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3,695,925

PROCESS FOR FLAMEPROOFING TEXTILES

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15 Claims

ABSTRACT OF THE DISCLOSURE

The present invention provides a process for flameproofing textiles which comprises passing a textile through an aqueous padding solution containing at least one vinylphosphonate monomer and at least one nitrogen containing derivative of acrylic or methacrylic acid, and curing said monomer and acrylic acid derivative on said textile, and thereby rendering the textile flame retardant.

This invention relates to a flame retardant textile finish. More particularly, this invention relates to a process for flameproofing textiles which comprises passing the textile through an aqueous solution containing a vinylphosphonate monomer and a nitrogen containing derivative of acrylic or methacrylic acid, and then curing the monomer and nitrogen containing derivative on the textile, to render the textile flame retardant.

By a textile is meant hereinafter a fabric, filament, staple, or yarn, or products made therefrom.

The flameproofing of textiles is of importance for improvement of the fire safety characteristics of apparel, bedding, protective clothing, tentcloth, carpets, home furnishings, aircraft and automobile interior fabrics, and industrial fabrics, which may be woven, knitted, tufted, and non-woven.

There are various methods known for flameproofing textiles, which include the application of chlorinated paraffins with antimony oxide or tris(dibromopropyl)phosphate plus a resinous binder. Such procedures generally have the disadvantage of requiring the addition of a large amount of solids with a resulting deleterious effect in the quality of the fabric and, furthermore, the resulting finishes are quite limited in their durability to laundering and dry cleaning. There have been finishes designed that are especially durable for cotton. For example, those based on tetrakis(hydroxymethyl)phosphonium chloride or on phosphonated N-methylamides, but these are of little value with other fabrics. Furthermore, they generally require high temperature, acid catalyzed curing conditions which are deleterious to cellulosic fibers and are found ineffectual on synthetic fibers such as polyesters or polypropylene.

In addition, it has been known to use bis(2-chloroethyl)vinylphosphonate alone as a flame retardant for flameproofing cellulosics. However, this compound is soluble and can readily be lost in the solution in which a fabric or textile is treated, or in subsequent laundering or dry cleaning.

It is therefore a very important object of the present invention to make available flame retardant finishes which can be used on all natural and synthetic textiles.

It is a further object to make available textile finishes which are durable to washing and dry cleaning.

Still another object of the present invention is to make available textile finishes which are curable under very

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mild conditions without excessive heating and without the need for acid catalysts.

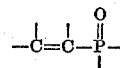
According to the present invention, there is provided a process for flameproofing all textiles with a finish which can be cured with a minimum of heat and which is durable when the textile is washed or dry cleaned.

The present flameproofing process comprises passing a textile through an aqueous padding solution containing a vinylphosphonate monomer and a nitrogen containing derivative of acrylic or methacrylic acid. Then, the solution is optionally dried and the monomer and nitrogen containing derivative are cured on the textile. According to the present invention, the solution mixture of the vinylphosphonate monomer and acrylic acid derivative may be cured on the textile either by a mild heating means, such as with steam, and preferably with a free radical catalyst present, or by means of radiation.

There are various vinylphosphonate monomers that may be used according to the present invention which include bis(2-chloroethyl)vinylphosphonate, diethylvinylphosphonate, dimethyl butadiene-1-phosphonate, tetramethyl butadiene-2,3-diphosphonate, tetramethylvinylidenediphosphonate, and the like. Suitable nitrogen derivatives of acrylic acid include acrylamide, acrylonitrile, N-methylolacrylamide, N-(alkoxymethyl)acrylamide, alpha-chloroacrylonitrile, and alpha-chloroacrylamide. The suitable nitrogen derivatives of methacrylic acid include methacrylonitrile, N-(alkoxymethyl)methacrylamide, methacrylamide, and N-methylolacrylamide.

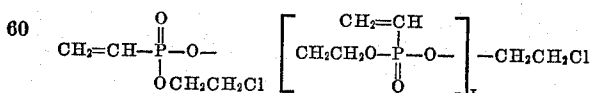
The padding bath, or aqueous solution, through which the textile is passed contains at least one vinylphosphonate monomer and at least one nitrogen containing derivative of acrylic or methacrylic acid, together with a wetting agent and water. In addition, to assist or aid the curing and polymerization of the monomers on the textile, a catalyst is preferably added to the bath solution, such as ammonium persulfate, although the catalyst may be omitted if radiation curing is used.

The vinylphosphonate monomers that may be used according to the present invention contain the linkage:



wherein the remaining valences of the carbon (C) atoms are substituted by hydrogen, methyl, vinyl, dialkylphosphono, or phosphonovinyl and the remaining valences on the phosphorus atom are substituted by alkoxy, haloalkoxy, hydroxyalkoxy, aryloxy, haloaryloxy, amino, alkyl-substituted amino, phenylamino or, where one or both of the valences on the phosphorus atom are substituted with a glycol residue, e.g. $-\text{OCH}_2\text{CH}_2-\text{O}-$, the other terminus of said glycol residue will be attached to a similar vinylphosphonate or both termini of the glycol residue are attached to the same phosphonate phosphorus atom thereby forming a ring.

The polycondensed vinylphosphonate that may be used in the role of vinylphosphonate monomer has the structure:

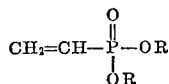


where x is an integer of 1 to 20. This is a preferred vinylphosphonate because of its water solubility, low volatility, and ability to give a very high level of durability.

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The polycondensed vinylphosphonate monomer can be prepared according to the process described in co-pending U.S. application, Ser. No. 828,781, filed May 29, 1969, now Patent No. 3,641,202. In that process, the monomer is prepared by reacting bis(2-chloroethyl) vinylphosphonate in the presence of a basic alkali metal or alkaline earth metal compound such as sodium carbonate, potassium carbonate, lithium carbonate, or the corresponding bicarbonate, calcium hydroxide and the like at a temperature of from about 140° C. to about 250° C. and removing the ethylene dichloride formed. The condensation can be stopped when the amount of ethylene dichloride liberated corresponds to the desired degree of condensation.

In addition, there can also be used as the vinylphosphonate monomer, dialkyl vinylphosphonates of the structure:



wherein each R is an alkyl radical or a halogen-substituted alkyl radical having from 1 to about 5 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, pentyl, 2-chloroethyl, 2,2,2-trichloroethyl, 2-bromoethyl, 2-fluoroethyl, 2-iodoethyl, 2,3-dibromopropyl, and the like. As examples of suitable dialkyl vinylphosphonates, one can mention dimethyl vinylphosphonate, diethyl vinylphosphonate, dipropyl vinylphosphonate, diisopropyl vinylphosphonate, dipentyl vinylphosphonate, bis(2-bromoethyl) vinylphosphonate, bis(2-chloroethyl) vinylphosphonate, bis(2,2,2-trichloroethyl) vinylphosphonate, bis(2,3-dibromopropyl) vinylphosphonate, bis(2,3-dichloropropyl) vinylphosphonate, bis(2-hydroxyethyl) vinylphosphonate, and the like.

The preferred nitrogen containing derivatives are the water soluble amides, particularly acrylamide, methacrylamide, N-methylolacrylamide, N-methylolmethacrylamide, N-(lower-alkoxymethyl)acrylamide and N-(lower-alkoxymethyl) methacrylamide.

The use of the vinylphosphonate monomers and the acrylic and methacrylic acid derivatives provides a textile finish which can be rapidly cured under mild conditions to a stable insoluble copolymer and therefore highly durable finish, i.e. durable to both laundering and dry cleaning.

The catalysts that may be optionally included in the padding bath in addition to the vinylphosphonate monomer and the acrylic or methacrylic acid derivative include such free radical generating materials as ammonium persulfate, potassium persulfate, sodium persulfate, sodium perborate, hydrogen peroxide, acetyl peroxide, peracetic acid, benzoyl peroxide, lauroyl peroxide, t-butylhydroperoxide, acetone peroxide, methylethylketone peroxide, t-butyl perbenzoate, azobisisobutyronitrile, azobisisovaleronitrile, and the like.

Where especially fast catalysis is desired, a reducing component such as a bisulfite, ascorbic acid, a ferrous salt, or the like may be added to the peroxygen compounds listed above. To avoid unduly short life of the aqueous padding bath, the oxidizing and reducing components may be added in separate padding operations.

It is not required in the method of this invention to use catalysts which may be deleterious to the textile being flameproofed.

A third monomer may optionally be present to modify the "hand" or other physical properties of the finish, to provide sites of attachment for dyes or durable press finishes, or impart soil release properties. Suitable termonomers of this sort include acrylic acid, methacrylic acid, alkyl acrylates or alkyl methacrylates, especially having alkyl of 1 to 8 carbon atoms, glycol acrylates or glycol methacrylates, vinylphosphoric acid, mono-2-chloroethylvinylphosphonate, and other lower alkyl acid vinylphosphonates, or vinyl lower-alkyl ethers. When a third monomer of this sort is present, it should comprise less than

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50% of the monomer content by weight, so as not to dilute unduly the flame retardant properties of the finish. The preferred monomers are those which are water-soluble and relatively low in volatility, namely the acid monomers named above and the glycol esters.

The presence of amide and/or carboxyl groups in the polymeric finishes of the invention makes it also possible to attach thereto various aminoplastic-forming reactants of the types well known in the textile art, such as melamine/formaldehyde condensates (e.g., trimethylolmelamine), ureaformaldehyde condensates, glyoxal-formaldehyde-urea condensates (e.g., dimethyloldihydroxyethyleneurea), N-hydroxymethyl dimethoxyphosphonopropionamide and methylolphosphines such as tetrakis (hydroxymethyl) phosphonium chloride or hydroxide. If such aminoplastic-forming reactants are to be attached, it may be advantageous to include in the formulation acidic or latent acidic catalysts such as ammonium chloride, zinc nitrate, magnesium chloride, oxalic acid, amine hydrochlorides, or phosphoric acid.

The finishing formulations of the invention may optionally contain other ingredients of the types per se known in the textile finishing art, for example, water and soil repellents, optical brighteners and colorants, softening agents (e.g., polyethylene emulsions), hand-modifying agents, buffering agents, and pH-controlling agents which may be acids or bases. Emulsified waxes, chlorowaxes, (chlorinated paraffins), polyvinyl chloride, polyvinylidene chloride, and other resinous finishing agents may be added in conjunction with the finishing agents of the invention. In cases where extremely high flame retardancy is required, it is possible to employ antimony oxide plus a resinous binder particularly a chlorine containing one such as chlorowax or polyvinyl chloride, along with the finishing system of the invention.

The amount of vinylphosphonate monomer to be used depends greatly on the nature of the textile and its weight and weave, the degree of flameproofing required and other technical and economical factors well understood by those skilled in the art of textile finishing. However, generally, the vinylphosphonate should be added to the padding solution in a sufficient amount so that about 0.2 to 8.0% phosphorus remains on the cloth or textile being treated, and preferably 0.4 to 4.0% phosphorus. Therefore, the amount of vinylphosphonate monomer added to the padding bath is greatly dependent upon the product desired, i.e. the amount of flame retardance of the flameproofed textile.

The amount of nitrogen derivative of acrylic or methacrylic acid to be used also depends upon the nature of the fabric, its weight and weave, and degree of flameproofing required. It has been found that the best results are obtained when the acrylic or methacrylic acid nitrogen derivatives and the vinylphosphonate monomer are present in an atomic ratio ranging from about 1:10 to about 10:1, and preferably in an atomic ratio ranging from about 1:5 to 5:1.

A catalyst such as ammonium persulfate may be added only in nominal amounts such as from about 0.1 to about 2.5% of the weight of the aqueous padding bath. As indicated, the finishing agents of the present invention can be applied by several means such as the use of the padding bath which is most useful in a continuous process where the textile is run through a mill. The textile may also be treated or finished with a flame retardant material by spraying or by any other technique which assures an even and complete distribution of the finishing solution on the textile. However, it is preferred to use the padding bath since it is most efficient in a continuous process.

According to the present invention, the textile is passed through the aqueous padding solution so as to have the monomers absorbed or coated thereon.

After the fabric has passed through the aqueous padding solution, the solution is dried on the fabric, and

the monomer and nitrogen containing derivative are cured so as to effect the polymerization of them with one another in situ on the textile to render it flame retardant. One method of drying and curing the flameproofing finish on the fabric is by heating the fabric with either steam or with hot gases. When using steam or another form of heat, it is preferable to have it at a temperature ranging from ambient to about 200° C., and preferably from about 70° to about 170° C. The monomers may be cured in a short period of time, in as little time as one-second, and as much as several days, or one week, depending upon the temperature and catalyst chosen. By using particular catalysts, such as oxidation-reduction systems described below, the curing of the monomers may be accomplished at room temperature within a short time.

The temperature at which the monomers are heated, and the particular catalyst added to the monomer will largely determine the period of time in which the finish will be cured.

Accordingly, depending upon which catalyst is used, the finish will be cured in a shorter time when subjected to the higher temperatures, such as from about 150° to about 200° C.

Generally, the rate of cure is adversely influenced by the presence of atmospheric oxygen, therefore, for optimum cure rate it is advantageous to exclude oxygen by use of an inert gas which can be steam, nitrogen, carbon dioxide, or the like. A particularly convenient way to accomplish this is to conduct the final drying of the finish at the cure temperature so that the steam being evolved forms an air-excluding blanket. In the textile mill this is easily accomplished by passing the cloth from the padder over heated "cans" at such a rate and temperature as to initiate curing while some moisture still remains.

Another suitable method, according to the present invention, of drying the solution on the textile and curing the finish on the textile is by radiation. With radiation, there is no need of using heat or a catalyst, either of which may be detrimental or destructive to the textile and the cure rate is relatively insensitive to the presence of oxygen. The radiation curing may be effected with beta rays, gamma rays, X-rays, ultra-violet rays, or by a corona discharge (cold plasma). It has been found that by the use of such radiation the finish, in addition to being flame retardant, will be tightly cured so as to provide it with greater durability to laundering and dry cleaning.

Another advantage of radiation curing is that it can be conducted without heating, and with great rapidity (i.e., from about 0.1 second to several minutes). A further advantage of radiation curing is that since catalysts and heating are not required, the fabric is generally found not to have undergone any degradation of its physical properties such as color, tear strength, and abrasion resistance.

Although it is possible to cure a finish without the use of a catalyst, i.e. thermally at a relatively high temperature, it is preferred to cure the finish by using a catalyst and/or by subjecting the finish to radiation.

The flame retardant textile provided by the process of the present invention comprises a fabric having a copolymer of at least one vinylphosphonate monomer and at least one nitrogen containing derivative of acrylic or methacrylic acid absorbed throughout or present on at least one surface of the fabric.

The textile after being treated with the flameproofing finish of this invention, may be tested for its flame retardant qualities. In the standard tests, the textile is placed at various positions ranging from vertical to horizontal and a flame is ignited on its bottom edge. If the textile is self-extinguishing in the vertical position, it is acceptable for stringent applications. If the textile is self-extinguishing when positioned at a 45° angle, it is acceptable for most applications. However, if a textile is only self-extinguishing when in a horizontal position, the finish is only acceptable for use in non-critical applications.

The flameproofing finish according to the present invention, may be effectively applied to various types of textiles including acetate rayon, viscose rayon, cuprammonium rayon, jute, linen, cotton, nylon, polyesters such as polyethylene terephthalate, polypropylene, acrylics, modacrylics, fiberglass containing flammable binders, and blends of more than one fiber, such as cotton-polyester blends (20% or more of cotton), cotton-nylon blends, and viscose-rayon polyester blends.

The application of the finishing reagent of the invention is not limited to woven or knitted fabrics but may also be employed on the broad class of fabrics known as non-woven fabrics which consist of continuous or discontinuous fibers bonded to form a fabric by mechanical entanglement, thermal interfiber bonding, or by use of adhesive or bonding substances. Such non-woven fabrics may contain a certain percentage of wood pulp as well as conventional fibers in which case part of the bonding is by hydrogen bonding between the cellulosic pulp fibers. In non-woven fabrics, the finishing agents of the invention can serve not only as flame retardant finishes but can contribute interfiber bonding and can serve as all or part of the adhesive or bonding resin. The same double role can be played by the finishing agents of the invention in fabric laminates where the finishing agent can at the same time serve as the interlaminar bonding agent and as the flame retardant. In both such systems, i.e. non-woven fabrics and laminated fabrics, the finishing agent of the invention can also be blended with the more customary bonding agents such as acrylic emulsion polymers, polyvinyl acetate emulsion, styrene-butadiene rubber emulsion, urethane resin emulsion, polyvinylchloride emulsion, polyvinylchlorideacrylate emulsions, polyacrylates modified by vinylcarboxylic acid comonomer, and the like.

The following examples will further show the advantages and various embodiments of the present invention.

EXAMPLE 1

Polycondensed bis(2-chloroethyl) vinylphosphonate plus acrylamide

Solutions were prepared consisting of 40 grams of acrylamide, 20 grams polycondensed bis(2-chloroethyl) vinylphosphonate (average degree of condensation 4), 40 grams of water, and 0.3 gram of ammonium persulfate. Cotton swatches were passed through this bath and steam cured at 100° C. The resultant finish contained 1.2 percent phosphorus after being washed in hot water. An accelerated laundering test, considered by the U.S. Department of Agriculture to be representative of 40 ordinary home launderings, lowered the percent of phosphorus only to 0.62 percent and at this level the cloth was still self-extinguishing in the horizontal position.

EXAMPLE 2

In the manner of Example 1, solutions were made containing the following ingredients (percent by weight):

	A	B	C	D	E	F
Polycondensed bis(2-chloroethyl) vinylphosphonate	20	30	40	20	30	40
Acrylamide	0	0	0	15	22.5	30
Ammonium persulfate	0.5	0.5	0.5	0.5	0.5	9.5
Triton X100 (wetting agent)	0.05	0.05	0.05	0.05	0.05	0.05
Water	80	70	60	65	47.5	30

Swatches of polyethylene terephthalate, acetate rayon, cotton, nylon, and polypropylene were passed through these solutions, then dried and cured at 100° C. for one hour. The advantage of the acrylamide copolymer was demonstrated by carrying out sufficient laundering of the acetate rayon to lower the percent of phosphorus to 0.86. In the case of the finish containing acrylamide, the cloth was self-extinguishing in the 45° position at this phosphorus level while in the corresponding finish without acrylamide, the cloth at 0.86% phosphorus was not self-extinguishing even in the horizontal position.

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On acetate rayon the finish obtained from solution D after hot water washing had 0.64% P; from solution E the washed finish had 0.74% P; from solution F the washed finish had 0.9% P; in all cases the fabric was self-extinguishing in the 45° position. From solutions A, B, and C, similar phosphorus add-ons of similar durability were obtained but the fabric was not self-extinguishing even in the horizontal position. In the case of polypropylene, the presence of the acrylamide also aided durability; the washed polypropylene from solution C had 0.4% P and was not self-extinguishing in the horizontal position whereas from solution F it had 0.8% P and was self-extinguishing in the 45° position.

Nylon treated with solution E had 0.7% P after washing and was self-extinguishing in the 45° position whereas nylon treated with solution C (which had a higher percent P in the treating bath) had only 0.3% P and was not self-extinguishing.

EXAMPLE 3

Bis(2-chloroethyl) vinylphosphonate and N-methylolacrylamide

A solution of 20 grams of bis(2-chloroethyl) vinylphosphonate, 24 grams of N-methylolacrylamide, 36 cc. of water, and 15 cc. of isopropanol was padded onto 8 oz. cotton twill. Then the cotton twill was dried at ambient temperature. The finish was cured by an electron beam irradiation (4 megarads). The treated cotton cloth was then laundered at an accelerated rate for one hour in boiling water with 0.5% soap and 0.2% soda-ash solution. The treated cotton was self-extinguishing before and after the laundering in the 45° position.

EXAMPLE 4

Diethyl vinylphosphonate and N-methylolacrylamide

An experiment similar to Example 2 was conducted using 8.7 parts by weight of diethyl vinylphosphonate, 16 parts N-methylolacrylamide, and 19 parts of water. After being cured with 2 megarads of 0.3 mv. electron beam radiation, the cloth was found to be durably self-extinguishing in the 45° position.

EXAMPLE 5

Polycondensed bis(2-chloroethyl) vinylphosphonate and N-methylolacrylamide

A solution of 20 grams of polycondensed bis(2-chloroethyl) vinylphosphonate (degree of condensation 4), 18 grams of N-methylolacrylamide, 62 grams of water, and 0.6 gram of ammonium persulfate was padded onto cotton cloth to obtain a dry add-on of 23 percent. The finish was dried and cured by heating for one hour at 100° C. The resultant finish had 1.60 percent phosphorus after hot water washing and 0.9 percent after the accelerated laundering. The cotton cloth was still self-extinguishing, after laundering in the 45° position.

Without the N-methylolacrylamide component, the finish was similarly durable but the laundered cloth was not self-extinguishing even in the horizontal position.

EXAMPLE 6

Dimethyl butadienyl-1-phosphonate and N-methylolacrylamide

A solution of 5.6 parts of dimethyl butadienyl-1-phosphonate, 6 parts of N-methylolacrylamide, 13.4 parts of water and 0.3 part of ammonium persulfate was heated with steam until trace gelation began. It was then filtered and to the filtrate, 0.2 part of zinc nitrate was added. The solution was padded onto cotton cloth. The original phosphorus analysis before laundering was 1.65 percent and after the accelerated laundering test of 3 hours in boiling water with 0.5 percent soap and 0.2 percent soda ash, the phosphorus content was 1.45 percent. With this

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phosphorus content, the cotton cloth was very slow-burning.

EXAMPLE 7

A padding bath was prepared containing 30% polycondensed bis-2-chloroethyl vinylphosphonate (average degree of condensation of 4) 22.5% acrylamide, and 47.5% water. Swatches of cotton, Dacron polyester (polyethylene terephthalate), and polypropylene were padded therein and dried at ambient temperature then cured by rapid passage (about 2 sec.) through a 0.3 mv. electron beam to expose them to 5 megarads of beta radiation. The cloths were then washed in hot water and laundered thereafter in a 0.2% soda (sodium carbonate)=0.5% soap solution (3 hr. boil). The durability of the finish was determined by phosphorus analysis and by measurement, on the laundered cloth, of the limiting oxygen index (LOI). This is a recognized test for fabric flammability in which is measured the minimum percent oxygen in an O₂-N₂ mixture required to permit burning of the fabric from the top downward. An LOI of 21 or above represents self-extinguishment in air of a vertical fabric ignited from the top, and a figure of 25 or better correlates with fabric capable of passing the usual 45° angle test of the AATCC. Higher LOI figures represent a very high order of flame retardance. Results are as follows:

Fabric	Percent			LOI after soap-soda
	Phosphorous before wash	Phosphorous after wash	Phosphorous after soap-soda	
Cotton.....	3.80	2.90	2.36	28.4
Polyester.....	2.16	1.50	1.40	22.0
Polypropylene.....	2.38	2.12	1.86	25.0

In a similar manner, a cotton-polyester fabric, a nylon fabric, and an acrylic fabric (i.e., polyacrylonitrile modified by a vinyl comonomer) were found to be durably flame retardant.

A similar treatment of cotton with the acrylamide omitted, gave a finish which at 2.4% phosphorus had a limiting oxygen index (LOI) of only 25.2.

EXAMPLE 8

Two padding baths were prepared having the following compositions (percent by weight):

	Bath #1	Bath #2
Polycondensed bis-2-chloroethyl vinylphosphonate.....	30	30
Acrylamide.....	22.5	22.5
Triton X100 (wetting agent).....	0.1	0.1
Potassium persulfate.....	2	2
Urea (buffer).....	10	10
Sodium bicarbonate (buffer).....	35.4	35.4
Water.....		

A cotton fabric and a polyester (polyethylene terephthalate) fabric were padded therein, partially dried at ambient temperature, and then pressed in a steam press for 3 minutes at 330° F. (surface temperature of press). The cured fabrics were then washed 1 hr. in hot water and then subjected to accelerated laundering by 3 hours of boiling in a 0.2% Na₂CO₃=0.5% soap solution. The durability of the finish was shown by phosphorus analysis, and the flame retardancy by the LOI determination.

Fabric	Bath No.	Percent			LOI
		Phosphorus before wash	Phosphorus after wash	Phosphorus after soap-soda	
Cotton.....	1	2.7	2.2	2.1	31.75
Polyester.....	1	3.3	3.3	2.5	22.41
Cotton.....	2	2.9	2.9	2.3	31.90
Polyester.....	2	3.6	3.6	3.4	22.83

EXAMPLES 9 THRU 13

Five different types of fabrics were treated with different flameproofing finishes according to the present in-

vention. The fabrics, the finishes used, and the results of the flame retardant test on the treated fabrics are recorded in the following table.

Example	Fabric	Composition of padding bath (percent by wt.)	Curing catalyst	Curing temp.	Result
9.....	Viscose-rayon.	Diethyl vinylphosphonate (20); acrylamide (10)	2.0 % (NH ₄) ₂ S ₂ O ₈ .	100° (Steam).	Self-extinguishing after laundering.
10.....	Polypropylene.	Tetraethyl butadiene-2,3-diphosphonate (20); Acrylamide (10).	0.2% benzoyl peroxide.	95° (N ₂ atmosphere).	Do.
11.....	Cotton-dacron blend.	Ethyl vinylphosphonate (20); Ethyl acrylate (5); Acrylamide (10).	Beta radiation, 4 megarads.	25° C.	Self-extinguishing after laundering; dimensionally stable to laundering.
12.....	Rayon non-woven fabric.	Bis-(2-chloroethyl) vinylphosphonate (20); Acrylonitrile (10); Acrylic acid (2).	Ultra violet radiation (mercury vapor lamp).	25° C.	Self-extinguishing after laundering.
13.....	Cotton-dacron blend.	Polycondensed bis (2-chloroethyl) vinylphosphonate (15); N-methylolacrylamide (10); Trimethylolmelamine (10); Dimethyloluron (5); Urea (2).	2.0% (NH ₄) ₂ S ₂ O ₈ , 0.1% ZnCl ₂ .	90-100° then 150°.	Do.

What is claimed is:

1. A process for durably flameproofing textiles, which comprises:

(a) applying an aqueous solution containing at least one vinylphosphonate monomer and at least one nitrogen containing derivative of acrylic or methacrylic acid to a textile; and

(b) curing the monomer and the nitrogen containing derivatives on said textile so as to effect the polymerization of said monomer and said nitrogen containing derivative with one another in situ on said textile so as to yield a stable, insoluble, flame retardant copolymer finish which is resistant to laundering and dry cleaning and which is absorbed throughout or present on at least one surface of said textile so as to render the textile flame retardant.

2. A process according to claim 1, wherein said monomer and said nitrogen containing derivative are cured on said textile at a temperature ranging from ambient to about 200° C. for a period of about one second to about one week.

3. A process according to claim 1, wherein the vinylphosphonate monomer is selected from the group consisting of bis(2-chloroethyl) vinylphosphonate, the condensation polymers of bis(2-chloroethyl) vinylphosphonate, diethyl vinylphosphonate, tetramethyl butadiene-2,3-diphosphonate, and mixtures thereof.

4. A process according to claim 1, wherein the textile is selected from the group consisting of rayon, wool, cotton, nylon, polyester, polypropylene, acrylic, modacrylics, cotton-polyester blends, cotton-nylon blends, and viscose-polyester blends.

5. A process according to claim 1, wherein the textile is a cotton-polyester blend of at least 20% cotton.

6. A process according to claim 1, wherein the nitrogen containing derivative of acrylic or methacrylic acid is selected from the group consisting of acrylamide, N-methylol acrylamide, acrylonitrile, methacrylonitrile, methacrylamide, alpha-chloroacrylamide, N-methacrylamide, N-(alkoxymethyl) methacrylamide, N-(alkoxymethyl) acrylamide, and alpha-chloro acrylonitrile.

7. A process according to claim 1, wherein the vinylphosphonate monomer is present in a sufficient amount to result in the application of from about 0.8 to about 8% phosphorus on said textile.

8. A process according to claim 1, wherein the nitrogen containing derivative of acrylic or methacrylic acid is present with respect to the vinylphosphonate monomer, in said solution in an atomic ratio ranging from about 1:10 to about 10:1.

9. A process according to claim 1, wherein said monomer and nitrogen containing derivative are cured on said textile at a temperature ranging from about 70° to about 170° C.

10. A process according to claim 1, wherein the monomer and nitrogen containing derivative are cured on said textile by means of radiation.

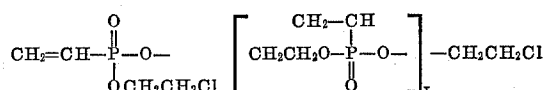
11. A process according to claim 10, wherein the radiation is carried out by means of beta rays, gamma rays, X-rays, ultra-violet rays, or a corona discharge.

12. A flame retardant textile comprising a fabric of rayon, wool, cotton, nylon, polyester, polypropylene, acrylic, modacrylics, cotton-polyester blends, cotton-nylon blends or viscose-polyester blends having a stable, insoluble flame retardant copolymer of at least one vinylphosphonate monomer and at least one nitrogen containing derivative of acrylic or methacrylic acid which is resistant to laundering and dry cleaning absorbed throughout or present on at least one surface of said fabric, with the proviso that at least one of the vinylphosphonate monomers is a condensation polymer of bis(2-chloroethyl) vinylphosphonate.

13. A textile according to claim 12, wherein the nitrogen containing derivative of acrylic or methacrylic acid is selected from the group consisting of acrylamide, N-methylol acrylamide, acrylonitrile, methacrylonitrile, methacrylamide, alpha-chloroacrylamide, N-methacrylamide, N-(alkoxymethyl) methacrylamide, N-(alkoxymethyl) acrylamide, and alphachloroacrylonitrile.

14. A textile according to claim 12, wherein the fabric is a cotton-polyester blend of at least 20% cotton.

15. A textile according to claim 12, wherein the vinylphosphonate monomer is a polycondensed vinylphosphonate having the structure:



wherein x is an integer of 1 to 20.

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CERTIFICATE OF CORRECTIONPatent No. 3,695,925Dated Oct. 3, 1972Inventor(s) Edward D. Weil

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

OFFICIAL PRINTER'S ERRORS

Column 2, line 29, the word "N-methylolacrylamide" should read -- N-methylolmethacrylamide --; line 36, the word "caotalyst" should read -- catalyst --.

Column 3, line 3, the word "may" should read -- May --.

Column 6, line 18, after the word "conventional" insert -- textile --.

Column 8, line 13, EXAMPLE 7, the words "(sodium carbonate)= 0.5%" should read -- (sodium carbonate) - 0.5% --; line 61, EXAMPLE 8, the formula " $\text{Na}_2\text{CO}_3=0.5\%$ " should read -- Na_2CO_3 - 0.5% --.

Column 9, line 25, Claim 1, the word "derivatives" should read -- derivative --.

Signed and sealed this 10th day of April 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
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