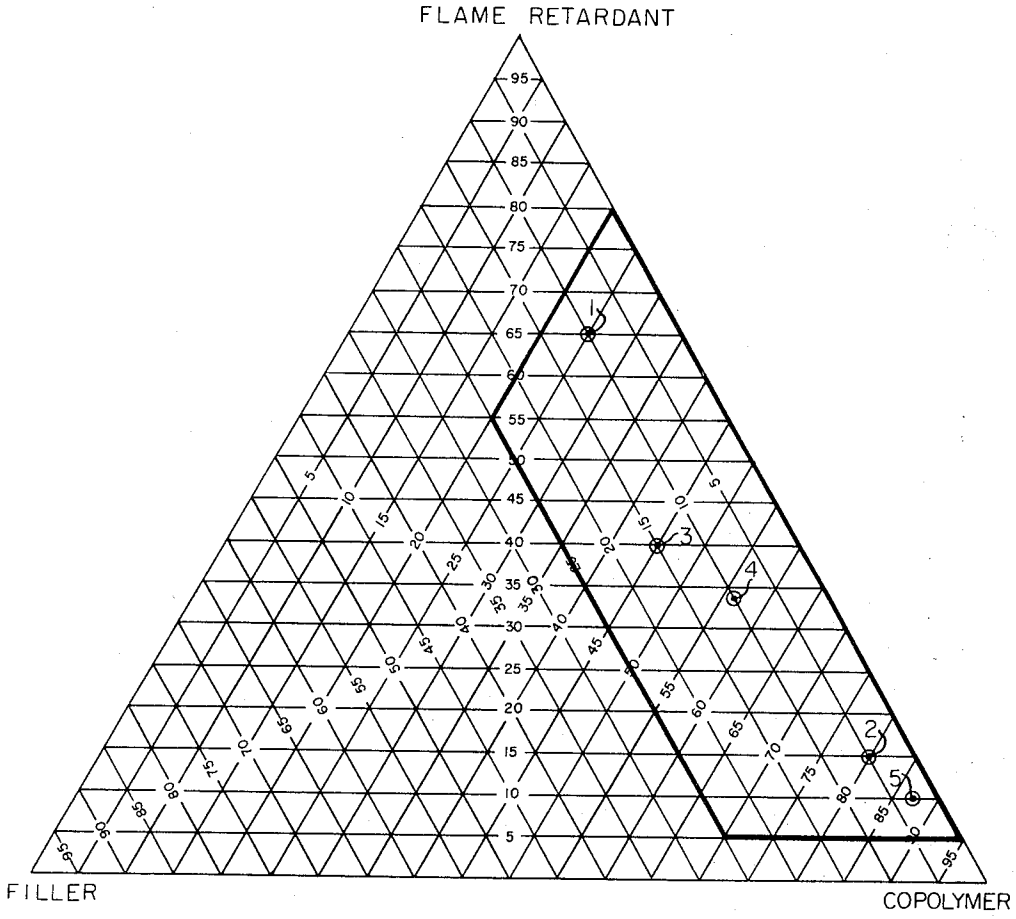
POLYESTER FABRICS COATED WITH ETHYLENE COPOLYMER DISPERSIONS

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POLYESTER FABRICS COATED WITH ETHYLENE COPOLYMER DISPERSIONS

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ABSTRACT OF THE DISCLOSURE

An aqueous dispersion of an ethylene copolymer, a halogenated alkyl phosphate and, optionally, a finely divided particulate matter filler is proxided. The dispersion contains as essential ingredients (1) about 20 to 95 percent by weight of an ethylene copolymer such as ethylene/vinyl acetate copolymer or an ethylene/methacrylate acid ionomer copolymer, (2) 0 to about 25 percent by weight of a filler, and (3) about 5 to 80 percent by weight of a halogenated alkyl phosphate such as tris-(2,3-dibromopropyl) phosphate. Polyester fabrics are rendered rainproof and fire-retardant when coated with particular dispersions.

This is a division of application Ser. No. 11,809, filed Feb. 16, 1970.

BACKGROUND OF THE INVENTION

Field of invention

This invention relates to stable aqueous dispersions of ethylene copolymers and polyester fabrics coated therewith. More particularly, this invention relates to stable aqueous dispersions of ethylene copolymers, finely divided particulate matter fillers and halogenated alkyl phosphates, useful as rainproof and fire-retardant coatings for polyester fabrics.

Prior art

Due to their low weight, high strength and durability, fabrics made from polyester fibers would be ideal candidates for use in tents, tarpaulins and awnings; however, these fabrics uncoated or coated with various materials have never possessed the necessary combined properties of flame-retardancy, rainproofness and breathability.

The common water-resistant mixtures with a paraffin wax base such as those taught in U.S. Pat. 2,015,865 issued to A. Müller on Oct. 1, 1935, U.S. Pat. 2,285,948 issued to J. B. Rust on June 9, 1942, and U.S. Pat. 2,386,631 issued to R. A. Pingree on Oct. 9, 1945, for cotton fabrics may also have utility for fabrics of polyester fibers, but are not at all flame-retardant. Actually, because of the paraffin content such coated fabrics burn more vigorously than do the uncoated fabrics. The flame-retardant auxiliaries such as the oxides of antimony, and the combinations of nitrogen and phosphorous compounds taught in U.S. Pat. 2,520,103 issued to A. M. Loukonsky et al. on Aug. 22, 1950, and U.S. Pat. 2,549,059 issued to J. W. Creely et al. on Apr. 17, 1951, are not satisfactory for polyester fabrics.

Attempts have been made to add fire retardants to water-resistant mixtures such as taught in U.S. Pat. 2,299,662 issued to W. Thaler on Oct. 20, 1942, which teaches mixing insoluble fire-retardant salts or oxides with a chlorinated organic vehicle. However, the great flammability of the water-resistant mixtures requires such a large amount of flame retardants that the resultant fabric is unsatisfactorily stiff and has insufficient breathability. For the cold nights of autumn and winter when tents are kept quite shut, a high order of breathability (well over 200 g. H_2O vapor permeability per 24 hours per square meter) is required. Those overcoated tents that do not meet this requirement are designed with vents which of course result in loss of heat and higher costs.

SUMMARY OF THE INVENTION

According to the present invention there is provided a stable aqueous dispersion comprising as essential ingredients: (1) about 20 to 95 percent by weight of an ethylene copolymer comprising at least 30 percent by weight ethylene and up to 70 percent by weight of at least one polar monomer, (2) 0 to about 25 percent by weight of a finely divided particulate matter filler and (3) about 5 to 80 percent by weight of a halogenated alkyl phosphate.

There is also provided an article of manufacture which comprises a polyester fabric coated with the dispersed phase of the above dispersion. Such a coating renders the polyester fabric rainproof and flame-retardant.

BRIEF DESCRIPTION OF DRAWING

The drawing is a three-component diagram showing the compositional ranges of the components contained in the dispersions of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The component ranges of dispersions of the present invention are shown in the drawing and are prepared by adding dispersion of the halogenated alkyl phosphate to a dispersion of the ethylene copolymer. The latter dispersion can be prepared by a post-dispersion process such as described in U.S. Pat. 3,296,172 issued to D. L. Funck and V. C. Wolff, Jr. on Jan. 3, 1967, U.S. Pat. 3,347,811 issued to T. C. Bissot on Oct. 17, 1967, and U.S. Patent application Ser. No. 801,741 filed by T. C. Bissot on Feb. 24, 1969. An optional, but highly preferred ingredient, is a finely divided particulate matter filler which can be blended as a dispersion with the ethylene copolymer dispersion and halogenated alkyl phosphate dispersion. When the ingredients are codispersed according to Ser. No. 801,741, conventional surfactants are not needed, but may be desirable; however, when separate dispersions are prepared and then blended, a conventional surfactant having an HLB number greater than 18 is preferred to aid in stabilizing the dispersion. Such surfactants are known to those skilled in the art. The resulting dispersions have a high solids content, on the order of 40 to 70 percent by weight, but are generally diluted down to 15 to 40 percent solids when applied as a coating on fabric. They are storage stable at room temperature and can be coalesced into films by removal of the aqueous medium either at room temperature or at elevated temperatures up to 180° C., as required for maximum strength of the particular film.

The ethylene copolymers useful in the present invention have an ethylene content of at least 30 percent by weight, preferably 60 percent by weight, and up to 70 percent by weight of at least one polar monomer. Among others, examples of monomers having polar characteristics are: vinyl esters of carboxylic acids such as vinyl formate, vinyl acetate, vinyl propionate and vinyl butyrate, unsaturated carboxylic acids such as acrylic acid, methacrylic acid, itaconic acid and maleic acid; acrylates and methacrylates such as methyl methacrylate, ethyl acrylate and isobutyl acrylate; halogenated vinyl compounds such as vinyl chloride and vinylidene chloride, vinyl alcohol (hydrolyzed vinyl acetate); acrylamide, β-dimethyl-aminoethyl methacrylate, β-hydroxyethyl acrylate and other adhesion-promoting monomers having carboxyl, amido, amino or hydroxyl groups.

One particularly preferred copolymer is a copolymer of ethylene and vinyl acetate having at least 60 percent by weight ethylene, 17 to 40 percent by weight vinyl ace-

tate and 0 to 5 percent by weight of an alpha, beta-ethylenically unsaturated carboxylic acid, such as acrylic acid or methacrylic acid. Such copolymers are generally prepared by high-pressure free-radical catalysis processes, but they can also be prepared by low-pressure coordination catalysis processes. Exemplary patents illustrating copolymer preparation are U.S. Pat. 2,703,794 issued to Milton J. Roedel on Mar. 8, 1955 and U.S. Pat. 3,215,657 issued to Aleksander Beresniewicz on Nov. 2, 1965. The molecular weight can be varied over a wide range; however, copolymers having molecular weights corresponding to melt indexes of 1 to 150, particularly under 15, are especially suited for use in this invention. Copolymer melt index is determined as described in ASTM–D–1238–65T.

Another particularly preferred copolymer is a copolymer of ethylene and an alpha, beta-ethylenically unsaturated carboxylic acid having at least 60 percent by weight, preferably 80 percent, ethylene and 0.3 to 40 percent by weight of the acid, preferably 0.3 to 20 percent, about 10 to 100 percent of the acid groups neutralized with alkali metal ions such as Na^+ or K^+. Typical acids are acrylic acid, methacrylic acid, fumaric acid, maleic acid, itaconic acid and aconitic acid. Acid derivatives of the aforesaid, such as esters, amides, anhydrides and the like also can be employed as monomers. While these derivatives must be convertible to a free carboxylic acid group prior to the formation of the dispersion, it is not necessary that all such derivatives be converted to free carboxyl groups. Prepartion of these dispersions with neutralization of the acid groups with sodium hydroxide is described in U.S. Pat. 3,296,172. The preferred acid monomer is methacrylic acid. Molecular weight preferences are as described above with reference to the copolymers of ethylene and vinyl acetate.

The halogenated alkyl phosphates useful in the present invention have 2 to 18 carbon atoms in the alkyl group with the halogen no more than 5 carbon atoms away from the phosphorus atom. Preferred materials are the chloro and bromo alkyl phosphates where in the alkyl group contains from 2 to 5 carbon atoms. A particularly preferred compound due to its commercial availability in dispersion form is tris-(2,3-dibromopropyl) phosphate.

While finely divided particulate matter fillers are particularly preferred in the dispersions of the present invention, to aid in fabric breathability, and the polyester coatings formed therefrom, they are not essential. When used, the following fillers can be employed and it is preferred that a majority of the particles be under about 2 microns so as to be stable in the dispersion. Tyical fillers are various types of clays such as the more or less impure hydrated aluminum silicates or clays upgraded by beneficiation procedures. Also, other mineral silicates can be used as fillers. Other useful fillers are metal oxides such as titanium oxide, zinc oxide, bismuth oxide and antimony trioxide; metal carbonates such as calcium carbonate; metal phosphates such as zinc phosphate; and metal borates such as zinc borate and magnesium borate. The fillers can be used by themselves or mixed together with other fillers or inorganic or organic pigments for tinting purposes. The pigments can also be used by themselves as fillers. Typical pigments beside the above titanium dioxide and calcium carbonate are "phthalocyanine green or blue," calcium yellow, chrome yellow, zinc yellow, molybdate red, ferric oxide, indanthrone blues and diazo pigments.

The dispersions of the present invention are especially suited for rendering polyester fabrics rainproof and flame-retardant. Polyester fabrics used can be manufactured from polyethylene terephthalate fibers as well as from fibers of poly 1,4, cyclohexalene dimethylene terephthalate and of polycondensation products with copolyesters structured from members of the group comprising adipic acid, terephthalic acid, hexahydroterephthalic acid, 2,6 - naphthalene dicarboxylic acid and bibenzoic acid. The dispersion is coated on the fabric according to the usual procedures so as to give a coating add-on, based on the weight of fabric, of about 15 to 75 percent, preferably about 20 to 50 percent. The amount of halogenated alkyl phosphate used in the dispersion and the dispersion used depends to a great extent upon the basis weight of the fabric, i.e., if the fabric is less than 5 ounces per square yard, the dispersion preferably contains about 5 to 25 percent of halogenated alkyl phosphate, about 1 to 10 percent filler and about 65 to 90 percent ethylene copolymer whereas for a fabric having a basis weight greater than 5 ounces per square yard, the dispersion preferably contains about 20 to 60 percent halogenated alkyl phosphate, about 1 to 10 percent filler and about 40 to 60 percent ethylene copolymer.

In the examples which follow, the following tests are used to determine fire-retardant properties, rainproofness and fabric breathability:

A. The fire-retardance test is conducted on impregnated and dried samples according to a modified ASTM D–626–55T. The test consists of clamping fabric samples 3.75 inches wide by 12.5 inches high vertically in a shielded chamber, ¾ inch above a Micro Bunsen Burner, and igniting the samples by applying a luminous flame of 1.5 inches in length for 12 seconds at the center of the lower edge of the test sample. After removing the burner, the after-flame and char lengths of the test samples are recorded. Samples having no after-flame are characterized as non-burning while samples having an after-flame of less than 2 seconds are characterized as self-extinguishing. The char-length shall not exceed 4.5 inches.

B. The rainproof test is conducted by flowing water at a rate of 270 inches/hour (1.5 gallons/min.) from a height of 60 inches onto a fabric sample 8 inches by 7.5 inches for 30 minutes and measuring the amount of water passing through the fabric. Fabric that passes less than 100 ml./30 min. is characterized as having satisfactory rainproofness.

C. The TAPPI water vapor permeability test, T–448–M49 is used to test fabric breathability. A small dish, containing water, is tightly covered with the fabric sample; and the loss of weight of this combination, kept at 73° F. and 50 percent R.H. for 24 hours, is recorded. The grams of water vapor lost per 24 hours per square meter of fabric surface is the water vapor permeability of the fabric sample.

D. The water repellency of a coated fabric sample is conducted in accordance with ASTM D–583–63. The test consists of spraying 250 ml. of water through the standardized spray nozzle onto a fabric sample (7″ x 7″), fastened at an angle of 45°, 6 inches below the nozzle. The spray rating is determined by comparing the test specimen with the photographic standards on a Spray Test Rating Chart in the standard.

The invention can be further illustrated by the following examples in which parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

This example will illustrate the use of a system with a high content of flame retardant.

An aqueous dispersion blend was prepared by thoroughly mixing 65 g. of tris-(2,3-dibromopropyl) phosphate, emulsified with the aid of sodium lauryl sulfate anionic surfactant ("Duponol") to a 65% aqueous emulsion, 50 g. of an ethylene/vinyl acetate copolymer dispersion (50% solids) in which the copolymer contains 28% vinyl acetate, and 10 g. of "Calcotone" organic yellow pigment as filler sold by Union Carbide Corp. This blend was diluted with 240 ml. water to a total of 400 g. dispersion containing 25% solids. The dispersion was stable and was used to impregnate 100% polyethylene terephthalate fabric (4.8 ozs./sq. yd.) to an add-on of 30 weight percent. The coating was coalesced at 150° C. for at least 60 seconds. This fabric is non-burning as determined by the fire retardance test ASTM–D–626–55T.

The same results were obtained when 10 g. of "Hydratex" clay or "Ultrawhite" 90 were substituted for the "Calcotone" yellow. "Hydratex" clay is a fine particle size (77 to 80% finer than 2 microns), white, insoluble, nonhygroscopic kaolin containing 44 to 46% silica and 37 to 40% alumina with other oxides in trace amounts. When added to water the clay dispersion has a pH of 4.5 to 5, "Ultrawhite" 90 has 92% of the particles finer than 2 microns and its dispersion has a pH of 6.3 to 7.

EXAMPLE 2

This example will illustrate the use of a system with a high content of ethylene/vinyl acetate copolymer.

An aqueous dispersion blend was prepared by mixing 80 g. of the ethylene/vinyl acetate copolymer dispersion of Example 1, 15 g. tris-(2,3-dibromopropyl) phosphate as a 65% aqueous dispersion, and 5 g. of Clay HT as filler. Clay HT is the same as "Hydratex" except 80% of the particles are finer than 2 microns and a resulting clay dispersion has a pH of 4 to 4.4. This blend formed a stable dispersion having a pH greater than 7. It was used to impregnate the polyester fabric of Example 1 to an add-on of 30% by weight. The coating was coalesced at 150° C. for at least 60 seconds. This fabric is self-extinguishing, having an after-flame of less than 2 seconds, as determined by the ASTM test D–626–55T.

EXAMPLE 3

Using the same technique as described in Example 1, a dispersion blend was prepared by mixing 45 g. of the ethylene/vinyl acetate copolymer in the form of a 50% aqueous dispersion, 40 g. of tris-(2,3-dibromopropyl) phosphate as a 60% aqueous emulsion, and 15 g. of phthalocyanine blue "Monastral" pigment as filler. This blend was shelf-stable for at least two months and can be used to coat polyester fabric.

Formulation A

Following the procedure of Example 1, 100 g. of the ethylene/vinyl acetate copolymer dispersion, 4 g. of "Calcotone" Yellow pigment aqueous dispersion (30% solids) and 10 g. of an aqueous dispersion of tris-(2,3-dibromopropyl) phosphate (45.5% solids) were mixed to form a stable aqueous dispersion in which the solids comprised 89.7% copolymer, 2.1% pigment and 8.2% tris-(2,3-dibromopropyl) phosphate. Two samples 8" x 10" of 100% polyethylene terephthalate fabric having a gray fabric weight of 4.8 and 4.9 ozs./sq. yd. were coated to an add-on of 23% and 35% respectively. The samples were dried at 160° C. for 180 seconds. The coating and test results are shown in Table I. The 4.9 ozs./sq. yd. fabric (uncoated) was one of the controls.

Formulation B

This formulation is the same as Formulation A except a "Monastral" blue pigment dispersion was used as filler and the tris-(2,3 - dibromopropyl) phosphate dispersion contained 60% solids. The resulting stable dispersion solids contained 87.4% copolymer, 2.1% pigment and 10.5% tris-(2,3-dibromopropyl) phosphate. A sample of polyethylene terephthalate fabric 8" by 10" and having a gray weight of 4.9 ozs./sq. yd. was coated to an add-on of 33%. The sample was dried at 160° C. for 180 seconds. The coating and test results are shown in Table I.

Formulation C

This formulation is the same as Formulation A except the fire retardant has been omitted. The solids of the resulting stable dispersion contained 97.7% copolymer and 2.3% pigment. A sample of polyethylene terephthalate fabric 8" by 10" and having a gray weight of 4.8 ozs./sq. yd. was coated to an add-on of 15%. As in Formulations A and B, the sample was dried at 160° C. for 180 seconds. The coating and test results are shown in Table I.

TABLE I.—PIGMENTED ETHYLENE/VINYL ACETATE COPOLYMER DISPERSION WITH FIRE-RETARDANT COATED ON FABRIC 100% OF POLYETHYLENE TEREPHTHALATE

Coating	Gray fabric weight (ozs./sq. yd.)	Coating components, percent of coated fabric				Water vapor perm.[1]	Rain test (ml./30 min.)	Flame time (sec.)	Char length (in.)
		Coating add-on	E/VA copolymer	Fire retardant	Pigment				
A	4.8	23	16.7	1.5	0.4	199	2	0	3.5
A	4.9	35	22.1	2.0	0.5	313	85	0	2.7
B	4.9	33	20.5	2.5	0.5	500		3	3.1
C	4.8	15	12.6		0.3		46		
Controls	4.9	None					Failed	7	3.5
Do	[3] 7.2	11				931	58	[3] 24	12.0

[1] g./24 hrs./sq. m. criteria is 200 g./24 hrs./sq. m.
[2] A commercial cotton tent fabric with paraffin-based waterproofing.
[3] 100% consumed with 182 sec. glow time. Other fabrics had zero glow time.

EXAMPLE 4

This is an example of a dispersion which will impart flame-resistance and water repellence at the same time.

An intimate dispersion was prepared by blending 56 g. of partially neutralized ethylene/methacrylic acid copolymer (89% ethylene, 11% methacrylic acid, 70% neutralized with NaOH) and wax dispersion (15% ethylene ionomer, 85% paraffin wax), 34 g. of tris-(2,3-dibromopropyl) phosphate as a 60% aqueous dispersion and 10 g. of "Monastral" blue pigment. This blend was diluted with water to the total solids content of 10% solids, and was used to impregnate the polyester fabric of Example 1 to an add-on of 25%. After a thorough curing cycle of at least 2 minutes at 165° C., the fabric was found to be flame-resistant as determined by the vertical test described in ASTM D–626–55T and water repellent as determined by the spray test described in ASTM D–583–63.

EXAMPLE 5

Three different formulations were prepared according to the procedure of Example 1. Formulations A and B are illustrative of the invention, while Formulation C does not contain a fire retardant.

What is claimed is:

1. An article of manufacture comprising: a polyester fabric and a coating thereon of the dispersed phase of a dispersion comprising as essential ingredients: (1) about 20 to 95 percent by weight of an ethylene copolymer comprising at least 30 percent by weight ethylene and up to 70 percent by weight of at least one polar monomer selected from the group consisting of vinyl esters of carboxylic acids, unsaturated carboxylic acids, acrylates, methacrylates, halogenated vinyl compounds, and adhesion-promoting monomers having amido, amino or hydroxyl groups, (2) 0 to 25 percent by weight of a finely divided particulate matter filler of clay, metal oxides, metal carbonates, metal phosphates, metal borates, metal silicates, inorganic pigments, organic pigments or mixtures thereof, and (3) about 5 to 80 percent by weight of a halogenated alkyl phosphate having 2 to 18 carbon atoms in the alkyl group with the halogen no more than 5 carbon atoms away from the phosphorus atom.

2. The article of claim 1 wherein the polyester fabric has a basis weight less than 5 ounces per square yard and is coated with the dispersed phase of a dispersion comprising as essential ingredients: (1) about 65 to 90 per-

cent by weight of an ethylene copolymer comprising at least 30 percent by weight ethylene and up to 70 percent by weight of at least one polar monomer selected from the group consisting of vinyl esters of carboxylic acids, unasturated carboxylic acids, acrylates, methacrylates, halogenated vinyl compounds, and adhesion-promoting monomers having amido, amino or hydroxyl groups, (2) 1 to 10 percent by weight of a finely divided particulate matter filler of clay, metal oxides, metal carbonates, metal phosphates, metal borates, metal silicates, inorganic pigments, organic pigments or mixtures thereof, and (3) about 5 to 25 percent by weight of a halogenated alkyl phosphate having 2 to 18 carbon atoms in the alkyl group with the halogen no more than 5 carbon atoms away from the phosphorus atom.

3. The article of claim 1 wherein the polyester fabric has a basis weight of greater than 5 ounces per square yard and is coated with the dispersed phase of a dispersion comprising as essential ingredients: (1) about 40 to 70 percent by weight of an ethylene copolymer comprising at least 30 percent by weight ethylene and up to 70 percent by weight of at least one polar monomer selected from the group consisting of vinyl esters of carboxylic acids, unsaturated carboxylic acids, acrylates, methacrylates, halogenated vinyl compounds, and adhesion-promoting monomers having amido, amino or hydroxyl groups, (2) 1 to 10 percent by weight of a finely divided particulate matter filler of clay, metal oxides, metal carbonates, metal phosphates, metal borates, metal silicates, inorganic pigments, organic pigments or mixtures thereof, and (3) about 20 to 60 percent by weight of a halogenated alkyl phosphate having 2 to 18 carbon atoms in the alkyl group with the halogen no more than 5 carbon atoms away from the phosphorus atom.

4. The article of claim 2 wherein the coating add-on is about 15 to 75 percent by weight, based on the weight of fabric.

5. The article of claim 3 wherein the coating add-on is about 15 to 75 percent by weight, based on the weight of fabric.

6. An article of manufacture comprising a fire-retardant coated polyester fabric having breathability of at least about 200 g. of water vapor per 24 hours per square meter and rainproofness of less than about 100 ml. of water per 30 minutes per 60 square inches comprising a polyester fabric and a coating thereon of the dispersed phase of a dispersion comprising as essential ingredients: (1) about 20 to 95 percent by weight of an ethylene copolymer comprising at least 30 percent by weight ethylene and up to 70 percent by weight of at least one polar monomer selected from the group consisting of vinyl esters of carboxylic acids, unsaturated carboxylic acids, acrylates, methacrylates, halogenated vinyl compounds, and adhesion-promoting monomers having amido, amino or hydroxyl groups, (2) 0 to 25 percent by weight of a finely divided particulate matter filler of clay, metal oxides, metal carbonates, metal phosphates, metal borates, metal silicates, inorganic pigments, organic pigments or mixtures thereof, and (3) about 5 to 80 percent by weight of a halogenated alkyl phosphate having 2 to 18 carbon atoms in the alkyl group with the halogen no more than 5 carbon atoms away from the phosphorus atom.

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