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FLAME-RESISTANT COMPOSITIONS OF ETHYLENE/VINYL CHLORIDE INTERPOLYMERS AND HYDRATED ALUMINA

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ABSTRACT OF THE DISCLOSURE

Flame-resistant compositions comprising ethylene/vinyl chloride interpolymer and finely-divided hydrated alumina.

This is a continuation of the now abandoned application Ser. No. 146,806, filed May 25, 1971.

This invention relates to flame resistant compositions comprising ethylene/vinyl chloride interpolymer and finely-divided hydrated alumina.

The term "nonwoven fibrous material" as used herein means a consolidated mass of fibers laid down by mechanical, chemical, pneumatic, electrical or vacuum means, or otherwise deposited, into the desired shape, either flat (webs, mats or sheets) or three-dimensional. The term "E/VCl/A" as used herein means ethylene/vinyl chloride/acrylamide.

The term "oxygen index" as used herein means the concentration of oxygen in an oxygen/nitrogen atmosphere below which combustion is not supported and above which combustion is supported for a given substance.

The flame resistant compositions of this invention exhibit an improved flame resistance which is totally unexpected from the teachings of the prior art. The use of finely-divided hydrated alumina as a flame resistant agent for various polymers such as styrene/butadiene/itaconic acid is well known to the art. However, the improvement in flame resistance of the S/BR as measured by oxygen index is generally limited to about 100%. The compositions of this invention exhibit an improved flame resistance of 300% or more as compared to the basic E/VCl/A terpolymer.

The ethylene/vinyl chloride interpolymers useful in the preparation of the flame resistant compositions of this invention generally contain about 5 to about 70 weight percent ethylene, about 30 to about 95 weight percent vinyl chloride, and about 0.1 to about 10 weight percent of an additional polar monomer component. The additional polar monomer component can be entirely acrylamide or a portion of the acrylamide can be replaced by one or more polar monomers selected from the group consisting of acrylonitrile, methacrylamide, N-(lower alkyl) acrylamide, N-(lower alkyl) methacrylamide and N-(hydroxy substituted lower alkyl) acrylamide containing from 1 to 3 carbon atoms in the lower alkyl groups, N-[2-(2-methyl-4-oxopentyl)]-acrylamide, acrylic acid, methacrylic acid, and alkali metal and ammonium salts of acrylic and methacrylacrylic acids, maleic acid, fumaric acid, half and complete alkali metal and ammonium salts of maleic and fumaric acid, aconitic acid, itaconic acid, citraconic acid, and alkali metal and ammonium salts thereof, acrylyl and methacrylyl esters of hydroxyalkanoic acids having from 2 to about 6 carbon atoms in the alkanoic acid moieties, acrylylamides and methacrylylamides of aminoalkanoic acids having from 2 to about 6 carbons in the aminoalkanoic acid, hydroxyethyl and hydroxypropyl esters of acrylic, methacrylic, maleic, and fumaric acids, vinyl esters of alkanoic acids having from 1 to 6 carbon atoms such as vinyl acetate, vinyl propionate, and lower alkyl (1 to 6 carbon atoms) sulfonic acid, vinyl esters of phenylsulfonic acids, and alkylphenylsulfonic acids and acrylyl and methacrylyl esters of hydroxyalkylsulfonic acids having from 1 to 6 carbon atoms in said alkyl moieties, and hydroxyalkylsulfonamides having from 1 to 6 carbon atoms in said hydroxyalkyl moieties. The polar monomer component generally contains at least 50 weight percent acrylamide and preferably at least 80 percent acrylamide.

Thus the interpolymers are at least terpolymers containing ethylene, vinyl chloride and acrylamide and may be a quaternary or higher polymer containing one or more of the above exemplified additional polar monomers in small quantities. Generally such additional polar monomers will not be present in the interpolymer in quantities greater than about 3 percent by weight.

It is preferred that the interpolymer contain from about 5 percent to about 70 percent ethylene, 30 percent to about 95 percent vinyl chloride, and from about 1 percent to about 5 percent acrylamide. A specific example of choice is a terpolymer containing from about 19 to about 23 percent ethylene, about 74 to about 78 percent vinyl chloride, and from about 2 to about 4 percent acrylamide.

The interpolymers used in accordance with this invention are generally unmodified, but modified interpolymers are also included for use in this invention. The interpolymers are particularly amenable to hydrolytic modification by the use of small quantities of a strongly alkaline material such as an alkali metal hydroxide, or a quaternary ammonium hydroxide such as tetramethyl ammonium hydroxide, or by a strong acid such as the mineral acids, e.g., hydrochloric, sulfuric, phosphoric, nitric. The base or acid used preferably has an ionization constant higher than 10^{-4} at 25° C.

The hydrolytic modification is carried out by treating an aqueous dispersion or polymer latex or the ethylene, vinyl chloride, and acrylamide with aqueous base or acid in an amount chemically equivalent to from about 0.1% to about 100 percent of the amide equivalent in the interpolymer.

Specific examples of polar monomers which can be used, as described above, to replace part of the acrylamide in the polar monomer component of the interpolymer useful in this invention include acrylonitrile, N-methacrylamide, N-ethylacrylamide, N-propylacrylamide, N-hydroxymethyl acrylamide, methacrylamide, acrylic, methacrylic, maleic, fumaric, itaconic, aconitic, and citraonic acids and alkali metal and ammonium salts of such acids, preferably the sodium, potassium or ammonium salts, alkyl esters of such acids, e.g., methyl acrylate, ethylacrylate, butyl acrylate, methyl methacrylate, butyl methacrylate, ethyl methacrylate, monoethyl maleate, dipropyl fumarate, acrylyl 3-hydroxypropionate, methacrylyl hexamide, 2-hydroxyethyl and 2-hydroxypropyl esters of acrylic, methacrylic, maleic, fumaric, itaconic, aconitic and citraconic acids, vinyl formate, vinyl acetate, vinyl hexanoate, vinyl and alkyl esters of propanesulfonic acid, vinyl phenylsulfonate, acrylyl and methacrylyl esters of 2-hydroxypropylsulfonic acid; and N-acrylyl and N-methacrylyl 2-hydroxypropanamides.

Illustrative of interpolymers which can be used in the bonding agent compositions for the flame retardant, bonded non-woven fibrous products of this invention are:

ethylene/vinyl chloride/acrylamide,
ethylene/vinyl chloride/hydroxyethylacrylate,
ethylene/vinyl chloride/acrylamide/N-isopropylacrylamide,
ethylene/vinyl chloride/acrylamide/N-ethylmethacrylamide,
ethylene/vinyl chloride/acrylamide/diammonium itaconate,

ethylene/vinyl chloride/acrylamide/monobutyl acid maleate,
ethylene/vinyl chloride/acrylamide/N-methacrylylpropionamide,
ethylene/vinyl chloride/acrylamide/N-methylolacrylamide, and
ethylene/vinyl chloride/acrylamide/sodium methacrylate.

In general, the finely-divided hydrated alumina can be used in any size which permits admixture with the ethylene/vinyl chloride interpolymers. In particular, finely-divided hydrated alumina having a particle size from about 8 to about 10 microns is preferred.

The flame-resistant compositions of this invention are prepared by any means known to the art as, for example, mixing or milling. The ethylene/vinyl chloride interpolymers and finely-divided hydrated alumina can be admixed by hand or with conventional mixing or milling equipment. For example, admixing can be carried out with mixing rolls, dough mixers, Banbury mixers, extruders and other mixing equipment. Admixture can be carried out by adding the finely-divided hydrated alumina to a solution of the interpolymer followed by solvent removal to obtain a homogeneous flame-resistant composition. Suitable solvents include dimethylformamide, dimethylacetamide, pyridine and the like. Admixture can also be carried out by adding the ammonium polyphosphate to an aqueous emulsion or dispersion of the interpolymer. In many applications the flame-resistant interpolymer in aqueous emulsion or dispersion will be used in latex form without further treatment.

The flame-resistant compositions of this invention generally contain from about 10 parts to about 1000 parts of weight of finely-divided hydrated alumina for every 100 parts by weight of ethylene/vinyl chloride interpolymer and preferably from about 50 to about 500 parts per each 100 parts of interpolymer.

When the flame-resistant compositions are used in the form of an aqueous dispersion, the dispersion generally contains from about 5 parts to about 2000 parts of aqueous media by weight and from about 50 parts to about 500 parts of finely-divided hydrated alumina by weight for each 100 parts by weight of ethylene/vinyl chloride interpolymer. Such dispersions preferably contain from about 50 parts to about 1000 parts by weight of aqueous media and from about 100 parts to about 300 parts of finely-divided hydrated alumina for each 100 parts by weight of interpolymer for ease of application by means of dipping, soaking, spraying and the like. The preferred flame-resistant compositions of this invention comprise ethylene/vinyl chloride/acrylamide terpolymers containing 15 to 70 weight percent ethylene, 30 to 85% vinyl chloride and 1 to 5% acrylamide, and from about 50 to about 500 parts of finely-divided hydrated alumina.

The ethylene/vinyl chloride interpolymers useful in this invention are readily prepared by various means well known to the art. The interpolymers can be prepared by first mixing ethylene and vinyl chloride in an aqueous medium in the presence of any suitable anionic or nonionic emulsifier and any initiator capable of generating free radicals in the chemical mixture at the chosen reaction temperature and pressure. The acrylamide, preferably in aqueous solution either alone or mixed with the appropriate amounts of other polar monomers, is added to the polymerizing ethylene and vinyl chloride mixture gradually throughout the reaction. The addition of the acrylamide is preferably begun after about 40 to 50 percent of the desired conversion of the ethylene and vinyl chloride has been reached. A shell-core latex in which the polar monomer is concentrated in the outer layers is produced.

The ethylene/vinyl chloride interpolymers used in this invention are preferably prepared by a process which comprises mixing ethylene and vinyl chloride monomers in the presence of an alkaline buffered reduction-oxidation (redox) initiator-catalyst system, water, and from about 1 percent to about 8 percent by weight based upon the monomer feed, or from about 4 percent to about 7 percent based upon the polymer product of an anionic or nonionic emulsifying agent having a hydrophilic-lipophilic balance (HLB) value of from about 10 to about 40, and reacting the mixture at a temperature and pressure and for a time sufficient to cause polymerization between the ethylene and vinyl chloride, and then to introduce acrylamide, either alone, or mixed with other monomers in minor amounts in an appropriate diluent such as water into the pressurized polymerizing reaction mixture of the ethylene and vinyl chloride. This process is described in detail in U.S. Pat. 3,428,582 and the subject matter thereof is expressly incorporated herein by reference.

The following examples will illustrate this invention. Parts and percent are by weight unless otherwise indicated.

EXAMPLE 1

This example illustrates the preparatioin of a 21/76/3 ethylene/vinyl chloride/acrylamide interpolymer latex.

Reaction Vessel Initial Charge

	G.
$K_2S_2O_3$ (KPS)	11.0
$NaHCO_3$	15.0
$Fe(NO_3)_3 \cdot 9H_2O$	0.8
Tetrasodium ethylenediamine-tetraacetate (Na_4EDTA)	1.5
Na lauryl sulfate (SLS)	1.2
H_2O to make 1700 ml.	
Vinyl chloride (VCl)	450
Ethylene (E)	150

The above ingredients are charged to a suitable reaction vessel and heated to 30° C. with stirring to give a reaction pressure of 850 p.s.i.g. Polymerization is started by adding a 1 M sodium formaldehyde sulfoxylate-$NaHSO_2 \cdot CH_2O \cdot 2H_2$(SFS)/1.5 M ammonium hydroxide (NH_4OH) solution to the mixture at a rate of 5.2 ml./hr. at the same time 18 ml./hr. of a 25 percent SLS solution is added and the pressure is kept constant by the addition of pure vinyl chloride as required. After three hours, a 50 percent solution of acrylamide in water solution is added at 40 ml./hr. The reaction stops after 5.5 hours and the feed streams are turned off. A total of 1330 g. of VCl, 95 ml. of the 50 percent acrylamide, 27 ml. of the 1 M SFS/1.5 M NH_4OH solution, and 92 ml. of the 25 percent SLS solution are added. The resulting polymer latex is vented out the bottom of the autoclave. A total of about 3500 g. of the ethylene/vinyl chloride/acrylamide polymer latex is obtained containing 47 percent total solids, and 1.5 percent sodium lauryl sulfate (based on the weight of the polymer). It has a pH of 7.7. The composition of the terpolymer is about 21/76/3 ethylene/vinyl chloride/acrylamide.

EXAMPLE 2

An aqueous dispersion of ethylene/vinyl chloride/acrylamide 21/76/3 terpolymer prepared substantially in accordance with Example 1 and containing about 45 weight percent polymer solids is coagulated by means of tetrahydrofuran. The terpolymer is washed with water and dried. About 100 parts of finely-divided hydrated alumina having a particle size range of about 8 to 10 microns are admixed with about 100 parts of the dry terpolymer to form a flame-resistant composition.

EXAMPLE 3

About 30 parts of the E/VCl/A terpolymer prepared in Example 2 are dissolved in 100 parts of dimethylformamide at 25° C. with moderate agitation. To this solution is added about 10 parts of finely-divided hydrated alumina having a particle size range of 8 to 10 microns with stirring. The solvent is removed by evaporation at reduced pressure with constant stirring to produce a flame-resistant composition.

EXAMPLE 4

An aqueous flame resistant composition comprising 100 parts of E/VCl/A (21/76/3) and 300 parts of finely-divided hydrated alumina having a particle size range of 8 to 10 microns is prepared by admixing the hydrated alumina with a 60 weight percent aqueous dispersion of E/VCl/A. A film is cast in a glass plate to a dry thickness of about 4.5 mils. The film is placed in a chamber having a variable oxygen/nitrogen atmosphere and is brought in contact with a small flame. The percent oxygen in the oxygen/nitrogen atmosphere is increased until it is sufficient to support combustion. The percent oxygen in the oxygen/nitrogen atmosphere at the point of combustion is termed the oxygen index. The E/VCl/A-hydrated alumina flame resistant film of this Example has an oxygen index of 0.866. A control sample of the same E/VCl/A without hydrated alumina has an oxygen index of 0.222 or just slightly above the oxygen concentration in atmospheric air.

This improvement of almost 300% in oxygen index is totally unexpected since hydrated alumina does not result in comparable improvements with other polymers such as styrene/butadiene/itaconic acid (57/38/5). The oxygen index of styrene/butadiene/itaconic acid (57/38/5) is 0.173. The oxygen index of a composition comprising 100 parts by weight of styrene/butadiene/itaconic acid terpolymer (57/38/5) and 300 parts of hydrated alumina having a particle size range of 8 to 10 microns is 0.330. Thus the improvement is only about 90 percent.

EXAMPLE 5

Preweighed samples of Hollingsworth and Vose nonwoven fabric composite comprising 75 weight percent cellulosic fiber and 25 weight percent nylon fiber are immersed in an aqueous dispersion of flame-resistant compositions comprising an ethylene/vinyl chloride interpolymer and finely-divided hydrated alumina. The impregnated fabrics are passed through a size press, weighed, dried for about three minutes at a temperature of about 118° C. The wet pickup of flame-resistant composition in each sample is about 270% based on the weight of the fabric. The bonded nonwoven fabrics are subjected to calendering through a single nip for smoothness and tested for flame resistance in accordance with TAPPI-T461 vertical flammability test. The ethylene/vinyl chloride/acrylamide interpolymer contains 76 weight percent ethylene, 21 weight percent vinyl chloride and 3 weight percent acrylamide and is prepared substantially in accordance with Example 1. The nonwoven fabric samples are 2.75 in. by 8.25 in. One dispersion of ethylene/vinyl chloride interpolymer which does not contain finely-divided hydrated alumina is used as control. Results and further details are given in the Table below.

TABLE

Finely-divided hydrated [a] Alumina in test fabric, percent by analysis	After glow, sec.	Char length, in.
0 (control)	Entire sheet consumed.	Entire sheet consumed.
10.4	None	2.

[a] Based on the weight of the fiber.

The flame-resistant compositions of this invention can also contain from about 1 to about 100 parts by weight per 100 parts by weight of interpolymer of a phosphate plasticizer, e.g. phosphoric acid derivatives such as triethyl phosphate, tributyl, phosphate, trioctyl phosphate, tri-(2-ethylhexyl) phosphate, tributoxyethyl phosphate, triphenyl phosphate, tricresyl phosphate, cresyl diphenyl phosphate, hexyl diphenyl phosphate, 2-ethylbutyl diphenyl phosphate, octyl diphenyl phosphate, 2-ethylhexyl diphenyl phosphate, isooctyl diphenyl phosphate, nonyl diphenyl phosphate, decyl diphenyl phoshate, 2-butyloctyl dihenyl phosphate, tridecyl diphenyl phosphate, tetradecyl diphenyl phosphate, octadecyl diphenyl phoshate, 2-ethylbutyl dicresyl phosphate, n-octyl dicresyl phosphate, isooctyl dicresyl phosphate, 2-ethylhexyl dicresyl phosphate, nonyl dicresyl phosphate, decyl dicresyl phosphate, 2-n-propyl-heptyl dicresyl phosphate, 2-butyloctyl dicresyl phosphate, tridecyl dicresyl phosphate, tetradecyl dicresyl phoshate, octadecyl dicresyl phosphate, trichloroethyl phosphate and tri-(dimethylphenyl) phosphate.

The flame-resistant compositions of this invention are also characterized by high tensile strength, good elongation, softness, good hand and flexibility, good drape and resistance to many common solvents and detergents. With these properties the flame-resistant compositions are useful as bonding agents for bonded nonwoven fibrous products suitable for use in a wide variety of end applications including, for example, paperboard, toweling, wrappings, wallpaper, mats napkins, tablecloths, heat or sound insulating materials, electrolytic condensers, luggage skin and interiors, glue coated tape stocks, pressure sensitive tape stocks, projection screens, waterproof wrapping paper, drapery headers, draperies, binders, hospital items such as caps, masks, gowns, jackets, scrub pants, capes, shoe covers, wash cloths, pillow cases, wipes, cubicle curtains, filters for food processing, motors, machines, air systems or liquid systems, electrical insulators, tapes ribbons, automobile head and arm rests, upholstery, stuffed pillows, fiberfills, sleeping bags, slip covers, bed spreads, blankets, curtains, window shades, carpeting (nonwoven), carpet backing, wearing apparel, clothing insulation, underwear, diapers, interfacing and interliners (collars and cuffs), automotive door panels, film backings and automotive padding.

The embodiments of this invention in which a particular property or privilege is claimed are defined as follows:

1. Composition comprising a flame resisting amount of finely-divided hydrated alumina and an interpolymer selected from the group consisting of (I) an ethylene/vinyl chloride interpolymer containing from about 5 to about 70 weight percent ethylene, about 30 to about 95 weight percent vinyl chloride, and about 0.1 to about 10 weight percent of an additional polar component selected from the group consisting of

(A) acrylamide, and

(B) acrylamide in combination with at least one additional polar monomer selected from the group consisting of acrylonitrile, methacrylamide, N-(alkyl) acrylamide, N-(hydroxy substituted alkyl) acrylamide, and N-(alkyl) methacrylamide having from 1 to 3 carbon atoms in each said alkyl group, acrylic acid, methacrylic acid and alkali metal and ammonium salts of acrylic and methacrylic acid, maleic and fumaric acids, itaconic and citraconic acids, half alkyl esters of maleic, fumaric, itaconic, and citraconic acids having from 1 to 6 carbon atoms in said alkyl groups, acrylyl and methacrylyl esters of hydroxyalkanoic acids having from 2 to 6 carbon atoms in said alkanoic acids, acrylylamide and methacrylylamides of aminoalkanoic acids having from 2 to 6 carbon atoms in said aminoalkanoic acid, hydroxyethyl and hydroxypropyl esters of acrylic, methacrylic, maleic, and fumaric acids, vinyl esters of alkanoic acids having from 1 to 6 carbon atoms and alkyl sulfonic acid having from 1 to 6 carbon atoms, phenylsulfonic acids, and acrylyl and methacrylyl esters of hydroxyalkylsulfonic acid having from 1 to 6 carbon atoms in said alkyl moieties and hydroxyalkylsulfonamides having from 1 to 6 carbon atoms in said hydroxyalkyl moieties;

and (II) interpolymers of the type described in (I) treated with an acid or a base having an ionization constant higher than about 10^{-4} in amounts equivalent to up to about 100 percent of the amide content of said interpolymer.

2. Composition of Claim 1 wherein the particle size of finely-divided hydrated alumina is from about 8 to about 10 microns.

3. Composition of Claim 1 wherein said finely-divided hydrated alumina is present in amounts of from about 10 parts to about 1000 parts by weight for each 100 parts by weight of interpolymer.

4. Composition of Claim 1 dispersed in aqueous media.

5. Composition of Claim 1 wherein the ethylene/vinyl chloride interpolymer contains from about 15 to about 70 percent ethylene, from about 30 to about 85 percent vinyl chloride and from about 0.1 to about 10 percent acrylamide.

6. Composition of Claim 1 wherein the ethylene/vinyl chloride interpolymer contains from about 19 to about 23 percent ethylene, from about 74 to about 78 percent vinyl chloride and from about 2 to about 4 percent acrylamide.

7. Composition of Claim 1 wherein the interpolymer is (II).

8. Composition of Claim 1 wherein the polar component of the interpolymer is a combination of acrylamide and N-hydroxymethylacrylamide.

9. Composition of Claim 1 together with from about 2 to about 2000 parts by weight of aqueous media for each 100 parts by weight of interpolymer wherein the ethylene/vinyl chloride interpolymer contains from about 15 to about 70 percent ethylene, from about 30 to about 85 percent vinyl chloride and from about 0.1 to about 10 percent acrylamide, and the finely-divided hydrated alumina is present in an amount from about 50 parts to about 500 parts by weight for each 100 parts by weight of interpolymer.

10. Composition of Claim 1 together with from about 2 to about 2000 parts by weight of aqueous media for each 100 parts by weight of interpolymer wherein the ethylene/vinyl chloride interpolymer contains from about 30 to about 85 weight percent vinyl chloride and from about 0.1 to about 10 weight percent of a combination of acrylamide and N-hydroxymethyl acrylamide, and the finely-divided hydrated alumina is present in an amount from about 50 parts to about 500 parts by weight for each 100 parts by weight of interpolymer.

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