG under the trademark NUVA FH or NUVA F. Fluoropolymer dispersions sold by Atochem SA under the trademark FORAPERLE, especially FORAPERLE 145 and 344, or Texchem UK Ltd Manchester, England under the trademark TEXFIN CPC may also be used. The weight percentage of fluorocarbon polymer (solids) to ammonium polyphosphate is usually 0.1-60% e.g. 1-30% but especially 2-60%.

The flame retardant medium preferably contains 7-18% e.g. 8-15% such as 9-13% ammonium polyphosphate, and usually 7-18% e.g. 8-15% such as 9-13% of the carbamic acid derivative e.g. urea, and 0.02-1.5% e.g. 0.1-1% and especially 0.3-0.8% fluoropolymer. However amounts of the ammonium polyphosphate of 7-24% such as 10-24% eg 15-24% and especially 15-23%, and amounts of 0-20% eg 1-20% or 0-15% eg 1-15% or 1-10% such as 1.5-4% of the carbamic acid derivative e.g. urea may be used. Advantageously the total content of the polyphosphate, carbamic acid derivative e.g. urea and fluoro polymer in the medium is not more than 26% e.g. 11-26% or 15-26% especially 20-24%.

The medium can also contain a non rewetting agent e.g. a volatile wetting agent such as an alcohol or an agent such as is sold by Warwick Chemicals under the trademark MYKON NRW; amounts of such non rewetting agents of 1-10g./l. are preferred. However if the substrate, which is to be flame retarded, has already been scoured or otherwise treated to aid penetration of liquids, then no such agent is required but one may be present if desired. The aqueous medium is usually in the absence of extenders or cationic polymers such as cationic synthetic resin waxes, such as are sold under the trademark CEROL by Sandoz, and is also usually substantially free of di, tri or tetra valent metal salts e.g. those of aluminium or zirconium. Some fluoropolymer dispersions are sold which contain also the extender or cationic polymer; these should preferably not be used. Fluoropolymer dispersions sold primarily to provide soil repellency, but not to provide soil and water repellency, are preferred as the latter tend to contain the cationic polymer and may be incompatible with the concentrated polyphosphate solution.

In one preferred embodiment particularly for use with subsequent curing at 120-147°C, the flame retardant composition is an aqueous medium comprising 7-24% e.g. 10-24% by weight of an ammonium or organic quaternary ammonium condensed phosphate, 1-10% by weight of the carbamic acid derivative e.g. urea, the weight percentage of urea to the polyphosphate being 5-30%, and a dispersed fluoropolymer in amount of 0.02-1.5% with a total content of the phosphate and urea of not more than 25%.

In another preferred embodiment particularly for use with subsequent curing at 147-170°C, the flame retardant composition is an aqueous medium comprising 8-15% e.g. 9-13% by weight of an ammonium or organic quaternary ammonium condensed phosphate, 8-15% by weight of carbamic acid derivative e.g. urea, the weight percentage of urea to polyphosphate being 50-200%, and a dispersed fluoropolymer in amount of 0.02-1.5% with a total content of the phosphate and urea of not more than 25%. In both these embodiments these compositions are preferably in the absence of cationic water soluble fluorine free polymers, and advantageously contain the fluoropolymer which has perfluoroalkylsulphonamide side chains.

The polyphosphate, preferably with the carbamic acid derivative, may be provided as a concentrated aqueous solution, for subsequent mixing with the fluoropolymer dispersion before or preferably after one or both has been diluted to the strength for the impregnation bath.

The fluoropolymer dispersion is preferably added to the medium when it is otherwise ready for use for impregnation. The medium is preferably used for impregnation within a few days though, especially in the case of anionic fluoropolymer dispersions, the medium may be stable for at least 1 week e.g. at least 1 month.

The aqueous medium may also contain other textile auxiliary agents of nature and in amount such that they are compatible with the other components of the medium, and are not significantly affected by the heat cure treatment e.g. to cause discoloration or loss of effect. Examples of such agents are softening or conditioning agents, which may be cationic, anionic, non ionic, amphoteric or reactive and usually contain at least 1 and often 2 alkyl chains of at least 10 carbon atoms. Examples of cationic softening agents are fatty quaternary ammonium salts, amino esters and amino amides and quaternary N acyl N polyoxyalkylene polyamines. Examples of anionic softening agents are fatty acid salts, soaps, sulphonated fats and oils, fatty alkyl sulphates and fatty acid condensation products, sulphosuccinates and sulphosuccinamates. Examples of amphoteric agents are alkyl imidazolines and betaines and salts thereof e.g. methosulphate, acyl amido betaines, acyl polyamines, amine oxides, substituted amino acids and sulpho betaines. Examples of non ionic softening agents are poly alkylene glycol ethers and esters and other polyoxyalkylene condensation products, and paraffin wax or polyethylene wax, these latter two being used in aqueous dispersion or emulsion, with non ionic, cationic or anionic, but especially amphoteric dispersing agents. Examples of reactive softening agents are N-methylol derivatives of fatty acid amides e.g. N-methylol stearamide or N methylol derivatives of fatty acid condensates with urea. The softening agent as such or as dispersion thereof may be used in amount of 0.01-5% e.g. 0.5-30% by weight of the total aqueous impregnation medium. The presence of the softening agent can enable the heat cure process to produce a treated fabric having improved flame retardance and with

other properties e.g. strength especially tear strength and colour substantially the same as those of the untreated fabric; the strength may even be improved.

The substrates to which the medium is applied may be woven or non woven. They are cellulosic based substrates e.g. textile fabrics or filaments, such as of cotton, linen, jute, hessian or regenerated cellulosic materials, such as rayon or viscose, but can also be paper, cardboard or wallpaper. The substrate can also be based on cellulosic material and other fibres coblendable or mixable therewith e.g. polyester or nylon, acrylics, acetate, polypropylene, silk or wool; these blends or mixtures of fibres may contain at least 50% of the cellulosic material e.g. 70-100% such as 50-80% thereof.

Fabric weights can be 50-1000 g/m<sup>2</sup>, e.g. 80-500g/m<sup>2</sup>. The fabric may be of pile or plain construction. The fabric may be plain or undyed or may be dyed or printed, especially with white or pastel shades. The fabric before impregnation is usually free of dirt, sizes, natural waxes and applied finishes though may contain an optical brightening agent.

The flame retardant medium usually at pH 5-8 e.g. 5.5-7.5 is applied to the substrate by conventional procedures e.g. padding, soaking or spraying usually to a wet pick up of 50-150% e.g. 60-100% The total solids add-on before drying and after squeezing off surplus liquid is usually 10-35% e.g. 10-20% or 13-25% (based on the dry initial weight of the fabric) After impregnation the substrate is then dried e.g. for textile substrates at 80-120°C for 2 to 40 minutes e.g. 2-10 minutes. The drying may be performed in any conventional drier e.g. a forced air drier or stenter. The solids pick-up after drying is usually 8-25% such as 10-20% (based on the original weight of the fabric).

The dried substrate is then cured eg by heating at a temperature of 120-170°C such as 130-170°C e.g. 140-170°C or 147-170°C for 6 to 0.5 or 5-0.5 minutes, the combination of longer times and higher temperature being avoided to decrease any tendency to discoloration. Preferred temperatures, especially with high proportions of carbamic acid derivative to polyphosphate, are 147-165°C such as 147-160°C or 147-155°C for 6-0.5 e.g. 5-2 minutes. To minimise risk of any colour formation especially with low proportions of carbamic acid derivative to polyphosphate the dried substrate is preferably cured by heating at 120-147°C for 6 to 0.5 minutes, the combination of longer times and higher temperature being avoided to decrease any tendency to discoloration. These preferred temperatures are 120-138°C such as 124-142°C or 128-138°C for 6-0.5 e.g. 6-1.5 minutes while at temperatures of 138-147°C times of 3.5-0.5 minutes such as 138-142°C or 142-147°C for 3.5-0.5 minutes can be used. Curing at 130-140°C for 4-2 eg 3.5-2.5 minutes is preferred.

The curing at 147-170°C with a higher proportion of carbamic acid derivative to polyphosphates usually has a higher cure efficiency than the lower temperature cure which has a higher proportion of polyphosphates and higher amount thereof in the impregnation bath, but the latter has a reduced tendency to discoloration especially with white or pastel fabrics. The presence of the fluoropolymer increases the durability to soaking of the fabric cured at 120-147°C or 147-170°C.

The curing which is usually continuous may be performed by radiant e.g. infra red heating or heating by injection of steam and/or hot air through the substrate, or by contact of the substrate with heated metal drums in a vertical stack, but preferably the curing is by heating from impact of hot air on the surface of the substrate, preferably on both surfaces to ensure uniformity of heating. Thus preferably the substrate is passed continuously on a stenter through a thermostated oven in which heated air flows are passed on to the top and bottom surfaces of the substrate. The stenter gives the most uniform curing with minimum scorching. In the case of the stenter oven, the cure temperature of the substrate is essentially the same as that of the heated air flow. Usually at the end of the curing the substrate is cooled rapidly by passing or drawing cool air through it.

The cured fabric as finished usually has a solids content of 6-25% such as 8-20% and usually contains 0.5-5%P e.g. such as 0.5-4%P preferably 1-3%P or 2-4%P. The fabric as finished has a reduced flammability compared to the untreated substrate and can pass the BS 5852 test with ignition sources 0 and 1. The fabric after leaching once in hard water at 40°C according to BS 5651 without final ironing usually has a solids content of 3-10% e.g. 4-9%, a % content of 0.4-3% preferably 0.9-3% eg 1-3%P and can pass the flammability test of BS 5852 Part 1 with ignition sources 0 and 1. The reduced flammability finish is usually durable for 1-3 washes in soft water at 74°C while some fire retardant effect is retained thereafter. The fabric as finished usually has a handle not significantly changed from that of the untreated fabric, and usually has a colour not significantly changed from that of the untreated fabric. The fabric as finished usually has some degree of water and oil repellency which may be resistant to one wash in softwater at 74°C, but is usually substantially removed on 3 washes. The synergistic combination of (i) fluoropolymer and (ii) condensed phosphate (with carbamic acid derivative if present) can give substrates of improved durability of flammability not possessed by substrates from (i) or (ii) alone.

The invention is illustrated in the following Examples. In Ex. 1-11, 13 and 14 the fluoropolymer was used as a 23% aqueous emulsion of fluoropolymer with a slight cationic character sold by 3M under the Trademark SCOTCHGARD FC 208 or Ciba Geigy under the Trademark SCOTCHGARD FC451. This fluoropolymer is believed to be a copolymer of 2 (N-propyl N-perfluoro octylsulphonyl amido) ethyl acrylate and 2-chloro- 1, 3-butadiene. In Ex 12 the fluoropolymer was an aqueous fluorocopolymer dispersion which was anionic, has a pH of 7.5-8.5 and was sold by Hoechst AG under the trademark NUVA FH and is believed to contain carboxyl and perfluoroalkyl groups. In Ex 15, 16, 19, 20, 23, 24 and Comp. Ex A-D the fluoropolymer was an aqueous acrylic fluoropolymer dispersion sold by Atochem S.A. under the trademark FORAPERLE 145; it is slightly cationic, has pH 4.5 ± 0.5 and is believed to contain perfluoroalkyl, carboxyl and sulphonamido groups. In Ex 17, 18, 21 and 22, the fluoropolymer was an aqueous fluoropolymer dispersion which is slightly cationic, has pH 6-8 and

is sold by Texchem UK Ltd, Manchester, England under the trademark Texfin CPC; it is believed to contain perfluoroalkyl and carboxyl groups.

The ammonium polyphosphate used in all the Examples was made by reacting polyphosphoric acid of 83-85%  $P_2O_5$  with ammonia according to BP 1504507, to produce a product which was adjusted, to give an solution at pH6.2 containing 45% solids, 30%  $P_2O_5$  and a specific gravity of 1.36.

In each case the same general procedure was adopted. The aqueous solution of the ammonium polyphosphate and urea was made and after dilution with water if desired, was mixed with stirring with the fluoropolymer emulsion, in amount (by weight of emulsion based on the of total weight of solution and emulsion), of 2% for Ex1-11, 13 -22 and 1.5% for Ex 12, and also in Ex1-13 0.5% of a non rewetting agent sold under the trademark MYKON NRW to give aqueous media containing the ammonium polyphosphate fluoropolymer and urea. The aqueous medium obtained was stable, but was preferably used without undue delay. The fabric was impregnated with the aqueous medium and squeezed and then the impregnated fabric dried at 90-100°C or 110°C in a forced air drier or stenter. Portions of the dried fabric were then moved on a stenter slowly but continuously through a thermostated stenter oven provided with heated air flows impinging on the fabric from top and bottom. The fabric was weighed after drying and after curing. The cured fabric was then tested according to the test of BS 5852 Part 1 with ignition sources 0 and 1 for flammability as finished and after leach once in hard water at 40°C according to BS 5651 Part 1 without final ironing.

Some finished fabrics were also submitted to a dry cleaning test with 3 commercial dry cleaning cycles in a charged solvent system charged with 10% water.

Some fabrics were also tested for oil and water repellency according to AATCC 118 and BS 3702 respectively and assessed for colour.

#### Example 1

The aqueous ammonium polyphosphate solution (94 parts) was mixed with urea (6 parts) and the mixture obtained diluted with water (122 parts) and then the fluoropolymer emulsion and NRW agent added to give the impregnation medium. The medium was applied in a pad mangle to a floral print cotton fabric of 230 g/m<sup>2</sup> and also to prescoured colour woven orange dyed cotton fabric of 410 g/m<sup>2</sup>, with wet pick-ups of 71%, and 81.5% respectively. The impregnated fabrics were then dried on a stenter at 100°C for 3.5 minutes and then cured at 135°C for 2.5 minutes. The floral and orange fabrics as finished contained 3.19% and 3.53%P respectively. All the fabrics as finished and after one leach in hard water passed the BS 5852 test with ignition sources 0 and 1. The floral and orange fabrics were also submitted to the BS 5438 test 2 flammability test with char lengths in mm. as shown in the Table below. After the hard water leach the floral and orange fabrics contained 0.99% and 1.43% P respectively.

Char Length

| Fabric | As Finished | Leached | Dry Cleaned |
|--------|-------------|---------|-------------|
| Floral | 108         | 124     | 92          |
| Orange | 84          | 74      | 75          |

Other Properties were as follows:-

| Fabric       | Finish    | Oil Repel-<br>lency<br>AATCC<br>118 | Water Repel-<br>lency BS<br>3702 |
|--------------|-----------|-------------------------------------|----------------------------------|
| Floral-print | Untreated | NT                                  | NT                               |
|              | Treated   | 3                                   | 70                               |
| Orange       | Untreated | NT                                  | NT                               |
|              | Treated   | 6                                   | 70                               |

NT - means not tested.

In the treated floral fabric, there were essentially no colour changes in the white or coloured parts of the floral print compared to those in the untreated fabric.

#### Example 2

The process of Ex 1 was repeated with a variety of fabrics of different weights and styles and tests for flammability performed according to BS 5852 ignition sources 0 and 1. In all cases the tests were passed. The fabrics were:-

- (1) 100% cotton, plain, velvet, print or colour woven of weights in the range 120-410 gm<sup>-2</sup>.

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(2) Cotton blends with linen (48:52), viscose (46:54) (55:45) or viscose/nylon (25:72:3) print, velour or colour woven of 330-540 gm<sup>-2</sup> weight.

(3) Cotton blends with polyester (53:47) colour woven of 300 gm<sup>-2</sup>.

(4) Mixed velvet fabrics with 63 cotton, 37 acrylic pile and 47 cotton 28 acrylic 25 polyester base of weight 540 gm<sup>-2</sup>, and with 100 viscose pile and 83 viscose, 10 cotton, 7 polyester base of weight 750 gm<sup>-2</sup>.

### Examples 3-8

The process of Ex 1 was repeated, with the following changes.

In these experiments the fabric was scoured cotton fabric of 220 g/m<sup>2</sup> fabric weight dyed red.

| Example                | 3    | 4    | 5    | 6    | 7    | 8    |
|------------------------|------|------|------|------|------|------|
| Cure temp °C           | 130  | 130  | 130  | 130  | 140  | 140  |
| Time minutes           | 2    | 3    | 4    | 5    | 2    | 3    |
| % wet pick up          | 81.7 | 81.5 | 81.8 | 81.6 | 80.8 | 81.2 |
| % dry solid pick up    | 15.8 | 16.2 | 16.2 | 15.8 | 15.7 | 16.2 |
| % Solids after cure    | 15.1 | 15.9 | 15.6 | 15.5 | 15.7 | 14.9 |
| % solids after 1 leach | 5.7  | 7.8  | 7.0  | 7.8  | 7.0  | 7.6  |

All the treated fabric after 1 leach passed the BS5852 ignition test with sources 0 and 1, and there was no significant colour change compared to the untreated fabric.

### Examples 9 and 10

The process of Ex 1 was repeated with a white cotton fabric of 270 g/m<sup>2</sup> which did not contain optical brightening agent. The cure conditions at 135°C were 3 min (Ex 9) and 3.5 min (Ex 10). The fabrics as finished and after one leach passed the BS5852 test with ignition sources 0 and 1. The fabrics as finished and after one leach showed no significant colour change compared to the fabrics before treatment.

### Example 11

The process of Ex 1 was repeated with changes to the aqueous medium, the fabric and cure conditions. The aqueous medium was made by mixing the aqueous ammonium polyphosphate solution (59 parts), urea (27 parts) and water (154 parts), followed by the fluoropolymer emulsion and NRW.

The fabric was a white cotton drill fabric of 268 g/m<sup>2</sup>. The fabric was padded to about 75% wet pick up, the drying was 2 minutes at 100°C and the cure conditions 2.5 minutes at 145°C. The fabric as finished contained 2.19%P, and the fabric after one leach contained 1.19%P. The fabric after the leach had a char length of 128 mm when tested by BS5438 test 2. The fabric as finished and after one leach showed no significant colour change compared to the fabric before treatment.

### Example 12

The process of Ex 1 was repeated with the NUVA fluoropolymer emulsion in amount of 1.5%. The impregnation medium was stable for at least 2 months at room temperature. The fabric impregnated was a red dyed cotton fabric of 220 g/m<sup>2</sup> and the wet pick up was 72.5%. After drying and curing as in Ex1, the fabric had a total solids add-on as finished of 15.8% and a total solids add-on after one leach of 5.6%. The fabric as finished and after one leach passed the BS 5852 test with ignition sources 0 and 1. The fabric as finished and after the leach showed no significant colour change compared to the fabric before treatment.

### Example 13

The process of Ex 1 was repeated with 3111 cotton drill fabric of 300g/m<sup>2</sup> and with and without the presence of 2% (based on the total weight of the impregnation medium) of a softening agent, which is an aqueous amphoteric dispersion of an aliphatic hydrocarbon, probably a paraffin wax or polyethylene wax, sold by Sandoz under the trade mark SANDOLUBE NV. The cure conditions were 135°C for 3 minutes. The cured fabric was tested for flammability and tested for tear strength in the warp and weft directions according to Elmendorf. The cured fabric as finished and after one leach passed the BS 5852 test with ignition sources 0 and 1, and showed no significant colour difference compared to the untreated fabric. The results of the tear strength work were as follows:-

## Tear Strength g.

| Fabric               | Warp | Weft |
|----------------------|------|------|
| Untreated            | 3162 | 4452 |
| Treated              |      |      |
| Without SANDOLUBE NV | 3174 | 3853 |
| With SANDOLUBE NV    | 5414 | 5619 |

## Example 14

The aqueous ammonium polyphosphate solution (59 parts) and urea (27 parts) and water (154 parts) were mixed and then the fluoropolymer emulsion and NRW added to give the impregnation medium. The medium was applied in a pad mangle to a floral print cotton fabric of 230 g/m<sup>2</sup> and also to a prescoured colour woven cotton fabric of 410 g/m<sup>2</sup>, dyed brown, with wet pick-ups of 71%, and 96.5% respectively. The impregnated fabrics were then dried on a stenter at 100°C for 3.5 minutes and then cured at 150°C for 3 minutes. The fabrics as finished contained 1.98 and 2.35% P respectively. All the fabrics as finished, after one leach in hard water and after dry cleaning passed the BS 5852 test with ignition sources 0 and 1. The floral and brown fabrics as finished, after one leach in hard water and after dry cleaning were also submitted to the BS 5438 test 2 flammability test with char lengths in mm. as shown in the Table below. After the hard water leach the fabrics contained 1.27 and 1.83%P respectively.

## Char Length Data

| Fabric | As Finished | Leached | Dry Cleaned |
|--------|-------------|---------|-------------|
| Floral | 98          | 102     | 91          |
| Brown  | 71          | 73      | 65          |

Other Properties were as follows:-

| Fabric       | Finish    | Oil Repel-<br>lency<br>AATCC<br>118 | Water Repel-<br>lency BS<br>3702 |
|--------------|-----------|-------------------------------------|----------------------------------|
| Floral-print | Untreated | NT                                  | NT                               |
|              | Treated   | 5                                   | 70                               |
| Orange       | Untreated | NT                                  | NT                               |
|              | Treated   | 5                                   | 70                               |

NT - means not tested.

The colours of treated fabrics were not significantly different from those of the untreated fabrics.

## Example 15, 16, 17 18

The process of Ex 1 was repeated with a floral print plain weave cotton fabric of 22Sg/m<sup>2</sup> and two different fluorocarbon polymer emulsions, one sold under the trademark FORAPERLE 145 (Ex 15, 16) and one sold under the trademark TEXFIN CPC (Ex 16, 17) in each case with (Ex 15, 17) and without (Ex 16, 18) the softening agent used in Ex 13. The impregnation bath was made from 34.8 parts of the ammonium polyphosphate solution, 2.2 parts of urea and 59.5 parts of water, with 2 parts of the fluoropolymer emulsion and with 1.5 parts of the softening agent or 1.5 parts of extra water. The fabric wet pick up was 76% and after drying at 110°C for 1 min, the dried fabric was baked at 135°C for 3 min. The finished fabrics were soaked in water according to the BS 5651 test and after drying were submitted to the BS 5438 test 2 flammability test. The finished fabrics were also tested for Tensile and Tear Strength according to Elmendorf and water and oil repellency. The results were as follows:-

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| Example  | Untreated | 15   | 16   | 17   | 18   |
|--|-----------|------|------|------|------|
| 5 Tensile strength, warp, N/5mm                    | 660       | 650  | 657  | 657  | 671  |
| Tensile strength, weft, N/50mm                     | 647       | 639  | 644  | 638  | 628  |
| 10 Tear strenght, warp, g                          | 3349      | 3360 | 2679 | 3349 | 2740 |
| Tear strenght, weft, g                             | 2410      | 2517 | 1920 | 2482 | 1860 |
| 15 Water repellency BS3702                         | NT        | 80   | 80   | 70   | 70   |
| Oil repellency AATCC118                            | NT        | 7    | 6    | 6    | 6    |
| 20 Flammability test after soaking, char length mm | NT        | 105  | 100  | 105  | 110  |
| N/50mm means Newtons                               |           |      |      |      |      |
| 25 NT = Not tested per 50mm wide fabric            |           |      |      |      |      |

Example 19-22

30 The process of Ex 14 was repeated with the same cotton fabric and fluorocarbonpolymer emulsions used in Ex 15-18, the FORAPERLE 145 emulsion being used in Ex 19 and 20, and the TEXFIN CPC emulsion used in Ex 21 and 22, and with (Ex 19, 21) and without (Ex 20, 22) the softening agents used in Ex 13. The impregnation bath was made from 20.6 parts of the ammonium polyphosphate solution, 9.28 parts of urea, 2 parts of the fluorocarbon polymer emulsion, 61.5 parts of water and 1.5 parts of the softening agent (or 1.5 parts of extra water in Ex 20, 22). The fabric wet pick up was 76% and after drying at 110°C for 1 min, the dried fabric was

35 baked at 150°C for 3 min. The finished fabrics were soaked in water according to BS 5651 test and after drying were submitted to the BS 5438 test 2 flammability test. The finished fabrics were also tested for tensile and tear strength and water and oil repellency. The results were as follows:

| Example   | Untreated | 19   | 20   | 21   | 22   |
|---|-----------|------|------|------|------|
| 40 Tensile strength, warp, N/50mm               | 660       | 621  | 614  | 606  | 626  |
| 45 Tensile strength weft, N/50mm                | 647       | 587  | 582  | 597  | 574  |
| Tear strength, warp, g                          | 3349      | 3306 | 2344 | 3215 | 2411 |
| 50 Tear strength weft, g                        | 2410      | 2304 | 1660 | 2217 | 1688 |
| Water repellency BS3702                         | NT        | 90   | 90   | 80   | 80   |
| 55 Oil repellency AATCC118                      | NT        | 7    | 7    | 6    | 6    |
| Flammability test after soaking, char length mm | NT        | 71   | 82   | 75   | 88   |
| 60 NT = Not tested                              |           |      |      |      |      |

Example 23 and Comparative Examples A and B

65 Fabrics treated by a method of the invention (for Ex 23), were compared for colour with those of fabrics

treated by different methods using curing conditions described in Examples 1 and 2 of BP1504507 (for Ex A and B). The fabric was that used in Ex 19. The impregnation bath and method for Ex 23 where the same as in Ex 19, while the comparative baths and processes for Comparative Ex A and 8 involved ammonium polyphosphate and urea in concentrations given in Ex 1 of BP1504507 but with wet pick ups, and drying conditions as in Ex 20 and cure for 7 min at 150°C (Comp Ex A) and cure for 5 min at 160°C (Comp. Ex B). The cured fabrics were tested for colour on a "1-5 grey scale" compared to the untreated fabric, 5 denoting little or no shade change and 1 denoting maximum change. The results were as follows: Ex 23, shade 4/5, Comp Ex A shade 2, and Comp Ex B shade 1.

#### Example 24 and Comparative Ex C and D

Fabrics treated by a method of the invention (Ex 24) with an aqueous medium containing both (i) ammonium polyphosphate and urea and (ii) fluorocarbon polymer were compared for flammability and water repellency before and after soaking with corresponding fabrics having been treated with aqueous media containing either (i) or (ii) (Comp C and D respectively). The fabric was as in Ex 19. The method in Ex 24 was as in Ex 20, while that in Comp Ex C was the same as in Ex20 but without the fluoropolymer and in Comp Ex D involved impregnation of the fabric with a 2% dispersion of the fluoropolymer emulsion and drying, followed by baking for 3 min at 150°C. The fabrics were tested for flammability according to BS 5438 and water repellency according to BS 3702. The soaking involved immersion of the fabrics for 30 min in a bath at 40°C of water containing 5g/l wetting agent. After the soaking the fabrics were dried and retested. The results were as follows.

| Example       | Char Length<br>mm | Water<br>Repellency |
|---------------|-------------------|---------------------|
| 24            | 73                | 100                 |
| 24 after soak | 77                | 50                  |
| C             | 73                | -                   |
| C after soak  | 103               | -                   |
| D             | -                 | 100                 |
| D after soak  | -                 | 50                  |

NB The water repellency scale goes from 100 (best) to 0.

#### Claims

1. An aqueous flame retardant composition comprising an ammonium or organic quaternary ammonium condensed phosphate in an amount of 7-24% (by weight) and a dispersion of a fluoro polymer.

2. A composition according to claim 1 which comprises a carbamic acid derivative.

3. A composition according to claim 2 wherein the carbamic acid derivative is urea and the condensed phosphate is a water soluble ammonium polyphosphate.

4. A composition according to any one of claims 1-3 wherein the fluoro polymer has a perfluoroalkyl side chain.

5. A composition according to claim 4 wherein the fluoro polymer is a polymer derived from an acrylic or methacrylic ester of an alcohol containing a perfluoroalkyl side chain.

6. A composition according to claim 4 or 5 wherein the fluoro polymer is one containing (N-alkyl-N-perfluorosulphonamido) alkylene side chains.

7. A composition according to any one of claims 1-6 which is substantially free of any cationic water soluble fluorine free polymer.

8. A composition according to any one of claims 3-7 wherein the weight percentage of urea to ammonium polyphosphate is 5-30%.

9. A composition according to any one of claims 3-7 wherein the weight percentage of urea to ammonium polyphosphate is 50-300%.

10. A composition according to claim 8 which comprises 10-24% ammonium polyphosphate, 1.5-4% urea and 0.1-1% of the fluoro polymer with a total of said polyphosphate urea and fluoropolymer of 15-26%.

11. A composition according to claim 9 which comprises 8-15% ammonium polyphosphate and 8-15% of urea and 0.1-1% of the fluoropolymer with a total of said polyphosphate, urea and fluoropolymer of 15-26%.

12. A composition according to any one of the preceding claims which also comprises a softening agent.

13. A two pack system having in one pack (i) an aqueous medium comprising an ammonium organic

quaternary ammonium condensed phosphate and in a second pack (ii) an aqueous dispersion of a fluoropolymer, the contents of the 2 packs being for mixing to produce an aqueous composition according to claim 1.

14. A method of flame retarding a substrate which comprises impregnation thereof with an aqueous composition comprising an ammonium or organic quaternary ammonium condensed phosphate, and a dispersion of a fluoro polymer, drying and curing at 120-170°C, the aqueous composition also comprising a carbamic acid derivative when the curing is at 147-170°C said derivative being in weight percentage (expressed as urea) of 50-300% to the weight of the condensed phosphate (expressed as ammonium polyphosphate).

15. A method according to claim 14 which comprises impregnation of a cellulosic substrate with an aqueous composition comprising urea and a water soluble ammonium polyphosphate.

16. A method according to claim 14 or 15, wherein the fluoro polymer is as defined in any one of claim 4-6.

17. A method according to any one of claims 14-16, wherein the substrate is impregnated with an aqueous composition comprising 8-15% ammonium polyphosphate, 8-15% urea and the fluoro polymer to give a total solids add on after drying of 10-20% (based on the original weight of the substrate with subsequent curing at 147-160°C for 6-0.5 minutes).

18. A method according to any one of claims 14-16 wherein the substrate is impregnated with an aqueous composition comprising 15-24% ammonium polyphosphate and 1-10% urea and the fluoro polymer to give a total solids add on after drying of 10-20% (based on the original weight of the substrate) with subsequent curing at 128-142°C for 6-1.5 minutes.