(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 449 159 A2**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **91104617.5**

(22) Date of filing: **23.03.91**

(51) Int. Cl.^{5}: **D06M 11/72**

(30) Priority: **26.03.90 GB 9006738**
29.05.90 GB 9011920

(43) Date of publication of application:
02.10.91 Bulletin 91/40

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

(71) Applicant: **Albright & Wilson Limited**
210-222 Hagley Road West
Oldbury Warley West Midlands B69 4PR(GB)

(72) Inventor: **Black, Robert William**
104 Norman Road
Warley, West Midlands, B67 5PU(GB)

(74) Representative: **Savidge, Roger Gordon**
Madgwick et al
c/o Albright & Wilson Limited, P.O. Box
2098,7 Stars Road
Oldbury, Warley, West Midlands B69
4PR(GB)

(54) Coating composition to impart flame retardation and process to apply such compositions.

(57) An aqueous composition comprising an insoluble ammonium polyphosphate, a surfactant and a heat curable resin, which may also contain a soluble ammonium polyphosphate and/or a carbamic acid derivative, forms a shearable paste which, when applied to the back of a fabric and heat cured, flame retards the fabric without exuding to the front face and causing resin and/or salt marks.

Rank Xerox (UK) Business Services

This invention relates to a coating and impregnation composition, especially for treating fabrics to render them flame retardant.

Cotton fabrics can be rendered flame retardant by incorporation therein of a wide variety of chemicals, which can provide durable or non-durable flame retardance. Among these chemicals are antimony compounds, organo halogen compounds and organic or non-organic phosphorus compounds such as water insoluble and soluble ammonium polyphosphates, which can be cured into the fabric by heating (eg see GB-P-1504507). In the treatment of many fabrics, especially for upholstery uses, it is essential that the look and handle of the fabric be substantially unaffected by any fire retardant treatment. For this reason many upholstery fabrics are fire retarded by back coating especially with a resin composition containing antimony oxide and an organo bromine compounds. Such compositions are undesirable for environmental reasons and secondly are only suitable for low fabric weight fabrics.

We have discovered a back coating composition, which is suitable for a wide range of fabric weights and is more acceptable to the environment.

The present invention provides a composition for flame retarding fabrics which comprises (i) an at least partly water insoluble ammonium polyphosphate, (ii) a surfactant, (iii) a heat curable resin and (iv) water. Preferably the composition contains (v) a water soluble ammonium polyphosphate and/or (vi) a carbamic acid derivative. There is also provided a method of flame retarding a fabric substrate which comprises impregnating the fabric with a composition comprising components (i) to (iv), and preferably also (v) and (vi), and then heat curing the impregnated fabric.

The invention also provides a fabric which as been flame retarded by impregnation with a composition comprising components i) to iv) and preferably also (v) and (vi) and curing the impregnated fabric.

The at least partly water insoluble (hereinafter referred to as insoluble) ammonium polyphosphate (i) usually has a water solubility of less than 10 g/100g water, at 20°C especially less than 7 or 5 g/100g, such as 0.1-5, 0.5-3 or 1.5-7g/100g water, wherein the solubility is as measured by the Manders test, as defined by the Manders paint company for ammonium polyphosphates used in paints and as hereinafter described. It may be considered as comprising a mixture of truly soluble and insoluble components, the soluble components of which can leach out on addition of or to water to produce an insoluble fraction of very high surface area to volume ratio, e.g. as a very fine powder and/or a honeycomb structure. It may be made by heating, eg at 200-400°C, mono or di ammonium polyphosphate alone or mixed with phosphorus pentoxide or ammonia. The phosphorus pentoxide may be replaced at least in part by phosphoric acid and the source of ammonia may be urea (see eg BP 1103772, 1184878, 1309873 and EP 49763). The insoluble polyphosphate may have a straight or branched chain structure and may be of general formula $(NH_4)_a H_{b-a+2} P_bO_{3b+1}$, where b has an average value of greater than 10, a/b is between 0.7-1.1 and the maximum value of a is b+2. The molecular weight of the insoluble polyphosphate is usually greater than 10,000, eg 10,000 to 2 million, such as 10,000 to 1,000,000 or 200,000 to 1.5 million. The water insoluble ammonium polyphosphate usually has a mean particle size of less than 50 microns, preferably less than 30 microns, such as 1-50, 5-50 or 10-30 microns. Preferably at least 60% of the particles are of less than 30 microns and especially at least 40% less than 10 microns. The polyphosphate usually contains 20-35% P, such as 23-32%P, preferably 25-32%P.

Examples of suitable insoluble polyphosphates are those sold by Albright & Wilson Limited under the Trade Marks AMGARD MC and AMGARD PI. The composition usually contains (based on the weight of components (i-vi)) 15-30%, eg 10-25% or 19-23%, of the water insoluble ammonium polyphosphate, while containing 15-30%, such as 20-28 or 21-25, and especially 24-27%, of the polyphosphate (based on the weight of components (i-iv)).

The surfactant (ii) is usually a poor wetting agent. It preferably comprises a strong foaming agent, especially one which can stabilise oil in water emulsions, with an hydrophilic lipophilic balance (HLB) figure of greater than 12, eg 12-20, especially 12-16, but may alternatively be suitable for stabilizing water in oil emulsions, with an HLB of figure less than 12, eg 1-8, especially 3-7. The composition may comprise a mixture of surfactants, eg an emulsifier for the resin and a strong foaming agent.

The surfactant may comprise at least one anionic, non-ionic, cationic, amphoteric and/or semi-polar component.

Surfactants for use in our invention typically contain hydrophobic groups such as alkenyl, cycloalkenyl, alkyl, cycloalkyl, aryl, alkyl/aryl or more complex aryl (as in petroleum sulphonates) moieties having from 8 to 22, preferably 10 to 20, typically 12 to 18, carbon atoms and a hydrophilic moiety. Other hydrophobic groups included in the invention are polysiloxane groups.

The surfactant may for example consist substantially of an at least sparingly water-soluble salt of sulphonic or mono esterified sulphuric acids, e.g. an alkylbenzene sulphonate, alkyl sulphate, alkyl ether sulphate, olefin sulphonate, alkane sulphonate, alkylphenol sulphate, alkylphenol ether sulphate, alkylethanolamide sulphate, alkylethanolamide ether sulphate, or alpha sulpho fatty acid or its esters each having at least one alkyl or alkenyl group with from 8 to 22, more usually 10 to 20, aliphatic carbon atoms.

The expression "ether" hereinbefore refers to compounds containing one or more glyceryl groups and/or an oxyalkylene or polyoxyalkylene group especially a group containing from 1 to 20 oxyethylene and/or oxypropylene units. One or more oxybutylene units may additionally or alternatively be present.
For example, the sulphonated or sulphated surfactant may be sodium dodecyl benzene sulphonate, potassium hexadecyl benzene sulphonate, sodium dodecyl dimethyl benzene sulphonate, scdium lauryl sulphate, sodium tallow sulphate, potassium oleyl sulphate, ammonium lauryl monoethoxy sulphate, or monoethanolamine cetyl 10 mole ethoxylate sulphate.

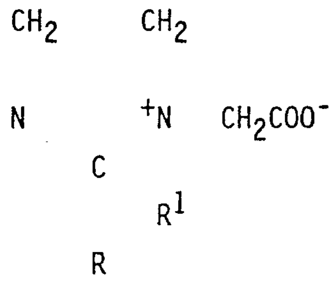
Other anionic surfactants useful according to the present invention include alkyl sulphosuccinates, such as sodium di-2-ethylhexylsulphosuccinate and sodium dihexylsulphosuccinate, alkyl ether sulphosuccinates, alkyl sulphosuccinamates, alkyl ether sulphosuccinamates, acyl sarcosinates, acyl taurides, isethionates, soaps such as stearates, palmitates, resinates, oleates or linoleates, and alkyl ether carboxylates. Anionic phosphate esters, alkyl phosphonate and alkyl amino and imino methylene phosphonates may also be used. In each case the anionic surfactant typically contains at least one aliphatic hydrocarbon chain having from 8 to 22, preferably 10 to 20 carbon atoms, and, in the case of ethers, one or more glyceryl and/or from 1 to 20 oxyethylene and/or oxypropylene and/or oxybutylene groups.

Preferred anionic surfactants are sodium salts. Other salts of commercial interest include those of potassium, lithium, ammonium, monoethanolamine, diethanolamine, triethanolamine and alkyl amines containing up to seven aliphatic carbon atoms.

The surfactant may optionally contain or consist of nonionic components. The nonionic surfactant may be, e.g. a C_{10-22} alkanolamide of a mono or di- lower alkanolamine, such as coconut monoethanolamide. Other nonionic surfactants, which may optionally be present, include tertiary acetylenic glycols, polyethoxylated alcohols, polyethoxylated mercaptans, polyethoxylated carboxylic acids, polyethoxylated amines, polyethoxylated alkylolamides, polyethoxylated alkylphenols, polyethoxylated glyceryl esters, polyethoxylated sorbitan esters, polyethoxylated phosphate esters, and the propoxylated or ethoxylated and propoxylated analogues of all the aforesaid ethoxylated nonionics, all having a C_{8-22} alkyl or alkenyl group and up to 20 ethyleneoxy and/or propyleneoxy groups. Also included are polyoxypropylene/polyethylene oxide copolymers, polyoxybutylene/polyoxyethylene copolymers and polyoxybutylene/polyoxypropylene copolymers. The polyethoxy, polyoxypropylene and polyoxybutylene compounds may optionally be end-capped with, e.g. benzyl groups to reduce their foaming tendency.

Compositions of our invention preferably contain at least one amphoteric surfactant.

The amphoteric surfactant may for example be a betaine, e.g. a betaine of the formula:- $R_3N^+CH_2COO^-$, wherein each R is an alkyl, cycloalkyl, alkenyl or alkaryl group and preferably at least one, and most preferably not more than one R, has an average of from 8 to 20, e.g. 10 to 18, aliphatic carbon atoms and each other R has an average of from 1 to 4 carbon atoms. Particularly preferred are the quaternary imidazoline betaines of the formula:



wherein R and R^1 are alkyl, alkenyl, cycloalkyl, alkaryl or hydroxyalkyl groups having an average of from 1 to 20 aliphatic carbon atoms. R preferably has an average of from 8 to 20, e.g. 10 to 18, aliphatic carbon atoms and R^1 preferably has 1 to 4 carbon atoms. Other amphoteric surfactants for use according to our invention include alkyl amine ether sulphates, sulphobetaines and other quaternary amines or quaternised imidazoline sulphonic acids and their salts, other quaternary amine or quaternised imidazoline carboxylic acids and their salts and Zwitterionic surfactants, e.g. N-alkyl taurines, carboxylated amido amines such as $RCONH(CH_2)_2N^+(CH_2CH_2CH_3)_2CH_2CO_2^-$, and amino acids having, in each case, hydrocarbon groups capable of conferring surfactant properties (e.g. alkyl, cycloalkyl, alkenyl or alkaryl groups having from 8 to 20 aliphatic carbon atoms). Typical examples include 2-tallow alkyl 1-tallow amido alkyl 1-carboxymethyl imidazoline and 2-coconut alkyl N-carboxymethyl 2-(hydroxyalkyl) imidazoline. Generally speaking any water soluble amphoteric or Zwitterionic surfactant compound which comprises a hydrophobic portion including a C_{8-20} alkyl or alkenyl group and a hydrophilic portion containing an amine or quaternary ammonium group and a carboxylate, sulphate or sulphonic acid group may be used in our invention.

Compositions of our invention may also include cationic surfactants.

The cationic surfactant may for example be an alkylammonium salt having a total of at least 8, usually 10 to 30, e.g. 12 to 24, aliphatic carbon atoms, especially a tri or tetra-alkylammonium salt. Typically alkylammonium surfactants for use according to our invention have one, or at most two, relatively long aliphatic chains per molecule (e.g. chains having an average of 8 to 20 carbon atoms each, usually 12 to 18 carbon atoms) and two or three relatively short chain alkyl groups having 1 to 4 carbon atoms each, e.g. methyl or ethyl groups, preferably methyl groups. Typical examples include dodecyl trimethyl ammonium salts. Benzalkonium salts having one C_{8-20} alkyl group, two C_{1-4} groups and a benzyl group are also useful.

Another class of cationic surfactants useful according to our invention are N-alkyl pyridinium salts wherein the alkyl group has an average of from 8 to 22, preferably 10 to 20 carbon atoms. Other similarly alkylated heterocyclic salts, such as N-alkyl isoquinolinium salts, may also be used.

Alkylaryl dialkylammonium salts, having an average of from 10 to 30 aliphatic carbon atoms are useful, e.g. those in which the alkylaryl group is an alkyl benzene group having an average of from 8 to 22, preferably 10 to 20, aliphatic carbon atoms and the other two alkyl groups usually have from 1 to 4 carbon atoms, e.g. methyl groups.

Other classes of cationic surfactant which are of use in our invention include alkyl imidazoline or quaternised imidazoline salts having at least one alkyl group in the molecule with an average of from 8 to 22, preferably 10 to 20, carbon atoms. Typical examples include alkyl methyl hydroxyethyl imidazolinium salts, alkyl benzyl hydroxyethyl imidazolinium salts, and 2-alkyl-1-alkylamidoethyl imidazoline salts.

Another class of cationic surfactant for use according to our invention comprises the amido amines such as those formed by reacting a fatty acid having 8 to 22 carbon atoms or an ester, glyceride or similar amide forming derivative thereof, with a di or poly amine, such as, for example, ethylene diamine or diethylene triamine, in such a proportion as to leave at least one free amine group. Quaternised amido amines may similarly be employed.

Typically the cationic surfactant may be any water soluble compound having a positively ionised group, usually comprising a nitrogen atom, and either one or two alkyl groups each having an average of from 8 to 22 carbon atoms.

The anionic portion of the cationic surfactant may be any anion which confers water solubility, such as formate, acetate, lactate, tartrate, citrate, chloride, nitrate, sulphate or an alkylsulphate ion having up to 4 carbon atoms, such as a methanesulphonate. It is preferably not a surface active anion, such as a higher alkyl sulphate or organic sulphonate.

Polyfluorinated anionic, nonionic or cationic surfactants may also be useful in the compositions of our invention. Examples of such surfactants are polyfluorinated alkyl sulphates and polyfluorinated quaternary ammonium compounds.

Compositions of our invention may contain a semi-polar surfactant, such as an amine oxide, e.g. an amine oxide containing one or two (preferably one) C_{8-22} alkyl groups, the remaining substituent or substituents being preferably lower alkyl, e.g. C_{1-4} alkyl, groups or benzyl groups.

Mixtures of two or more of the foregoing surfactants may be used. In particular mixtures of non-ionic surfactants with cationic and/or amphoteric and/or semi polar surfactants or with anionic surfactants may be used.

The compositions usually contain 0.1-5%, eg 1.0-3.5%, of the surfactant (or surfactant mixture) especially with 0.2-1.5%, eg 0.4-1%, added surfactant in addition to any emulsifier present in the resin dispersion, which may be in amount of 0.2-3.5%, such as 0.5-2.5%, of components (i-vi). Added surfactant may be 0.5-0.9% based on components (i-iv). The emulsifier in the resin dispersion is preferably non ionic or anonic, eg an alkyl sulphate or alkyl ether sulphate, while the added surfactant is preferably a betaine.

Examples of suitable surfactants are the alkyl dimethyl betaine surfactants, sold by Albright & Wilson Limited, Birmingham, England under the Trade Mark EMPIGEN BB, those sold by Texchem UK Manchester, England under the Trade Name TEXFIN TA, which are believed to have a high HLB and the amphoteric surfactant OSCOL 459 sold by Oils and Soaps Ltd, Lancs, England.

The resin (iii) is derived from at least one ethylenically unsaturated monomer and may be a homopolymer, but is preferably is a copolymer. Examples of suitable monomers are ethylene and mono substituted ethylenes, eg vinyl carboxylate esters, eg of 4-8 carbons, such as vinyl acetate, mono and di carboxy substituted ethylenes and esters thereof, such as acrylic acid, methacrylic acid, maleic acid and their esters, such as ethyl acrylate, chloroethylenes, such as vinyl chloride and cyanoethylenes, such as acrylonitile. Preferred resins are copolymers comprising acrylic monomer units with each other or acrylonitrile or vinyl chloride, or vinyl acetate/ethylene copolymers. Examples of suitable resins are those sold under the trade marks REVACRYL 274 by Harlow Chemical Co, England, VINAMUL 3306 by Vinamul Ltd, Surrey, England and LUTOFAN LA560S, LUTOFAN 300D and ACRONAL DS 2272 by BASF, West Germany. The resin is usually commercially available as an aqueous dispersion or emulsion with an emulsifier, which may be anionic such as an alkyl sulphate and/or alkyl ether sulphate, a mixture of which is present in the case of the REVACRYL 274 resin, or non-ionic as in the case of the ethylene/vinyl acetate copolymer sold as VINAMUL 3306. The dispersions usually contain 40-55% solids content of the resin. While the emulsifier added with the resin may be sufficient to provide the sole surfactant for use in the compositions of this invention (as in the case of the vinyl chloride acrylic copolymer sold as LUTOFAN 560S), preferably a separate surfactant, which is preferably a foaming agent, is added as well. The resins are usually ones with T_G of less than 30° C, eg -40 to +30° C, especially 0 to - 30° C. The resins are self curable by heat, eg at 80-180° C, especially 120-170° C. The compositions of the invention usually contain 10-30% or 15-30%, such as 20-25%, 21-24% or 21.5-23.5% resin (expressed as resin solids on the total weight of the components (i-vi)), or 10-30%, eg 14-23%, such as 17-21% or 14-18% (based on the weight of a composition containing components (i-iv) but not (v) or (vi)).

The compositions also contains as component (iv) water in weight amount usually of 40-51%, such as 42-50 or 44-49% (based on the weight of components (i-vi) or 50-60%, such as 56-58% (based on the weight of components (i-iv) in the absence of (v) and (vi)). These figures include any water added with the other components such as resin or surfactant, as well as water added separately.

The water soluble ammonium polyphosphate (v), which is preferably present in the compositions of the invention, is usually 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 has a linear, branched or cyclic structure. Preferably the salts contain nitrogen and phosphorus 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, e.g. 5-12, such as 5-9, 6-8 or 6.5-7.5. Ammonium polyphosphate mixtures which may be used are described in BP 1504507 and may be made as described therein. This added ammonium polyphosphate usually has a (true) water solubility of at least 50 g/l, e.g. at least 100g/l, in water at 20° C. Examples of suitable soluble polyphosphates are these mixed with urea and sold by Albright & Wilson Ltd under the Trade Mark AMGARD LR2. The composition usually contains 0-10%, such as 2-8%, eg 4-6%, of the water soluble ammonium polyphosphate.

The flame retardant composition of the invention usually also contains a carbamic acid derivative (vi) 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%. However 50-300%, e.g. 50-200%, and especially 75-125% are preferred. 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. The composition usually contains 0-10%, such as 2-8%, eg 4-6%, of the carbamic acid derivative (expressed as urea).

The compositions of the invention are usually thixotropic pastes, which are pourable when freshly made, form a gel on standing, but are converted to a pourable emulsion on shearing. The stable emulsions may be water in oil emulsions, but are preferably oil in water emulsions. On contact with a cotton fabric under the influence of gravity only, the compositions tend not to pass through the fabric nor to lose water rapidly into the fabric. On shearing the composition in contact with the fabric, eg under the pressure of a knife edge, it is believed that the compositions shear allowing them to penetrate the fabric, wherein they regel rapidly, but do not pass through the fabric and exude from the opposite side. The compositions may be made by mixing the components in any order, but usually in order of resin first, then insoluble ammonium polyphosphate, followed preferably by soluble ammonium polyphosphate and carbamic acid derivative, then water and finally any extra surfactant. The mixing is usually dcne with a high speed stirrer.

The compositions of the invention containing components (i) - (iv) usually contain these in weight proportions of 20-28 : 0.1-5 : 14-30 : 50-60. The compositions of the invention containing components (i-vi) usually contain these in weight proportions of 15-30 : 0.1-5 : 15-30 : 40-51 : 2-8 : 2-8.

The substrates to which the composition is applied may be woven or non woven. They are usually cellulosic based substrates, e.g. textile fabrics, such as cotton, linen, jute or hessian or regenerated cellulosic materials, such as rayon or viscose, alone or with other fibres coblendable or mixable therewith, e.g. polyester, nylon, acrylics, acetate, polypropylene, silk or wool. These blends or mixtures of fibres may contain at least 10%, or at least 20%, such as 15-100% or 30-90%, but preferably at least 40%, such as 40-75%, of the cellulosic material.

Preferred are fabrics from intimate blends or non-blended mixtures of cellulosic material, eg cotton, and synthetic polymer, eg polyester, nylon or acrylics. The fibres used to form at least part of the fabrics may if desired be of core sheath construction but are preferably not so. The fabrics may be of union construction, for example with at least one of the weft and especially the warp being predominantly (eg 50-100%), especially essentially completely, of synthetic polymer fibres. Those with a warp predominantly of polyester or nylon and a cotton weft, especially with embossed cotton designs and/or colour woven cotton are preferred. The flame retardant compositions of the invention and the method of the invention enables one more uniformly to flame retard, at least semidurably, such union fabrics, preferably embossed ones, but especially ones with non uniform distribution of synthetic polymer and cellulosic material on a surface thereof (hereinafter called "differential surface fabrics"). Particularly important differential surface fabrics are ones with a front side with a different (usually lower) proportion of the cellulosic material to synthetic material from that on the back side, as well usually as having a face or front side having significant areas of predominantly (eg 50-100%) fibres of synthetic polymer on the surface, as well usually as significant areas of predominantly (eg 50-100%) fibres of the cellulosic material. Examples of such differential surface fabrics are ones with a polyester warp and dyed cotton weft, especially with more than one differently coloured cotton weft, with the fabrics woven with front designs of such dyed cotton on a background of the polyester warp and a nondesigned back with a substantial cotton surface. Such differential surface fabrics may be used as upholstery fabrics. Other useful fabrics are pile fabrics, especially with a cotton base fabric back and an acrylic pile face. In the cases of the union fabrics and pile fabrics each having a face and a back, the compositions are applied to the back of the fabrics.

In addition to upholstery fabrics, the flame retardant composition can be applied to other furnishing fabrics, such as curtains, which are not subjected to frequent washing, and which are for use in, for example, domestic, office, institutional or public buildings. The ability to treat different types of fabric makes it useful where various fabrics bear the same, or similar, designs for use in situations which have "colour-coordinated" decor.

Fabric weights can be 0.050-1.0kg/m^2, e.g. 0.080-0.700kg/m^2, or 0.400-0.700 kg/m^2, typically 0.200-0.400 kg/m^2, especially with fabrics containing at least 30% of non cellulosic fibres. Each of the components of the fabric may be plain or undyed or may be dyed, especially with white or pastel shades. The fabric before impregnation is usually free of dirt, sizes, natural waxes and applied finishes though it may contain an optical brightening agent.

The flame retardant finishing may also be used to treat carpeting (by back coating), which can weigh up to 2kg/m^2.

The flame retardant composition, usually at pH 2-8, e.g. 5.5-7.5, is applied to the fabric substrate by a back coating procedure, such by spreading with a knife over a roller or air or, preferably, by using a rotary screen, optionally in combination with said knife, to give an application rate of 35-150% or 50-150% (on weight of fabric), such as 60-80% on pile fabrics or 80-120% on intimate blend or union fabrics. The minimum application rate necessary to provide adequate flame retardant properties is typically that required to saturate the fabric (especially the pores of the fabric) or a minimum of 95%, whichever is the lesser.

If desired, after impregnation the substrate may be dried, e.g. at 80-120°C for 0.1 to 10 minutes. The drying may be performed in any conventional drier, e.g. a forced air drier or stenter.

The impregnated substrate after drying, if desired, is then heat cured, eg by heating at a temperature of at least 80°C, such as at least 120°C, e.g. 120-170°C preferably 140-170°C or 140-165°C, e.g. for 6 to 0.5 minutes, the combination of longer times and higher temperature preferably being avoided to decrease any tendency to discoloration. Preferably the drying and curing steps are combined.

The curing, which is usually continuous, may be performed by radiant, e.g. infra red, heating but preferably the curing is by heating from impact of hot air on the surface of the substrate and 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 30-60%, such as 35-45% for pile fabrics, or 50-60% for union or other non pile fabrics, and usually contains 3-10% P, preferably 5-8% 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 can pass the flammability test of BS 5852 Part 1 with ignition sources 0 and 1. The reduced flammability finish can be durable for 1-3 washes in soft water at 74° C or to 10 dry cleaning operations depending primarily on the nature of the resin. The fabric as finished usually has a face handle not significantly changed from that of the untreated fabric and shows no surface salt deposits or resin marks. It usually has a colour not significantly changed from that of the untreated fabric.

The synergistic combination of the components (i)-(iv) especially with components (v) and (vi), can give treated fabrics with improved flame retardant properties and, particularly with fabrics having a face and back, without salt or resin deposits on the face, when the composition is applied to the back. It is believed that some of the water and any water soluble ammonium polyphosphate, added as such or as part of the water insoluble polyphosphate, migrates from the back towards the face but does not reach the face.

In this specification all parts and percentages are by weight.

The invention is illustrated in the following Examples. In Examples 1 to 23 the following fabrics were used:

Fabric A was an intimate blend fabric of 20% viscose, 40% polyester, 20% acrylic and 20% polypropylene of 0.320 kg/m^2 fabric weight.

Fabric B was a 50:50 cotton polyester union fabric with cotton weft and polyester warp of 0.240 kg/m^2 weight.

Fabric C was a 100% viscose pigment print of 0.230 kg/m^2 weight.

Fabric D was a 65:35 cotton polyester union fabric with cotton weft and polyester warp of 0.470 kg/m^2 weight.

Fabric E was a 50:50 cotton acrylic pile fabric with acrylic pile and a cotton base, of 0.540 kg/m^2 total fabric weight.

Fabric F was an intimate blend 40:60 cotton polyester fabric of 0.380 kg/m^2 weight.

Fabric G was an intimate blend 65:35 viscose/polyester fabric of 0.220 kg/m^2 weight.

Fabric H was a 100% cotton vat printed fabric of 0.240 kg/m^2 fabric weight.

Fabric I was a 50:50 cotton acrylic pile fabric with acrylic pile and a cotton base of 0.320 kg/m^2 total fabric weight.

In each case the composition of the invention was prepared and applied to the fabric on a supporting surface with the aid of a knife which spread the composition onto the fabric and forced it into the fabric; in the cases of fabrics B, D, E and I the composition was applied to the back of the fabric. The supporting surface under the fabric became cool but not damp in this procedure, showing that water did not exude from the underside of the fabric. The impregnated fabric was then heated in a stenter at 150° C for 90 secs to provide a combined drying and curing operation. The cured fabric was then tested for flame retardancy as finished and after one leach in hard water at 40° C according to BS 5651 part 1 without final ironing.

The solubility of the water insoluble ammonium polyphosphate as used in the text and Examples is that determined by the Manders test, in which 5g of solid is shaken with 50ml of water at ambient temperature and then 10 ml of solution is removed, weighed and evaporated to dryness to leave a residue. The solubility is given as 10 times the weight in g of the residue.

Example 1 - 5

A composition was made up by thoroughly mixing in the following order the following ingredients : 50 parts of a 45.5% solids content aqueous emulsion of a self cross linking heat curable acrylic copolymer containing some acrylonitrile monomer units, whose T_G was -24° C, sold as REVACRYL 274 by Harlow Chemical Co. England (an emulsifier was also present in the emulsion), 21 parts of a water insoluble ammonium polyphosphate of mean particle size 15 microns with a particle size distribution of 98% less than 32 microns, 90% less than 30, 75% less than 22, 50% less than 13, 25% less than 6 and 10% less than 1.6 microns and containing 30% P and a Manders solubility of about 2g/100g water at 20° C, 5.1 parts of urea and 5.1 parts of water soluble ammonium polyphosphate made according to the process of BP 1504507, 8.8 parts of water, extra water as specified below and various amounts of a 40% aqueous solution of an alkyl dimethyl ammonium betaine amphoteric emulsifier sold, as a foaming agent with some surface activity, as TEXFIN TA by Texchem Ltd England. The insoluble polyphosphate was obtained by milling the product sold by Albright & Wilson Limited under the trade mark AMGARD MC.

The composition was a pourable stable emulsion which on standing thickened to a gel, which was reconverted to the emulsion on shearing.

For fabrics A-D, F,G and H the composition was applied with an application rate of 96%, while for pile fabrics E and I the rate was 70%.

Details of the compositions and the fire retardant effect on the various fabrics were as follows.

With compositions containing 1, 2, 3 and 4 parts of the extra TEXFIN emulsifier solution and 9, 8, 7 and 6 parts respectively of added water all the fabrics passed the BS 5852 ignition source 0 and 1 tests before and after the soaking; cured fabrics D and E which had been treated by forcing into the back of the fabric corresponding compositions containing no TEXFIN emulsifier but 10 extra parts of water also passed the FR tests. All the fabrics passed the ignition source 0 tests.

In all cases the cured fabric showed no salt deposits or resin marks on their faces or on the surface opposed to that on which the composition was applied. The face handle of the fabrics was substantially unaffected by the treatment.

Examples 6 and 7

The process of Examples 1-5 were repeated with different amounts of added water. For fabrics A, B, C, D, F, G and H the composition contained 2 parts of the TEXFIN emulsifier solution and 8.33 and 12.5 extra parts of water and was applied at a loading of 96% (on weight of fabric). For pile fabrics E and I the composition contained 2 parts of the TEXFIN emulsifier solution and 11.43 and 17.14 extra parts of water and was applied at a loading of 70% to the back of the fabric. In all cases (apart from Fabrics C and F and 17.14 part water) the cured fabrics passed the BS 5852 ignition source 0 and 1 tests before and after soaking. All the fabrics passed the ignition source 0 test. Again there were no salt deposits nor resin marks on the faces of the fabric and the facial handles were substantially unaffected.

Example 8-11

The process of Ex 2 was repeated with equal weights of other self cross linking copolymer resin emulsions replacing the REVACRYL 274 resin emulsion. The resins were as follows; an aqueous vinylacetate ethylene copolymer emulsion containing 50% solids of T_G -18° C containing also a non ionic surfactant, sold under the trade mark VINAMUL 3306 by Vinamul Ltd of Carshalton, Surrey, England; an aqueous carboxylated vinyl chloride acrylic copolymer emulsion containing 51% solids of T_G -3° C with a synthetic emulsifier, sold under the trade mark LUTOFAN LA5605 by BASF A.G. of West Germany; an aqueous vinyl chloride copolymer emulsion containing 50% solids of T_G +26° C, sold under the trade mark LUTOFAN 300D by BASF; and an aqueous ethyl acrylate copolymer emulsion containing 45% solids, sold under the trademark ACRONAL DS 2272 by BASF.

In each case the composition was a thixotropic paste shearable to a stable pourable emulsion. Each of the compositions as applied to each of the fabrics as in Ex 2 and cured for 2 mins at 150° C; in all cases the cured fabrics passed the FR tests before and after one soak in hard water.

In the case of the LUTOFAN LA560S resin, the corresponding composition without the added TEXFIN emulsifier was also a thixotropic paste shearable to a pourable emulsion. The composition was applied and cured as in Ex 2; again all the FR tests were passed and there were no salt or resin marks on the face nor any adverse facial handle.

Examples 12-16

In these examples only Fabric B, D, E, H and I were treated. The compositions used for Fabrics B, D and H contained (for Ex 12) 50 parts of the REVACRYL 274 resin emulsion used in Ex 1, 2.08 parts of the TEXFIN TA emulsifier solution, 25 parts of the insoluble ammonium polyphosphate and 35.4 parts of extra water and in a second Example (Ex 13) the amounts of the insoluble polyphosphate and extra water were changed to 29.2 parts and 41.7 parts respectively. In the compositions used for Fabrics E and I, the compositions were as for Ex 12 but the amounts of insoluble polyphosphate and extra water were changed to 34.3 parts and 48.6 parts respectively in one case (Ex 14) and to 40 parts and 57.1 parts respectively in another case (Ex 15). All 4 compositions were stable thixotropic pastes shearable to stable emulsions.

The compositions were otherwise applied and cured as in Example 1 to give cured fabrics which passed the FR tests as before.

In the case of Fabrics D and E compositions were also used(for Ex 16) in which the amounts of insoluble polyphosphate and extra water were 20.8 parts and 29.2 parts respectively. The compositions were stable thixotropic pastes shearable to stable emulsions. They were applied to Fabrics D and E as before and cured as in Ex 1 to give cured fabrics which passed the FR tests as before, and showed no salt or resin marks on the faces nor any adverse facial handle.

Examples 17 and 18

Samples of fabric H were treated at an application rate of 96% in a similar manner to that in Example 1 with a composition consisting of:-

50 parts of Revacryl 274 resin emulsion;
5.1 parts of the soluble ammonium phosphate;
5.1 parts of urea;
2-parts of a 30% aqueous solution of a C_{12-14} alkyl dimethyl betaine, sold by Albright & Wilson Limited as under the Trade Mark EMPIGEN BB;
16.8 parts of water; and
20 parts of an insoluble ammonium phosphate having the following properties:-

Example	%P	Manders solubility	Particle Size
17	30.2	3.51	98% < 32um
18	31.8	0.5	95% < 10um

In each case the fabric passed the FR test and exhibited no facial marks or adverse handle.

Example 19

Samples of fabric B were treated at an application rate of 96% in a similar manner to that in Example 1 with a composition consisting of:-

50 parts of Revacryl 274 resin emulsion;
4.8 parts of the soluble ammonium phosphate;
4.8 parts of urea;
2 parts of a 30% aqueous solution of a C_{12-14} alkyl dimethyl betaine, sold by Albright & Wilson Limited as EMPIGEN BB;
16.3 parts of water; and
20 parts of the insoluble ammonium phosphate of Example 17.

In each case the fabric passed the FR test and exhibited no facial marks or adverse handle.

Example 20-21

Samples of fabrics E and I were treated at application rates of 70% with the composition containing 2 parts of TEXFIN TA foaming agent (as used in examples 1 to 5) with respectively 8.33 parts and 12.5 parts of added water.

In each case the fabric passed the FR test and exhibited no facial marks or adverse handle.

Examples 22-23

Samples of fabrics E and I were treated at application rates of 70% as in Examples 12 and 13 but using 25 and 29.2 parts of added water and 35.4 and 41.7 parts of insoluble phosphate respectively.

In each case the fabric passed the FR test and exhibited no facial marks or adverse handle.

Examples 24-26

The following fabrics

i) 75/25 cotton/polyester union of 0.336kg/m^2 fabric weight;
ii) 55/45 cotton/polyester union of 0.321 kg/m^2 fabric weight; and
iii) 55/45 cotton/polyester union of 0.324 kg/m^2 fabric weight;

were treated with a composition comprising:-

51 parts of Revacryl 274 resin emulstions;

5 parts of soluble phosphate;
5 parts of urea;
1 parts of Texfin TA foaming agent;
13 parts of water; and
25 parts of insoluble phosphate.

The final applied solids levels were 30% for fabrics i) and iii) and 38% for fabric (ii).

Drying and curing were carried out as in previous Examples and all treated fabrics passed the BS5852 test with ignition sources 0 and 1 following a water soak as specified in BS5651.

Claims

1. A composition for flame retarding fabrics which comprises:
   (i) an at least partly water insoluble (as hereinbefore defined) ammonium polyphosphate;
   (ii) a surfactant;
   (iii) a heat curable resin; and
   (iv) water.

2. A composition according to claim 1 also comprising:-
   (v) a water soluble ammonium polyphosphate; and/or
   (vi) a carbamic acid derivative.

3. A composition according to claim 1 or 2 wherein the solubility of (i), as defined by the Manders test, is less than 10g/100g water at 20° C.

4. A composition according to claim 3 wherein the solubility is from 0.5 to 3g/100g.

5. A composition according to any one of claims 1 to 4 wherein the mean particle size of (i) is less than 50 microns.

6. A composition according to claim 5 wherein the mean particle size is from 10 to 30 microns.

7. A composition according to any one of claims 1 to 6 wherein at least 60% of the particles of (i) are less than 30 microns in size.

8. A composition according to any one of claims 1 to 7 wherein at least 40% of the particles of (i) are less than 10 microns in size.

9. A composition according to any one of claims 1 to 8 wherein the molecular weight of (i) is from 10,000 to 2 million.

10. A composition according to any one of claims 1 to 9 wherein (i) contains from 20 to 35% by weight of phosphorus.

11. A composition according to claim 1 or 2 which contains 15 to 30% by weight of (i).

12. A composition according to claim 1 which contains 24 to 27% by weight of (i).

13. A composition according to claim 2 which contains 19 to 23% by weight of (i).

14. A composition according to any one of claims 1 to 13 wherein (ii) comprises at least one anionic, nonionic, cationic, amphoteric and/or semipolar surfactant.

15. A composition according to claim 14 wherein (ii) is derived at least in part from an aqueous emulsion of (iii).

16. A composition according to claim 14 or 15 wherein (ii) is an alkyl dimethyl betaine.

17. A composition according to claim 1 or 2 which contains 0.1 to 5% by weight of (ii).

18. A composition according to any one of claims 1 to 17 wherein (iii) is an acrylic copolymer containing acrylonitrile monomer units, a vinyl acetate / ethylene copolymer, a carboxylated vinyl chloride / acrylic copolymer or an ethyl acrylate copolymer.

19. A composition according to claim 1 or 2 which contains 10 to 30% by weight of (iii).

20. A composition according to claim 1 which contains 14 to 23% by weight of (iii).

21. A composition according to claim 2 which contains 20 to 25% by weight of (iii).

22. A composition according to any one of claims 2 to 21 wherein (v) has true water solubility of greater than 50g/l in water at 20° C.

23. A composition according to any one of claims 2 to 22 wherein (v) has an atomic ratio of nitrogen to phosphorus of 0.5 to 2:1.

24. A composition according to claim 23 wherein the ratio is about 1:1.

25. A composition according to any one of claims 2 to 24 wherein (v) has a mean degree of condensation of from 3 to 30.

26. A composition according to claim 2 which contains less than 10% by weight of (v).

27. A composition according to claim 26 which contains 4 to 6% by weight of (v).

28. A composition according to any one of claims 2 to 27 wherein (vi) is urea.

29. A composition according to claim 2 which contains less than 10% by weight of (vi).

30. A composition according to claim 29 which contains 4 to 6% by weight of (vi).

31. A composition according to any one of claims 2 to 30 wherein the weight proportion of (v) to (vi) is from 0.5 to 300% by weight.

32. A composition according to claim 31 wherein said proportion is from 75 to 125%.

33. A composition according to claim 1 wherein (i), (ii), (iii) and (iv) are in weight proportions of 20-28 : 0.1-5 : 14-30 : 50-60.

34. A composition according to claim 2 wherein (i), (ii), (iii), (iv), (v) and (vi) are in weight proportions of 15-30 : 0.1-5 : 15-30 : 40-51 : 2-8 : 2-8.

35. A method of flame retarding a fabric which comprises impregnating the fabric with a composition according to any of claims 1 to 34 and then heat curing the impregnated fabric.

36. A method according to claim 35 wherein the impregnation is carried out by applying the composition to the surface of the fabric and then imposing a shearing force on the applied composition to force it into the body of the fabric.

37. A method according to claim 36 wherein the application and imposition of shear are carried out in a single combined step.

38. A method according to claim 37 wherein the single step is carried out by using a knife applicator and/or a rotary screen.

39. A method according to any one of claims 35 to 38 wherein the fabric comprises cellulosic and non-cellulosic components.

40. A method according to claim 39 wherein the fabric comprises 40 to 75% by weight of cellulosic material.

41. A method according to any one of claims 35 to 40 wherein the fabric is a union fabric.

42. A method according to claim 41 wherein the application rate 80 to 120% by weight.

43. A method according to any one of claims 35 to 41 wherein the fabric is a differential surface fabric (as hereinbefore defined).

44. A method according to any one of claims 35 to 41 wherein the fabric is a pile fabric.

45. A method according to claim 44 wherein the application rate is from 60 to 80% by weight.

46. A method according to any one of claims 35 to 45 wherein the fabric weight is from 0.05 to 2 kg/m^2.

47. A method according to any one of claims 35 to 46 wherein the curing is carried out at 120 to 170° C for 6 to 0.5 minutes.

48. A method according to any one of claims 35 to 47 wherein the finished fabric has a solids content of 30 to 60 % by weight.

49. A method according to any one of claims 35 to 48 wherein the finished fabric has a phosphorus content of 3 to 10 % by weight.

50. A fabric treated by a method according to any one of claims 35 to 49.

51. A composition according to claim 1 as exemplified by that used in any one of Examples 1 to 23.

52. A method according to claim 35 as exemplified by any one of Examples 1 to 23.