PATENT REQUEST: STANDARD PATENT/PATENT OF ADDITION

We, being the person(s) identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Full application details follow.

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[54] Invention Title: "COATING COMPOSITION AND PROCESS"

[72] Name(s) of actual inventor(s): ROBERT WILLIAM BLACK

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BASIC CONVENTION APPLICATION(S) DETAILS

90 11921.5 United Kingdom GB 29th May 1990

TICK IF APPLICABLE

☐ I am an eligible person described in Sections 33 - 36 of the Act.

☐ For the purposes of Section 40, the specification relies on Section 6 of the Act (Microorganisms).

Drawing number recommended to accompany the abstract

By our/my Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

______________________________
D. B. Mischlewski
Registered Patent Attorney
COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

DECLARATION IN SUPPORT OF A CONVENTION
APPLICATION FOR A PATENT OR PATENT OF ADDITION

In support of the Convention Application made by (1) ALBRIGHT & WILSON LIMITED, a British company, of 210-222 Hagley Road West, Oldbury, Warley, West Midlands, England (hereinafter referred to as the applicant) for a Patent for an invention entitled: 'Coating Composition and Process'

I, ROGER GORDON MADGWICK SAVIDGE of Albright & Wilson Patents Department, P.O. Box 2098, Seven Stars Road, Oldbury, Warley, West Midlands, B69 4PR, England do solemnly and sincerely declare as follows:

1. I am authorised by the applicant for the patent to make this declaration on its behalf.

2. The basic application as defined by Section 141 of the Act was made in (4) United Kingdom on the 29th day of May, 1990, by Albright & Wilson Limited on the day of 19...

3. ROBERT WILLIAM BLACK, a British subject, of 104 Norman Road, Warley, West Midlands, B67 5PU, England is the actual inventor of the invention and the facts upon which the applicant is entitled to make the application are as follow:

   The applicant is entitled to apply under the provisions of Section 34(1)(FA) because it is entitled by contract to have any patent granted to the inventor assigned to it.

4. The basic application referred to in paragraph 2 of this Declaration was 9011921.5 the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at Oldbury, West Midlands, England on the 1st day of May, 1991.
An aqueous composition comprising an insoluble ammonium polyphosphate, an anti-foaming agent and a heat curable resin, which may also contain a surfactant, 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.

Claim: Indefinite
The following statement is a full description of this invention, including the best method of performing it known to us.
This invention relates to a coating and impregnation composition especially one 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 P 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 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) an antifoam agent (iii) a heat curable resin and (iv) water. It is especially preferred that the composition contains (v) a surfactant. Preferably the composition also contains (vi) a water soluble ammonium polyphosphate and/or (vii) 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 especially also (v), (vi) and/or (vii), and then heat curing the impregnated fabric.
The invention also provides a fabric which has been flame retarded by impregnation with a composition comprising components i) to (iv) and preferably also (v), (vi) and/or (vii) and curing the impregnated fabric.

The at least partly water insoluble (hereinafter referred to as insoluble) ammonium polyphosphate usually has a water solubility of less than 10 g/100 g water at 20°C, especially less than 8 or 5 g/100 g, such as 0.1-5, 0.5-3 or 1.5-7 g/100 g 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 at, eg 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 \((\text{NH}_4)_a \text{H}_b-a+2 \text{P}_b\text{O}_{3b+1}\), where b has an average value of greater than 10, \(a/b\) is 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 or AMGARD PI.
The composition usually contains (based on the weight of components (i-vii)) 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)).

An antifoam agent is a material which interacts with a liquid which is foaming or capable of doing so and which contains a surfactant by interacting with the surfactant molecules and/or the liquid/vapour interface in order to destroy the foam or prevent its formation. Examples of such agents are soaps, alkyl phosphate esters and mineral oil, wax, vegetable oil or silicone based formulations. The silicone based formulations comprise polysiloxane liquids which may be fluoro or alkyl siloxanes optionally possessing amino substituents and are preferably dimethyl siloxane polymers and preferably also contain finely divided silica which may be formed in situ by the hydrolysis of tetra alkoxy silanes. A preferred antifoam agent for use in the current invention is that sold by Wacker-Chemie GmbH under the name S132.

The composition usually contains 0.01-0.5%, e.g. 0.02-0.4%, preferably 0.05-0.2%, of the antifoam agent.

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, chlooroethylenes such as vinyl chloride and cyanoethylenes such as acrylonitrile. 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 sold by Vinamul Ltd, Surrey, England LUTOFAN LA560S and LUTOFAN 300d and ACRONAL DS 2272 sold by BASF, West Germany.
The resin is usually commercially available as an aqueous dispersion or emulsion which usually contains 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 emulsifier for use in the compositions of this invention (as in the case of the vinyl chloride acryl copolymer sold as LUTOFAN 560S), a separate emulsifier can be added as well. The resins are usually ones with T_G of less than 30°C, eg -40 to +30°C, and especially 0 to -30°C. The resins are self curable by heat, eg at 80-180°C, but 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-vii)), or 10-30%, eg 14-23% such as 17-21% or 14-18% (based on the weight of a composition containing components (i-v) but not (vi) or (vii)).

The compositions also contain 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-vii)) or 50-60% such as 56-58% (based on the weight of components (i-iv) in the absence of (v), (vi) and (vii)). These figures include any water added with the other components such as resin or surfactant, as well as water added separately.

The surfactant (v) is usually a poor wetting agent but with some surface activity. It preferably comprises strong foaming agent, especially one stabilizing oil in water emulsions with an hydrophilic lipophilic balance (HLB) figure of greater than 12, e.g. 12-20 eg 12-16, but may alternatively be suitable for stabilizing water in oil emulsion with an HLB of figure less than 12, eg 1-8, especially 3-7. The composition may comprise a mixture of surfactants, e.g. as an emulsifier for the resin.
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 sulphonate, alkylphenol ether sulphonate, alkylethanolamide sulphate, alkylethanolamide ether sulphonate, 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 groups. One or more oxybutylene groups 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, sodium 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, linoleates, and alkyl ether carboxylates. Anionic phosphate esters, alkyl phosphonates 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 surfactants. 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: \( R_3 N^+ CH_2 COO^- \), 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:

\[
\begin{align*}
\text{CH}_2 & \text{CH}_2 \\
N & = \text{C} \\
& \text{N}^+ \text{CH}_2 \text{COO}^- \\
R & \\
& R^1
\end{align*}
\]

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 amine or quaternised imidazoline sulphonics acids and their salts, and 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\(_2\))\(_2\)N\(^+\)(CH\(_2\)\(_2\)CH\(_3\))\(_2\)CH\(_2\)CO\(_2\)^-, 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 sulphonie 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 C8-20 alkyl group, two C1-4 alkyl 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 a 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 alkylsulphonate 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 group, 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 surfactant is usually present in the resin-containing emulsion but made additionally or alternatively be added separately, if desired.

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-vii). Added emulsifier may be 0.5-0.9% based on components (i-v). The emulsifier in the resin dispersion is preferably non ionic or anionic, eg an alkyl sulphate and/or alkyl ether sulphate.

The water soluble ammonium polyphosphate (vi), 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 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, 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 contains a carbamic acid derivative (vii) 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 the defoamer. The mixing is usually done with a high speed stirrer.

The compositions of the invention containing components (i) - (iv) usually contain these in weight proportions of 20-28 : 0.01-5 : 14-30 : 50-60. The compositions of the invention containing components (i-vii) usually contain these in weight proportions of 15-30 : 0.01-5 : 15-30 : 40-51 : 0.1-5 : 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, hessian or regenerated cellulosic materials, such as rayon or viscose, alone 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 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/m², e.g. 0.080-0.700kg/m², or 0.400-0.700 kg/m², typically 0.200-0.400 kg/m², 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 composition may also be used to treat carpeting (by back coating) which can weigh up to 2kg/m².

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 spreading with a knife over a roller or air 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 amount 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, e.g. 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, 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), (vi) and (vii), 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 which the following fabrics were used:

Fabric A was a 50:50 cotton polyester union fabric with cotton weft and polyester warp of 0.240 kg/m² weight.

Fabric B was a 65:35 cotton polyester union fabric with cotton weft and polyester warp of 0.470 kg/m² 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. 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**

A composition was made up by thoroughly mixing in the following order the following ingredients: 48 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 $-24^\circ$C, sold as REVACRYL 274 by Harlow Chemical Co. England (an emulsifier comprising alkyl ether sulphate and alkyl benzene sulphonate was also present in the emulsion); 20 parts of a water insoluble ammonium polyphosphate with a particle size distribution of 98% less than 32 microns, containing 30.2% P and a solubility of about 3.5g/100g at 20°C; 4.9 parts of urea; 4.9 parts of water soluble ammonium polyphosphate made according to the process of BP 1504507; 8.4 parts of water; and 0.1 parts of a 50:50 silicone oil(poly dimethyl siloxane)/hydrophobic silica antifoam agent, sold as S132 by Wacker-Chemie GmbH. 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 itself was reconverted to the emulsion on shearing and was applied to fabric A with an application rate of 90%.

The cured fabric samples passed the ignition source 0 and 1 tests and 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 fabric was substantially unaffected by the treatment.
Example 2

By proceeding in a similar manner to Example 1, but replacing the insoluble ammonium polyphosphate by 24 parts of one having a phosphorus content of 27.1%, a size distribution of 100% <32 μm and a solubility of 6.32/g/100g, and using an application rate of 94%, cured samples of fabric A again passed the FR tests, showed no salt or resin marks and exhibited an essentially unchanged handle.

Examples 3-16

Samples of fabric B were treated with compositions similar to those in Examples 1 and 2, but containing 20 or 24 parts of insoluble ammonium polyphosphate having the following properties:

<table>
<thead>
<tr>
<th>Examples</th>
<th>%P</th>
<th>Solubility (g/100g)</th>
<th>Particle Size (100% less than)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3, 4</td>
<td>27.1</td>
<td>6.32</td>
<td>30 μm</td>
</tr>
<tr>
<td>5, 6</td>
<td>26.7</td>
<td>5.55</td>
<td>32 μm</td>
</tr>
<tr>
<td>7, 8</td>
<td>27.3</td>
<td>3.55</td>
<td>32 μm</td>
</tr>
<tr>
<td>9, 10</td>
<td>27.5</td>
<td>3.33</td>
<td>32 μm</td>
</tr>
<tr>
<td>11, 12</td>
<td>27.9</td>
<td>3.16</td>
<td>32 μm</td>
</tr>
<tr>
<td>13, 14</td>
<td>27.3</td>
<td>2.96</td>
<td>32 μm</td>
</tr>
<tr>
<td>15, 16</td>
<td>27.9</td>
<td>2.58</td>
<td>32 μm</td>
</tr>
</tbody>
</table>

All cured samples again passed the FR tests, and exhibited no salt or resin marks or adverse change in handle.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A composition for flame retardant fabrics which comprises:

   (i) an at least partly water insoluble (as hereinbefore defined) ammonium polyphosphate;

   (ii) an anti-foam agent;

   (iii) a heat curable resin; and

   (iv) water

2. A composition according to Claim 1 also comprising:

   (v) a surfactant;

   (vi) a water soluble ammonium polyphosphate; and/or

   (vii) 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 any one of Claims 1 to 6 wherein at least 60% of the particles of (i) are less than 30 microns in size.

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) is a soap, an alkyl phosphate ester or a mineral oil, wax, vegetable oil or silicone based formulation.

15. A composition according to Claim 14 wherein (ii) comprises a polysiloxane.

16. A composition according to Claim 15 wherein the polysiloxane is polydimethylsiloxane.
17. A composition according to Claim 15 or 16 wherein (ii) also comprises finely divided silica.

18. A composition according to Claim 1 or 2 which contains 0.01 to 5% by weight of (ii).

19. A composition according to any one of Claims 1 to 18 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.

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

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

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

23. A composition according to any of Claims 2 to 22 which contains 0.1 to 5% by weight of (v).

24. A composition according to any one of Claims 2 to 23 wherein (vi) has true water solubility of greater than 50g/l in water at 20°C.

25. A composition according to any one of Claims 2 to 24 wherein (vi) has an atomic ratio of nitrogen to phosphorus of 0.5 to 2:1.

26. A composition according to Claim 25 wherein the ratio is about 1:1.

27. A composition according to any one of Claims 2 to 26 wherein (vi) has a mean degree of condensation of from 3 to 30.
28. A composition according to Claim 2 which contains less than 10% by weight of (vi).

29. A composition according to Claim 28 which contains 4 to 6% by weight of (vi).

30. A composition according to any one of Claims 2 to 29 wherein (vii) is urea.

31. A composition according to Claim 2 which contains less than 10% by weight of (vii).

32. A composition according to Claim 31 which contains 4 to 6% by weight of (vii).

33. A composition according to any one of Claims 2 to 32 wherein the weight proportion of (vi) to (vii) is from 0.5 to 300% by weight.

34. A composition according to Claim 33 wherein said proportion is from 75 to 125%.

35. A composition according to Claim 1 wherein (i), (ii), (iii) and (iv) are in weight proportions of 20-28 : 0.01-5 : 14-30 : 50-60.

36. A composition according to Claim 2 wherein (i), (ii), (iii), (iv), (v), (vi) and (vii) are in weight proportions of 15-30 : 0.01-5 : 15-30 : 40-51 : 0.1-5 : 2-8 : 2-8.

37. A method of flame retarding a fabric which comprises impregnating the fabric with a composition according to any of Claims 1 to 36 and then heat curing the impregnated fabric.

38. A method according to Claim 37 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.
39. A method according to Claim 38 wherein the application and imposition of shear are carried out in a single combined step.

40. A method according to Claim 39 wherein the single step is carried out by using a knife applicator.

41. A method according to any one of Claims 37 to 40 wherein the fabric comprises cellulosic and non-cellulosic components.

42. A method according to Claim 41 wherein the fabric comprises 40 to 75% by weight of cellulosic material.

43. A method according to any one of Claims 37 to 42 wherein the fabric is a union fabric.

44. A method according to Claim 43 wherein the application rate is from 80 to 120% by weight.

45. A method according to any one of Claims 37 to 43 wherein the fabric is a differential surface fabric (as hereinbefore defined).

46. A method according to any one of Claims 37 to 43 wherein the fabric is a pile fabric.

47. A method according to Claim 46 wherein the application rate is from 60 to 80% by weight.

48. A method according to any one of Claims 37 to 47 wherein the fabric weight is from 0.05 to 2 kg/m².

49. A method according to any one of Claims 37 to 48 wherein the curing is carried out at 120 to 170°C for 6 to 0.5 minutes.

50. A method according to any one of Claims 37 to 49 wherein the finished fabric has a solids content of 30 to 60% by weight.
51. A method according to any one of Claims 37 to 50 wherein the finished fabric has a phosphorus content of 3 to 10% by weight.

52. A fabric treated by a method according to any one of Claims 37 to 51.

53. A composition for flame retarding fabrics substantially as hereinbefore described with reference to any one of Examples 1 to 16.

54. A method for flame retarding fabrics substantially as hereinbefore described with reference to any one of Examples 1 to 16.

DATED this 27th day of May 1991.

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ABSTRACT

An aqueous composition comprising an insoluble ammonium polyphosphate, an anti-foaming agent and a heat curable resin, which may also contain a surfactant, 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.
ABSTRACT

An aqueous composition comprising an insoluble ammonium polyphosphate, an anti-foaming agent and a heat curable resin, which may also contain a surfactant, a soluble ammonium polyphosphate and/or a carbamic acid derivative, forms a sheearable 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.