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**Ottinger et al.**

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[54] **FLAME-RETARDANT, BONDED NONWOVEN FIBROUS PRODUCT EMPLOYING A BINDER COMPRISING AN ETHYLENE/VINYL CHLORIDE INTERPOLYMER AND AN AMMONIUM POLYPHOSPHATE**

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[57] **ABSTRACT**

Flame-retardant, bonded nonwoven fibrous products employing an ethylene/vinyl chloride interpolymer bonding agent having incorporated therein a phosphorus and nitrogen flame retardant.

**28 Claims, No Drawings**

# FLAME-RETARDANT, BONDED NONWOVEN FIBROUS PRODUCT EMPLOYING A BINDER COMPRISING AN ETHYLENE/VINYL CHLORIDE INTERPOLYMER AND AN AMMONIUM POLYPHOSPHATE

This invention relates to flame retardant, bonded nonwoven fibrous products employing a bonding agent composition comprising an ethylene/vinyl chloride interpolymer and an ammonium polyphosphate.

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.

Nonwoven fibrous material can be formed by both a wet process and a dry process. In the wet process, the fibers are slurried in water or similar inert liquid. The slurry is spread on a flat surface, the inert liquid drained off, and the web dried under pressure to form the loosely consolidated mass of randomly distributed fibers. In the dry process the fibers in the dry state are laid on a solid, flat surface, for example, a conveyor, by mechanical means or pneumatic means, for example, a carding machine or an air-lay machine. The dry process can be used to lay down the fibers in either a random distribution or an oriented distribution. A thorough discussion of the formation of nonwoven fabrics is presented in "Non Woven Fabrics" by F. N Buresh-Reinhold Publishing Company, New York, New York, (1962).

Regardless of the method employed to form the nonwoven fibrous material, the material is at this point only a flimsy structure having virtually no tensile strength and is unable to remain as a unitary piece without support. In order that the nonwoven fibrous material possess the necessary tensile strength and cohesion required for practical applications, it is necessary that the fibers be bonded and interlocked in some fashion. The usual and most economical means of accomplishing the bonding and interlocking of the fibers is to impregnate or saturate the nonwoven fibrous material with a bonding agent followed by heating or other means of activation in order to coalesce and fuse the bonding agent, and bond and interlock the fibers.

In many applications, it is essential that bonded nonwoven products exhibit good elongation, resistance to oils and solvents, good drape and hand characteristics, good flame resistance, and non-discoloration, as well as high tensile strength.

Various general purpose synthetic polymers and copolymers have been used as bonding agents for nonwoven fibrous products. Some of the prior art polymers produce undesirably stiff products which are unsuitable for textile use because of poor draping qualities and harsh feel or hand. Other prior art polymers result in discoloration and loss of strength upon exposure to bleach during washing. Still other prior art polymers result in bonded nonwoven fibrous products which exhibit acceptable tensile strength and elongation but which lack acceptable flame retardancy. In general, the bonding agents employed heretofore have not been entirely satisfactory.

In accordance with this invention, it has been found that flame retardant, bonded nonwoven fibrous products which exhibit good flame retardancy and the desirable combination of high tensile strength and elongation, as well as good hand and drape characteristics, are obtained by using a bonding agent composition comprising an ethylene/vinyl chloride interpolymer and an ammonium polyphosphate flame retardant for the nonwoven fibrous material.

The flame retardants useful in the preparation of the flame retardant, bonded nonwoven fibrous products of this invention are the substantially water-insoluble ammonium polyphosphates of the general formula

$$H_{(n-m)+2}(NH_4)_mP_nO_{3n+1}$$

wherein $n$ is an integer having an average value greater than 10, $m/n$ has an average value between 0.7 and about 1.1 and $m$ has an average value equal to *n+b 2*. These polymeric polyphosphates have P-O-P type linkages and the average value of $n$ being greater than 10 is evidenced by the paper chromatography method [Karl-Kroupa, *Anal. Chem.*, 28, 1091 (1956)], and the polymeric P-O-P type linkage is evidenced by *n.m.r.* spectra which indicates substantially no ammonium polyphosphates type linkages and no ortho, pyro or short chain P-O-P type groups and by infra-red spectra which indicates P-O-P type linkages but does not indicate substantially any P-N type linkages.

These polymeric ammonium polyphosphates can be either straight chain structures or branched chain structures. It should be noted that substantially all of the nitrogen in these ammonium polyphosphates is present as the ammoniacal nitrogen and there is substantially no nuclear nitrogen present in the polyphosphates. Although theoretically the ammoniacal nitrogen to phosphorus molar ratio for the polyphosphates of the instant invention approaches about 1, when the polyphosphates are completely ammoniated, in some cases the molar ratio of ammoniacal nitrogen to phosphorus is less than 1 and it is intended that this invention include only those polymeric ammonium polyphosphates having a molar ratio of not less than about 0.7 In addition, when the polyphosphates of the instant invention are characterized herein as being substantially water-insoluble it is intended to mean that the solubility of a slurry of 10 grams of solids/100 cc of water after 60 minutes at 25° C is about 5 grams/100 cc of water or less. Specifically, for purposes of the present invention an ammonium polyphosphate having a solubility of a specified value refers to the solubility value in grams per 100 cc of water when 10 grams of said polyphosphate is slurried in 100 cc of water for 60 minutes at 25° C.

The degree of polymerization of the substantially water-insoluble ammonium polyphosphates is difficult to determine since known methods for determining such are "so-called" solution methods, that is, they employ solution techniques for polymerization measurements. For example, as determined by the end group titration method [Van Wazer, Griffith and McCullough, *Anal. Chem.*, 26, 1755 (1954)] after converting the ammonium polyphosphate to the acid form by ion exchange resins [Van Wazer and Holst, *J. Am. Chem. Soc.*, 72, 639 (1950)], the average numerical value of $n$ is from about 20 to about 400, preferred from about 40 to about 400; whereas, as determined by the method of light scattering or viscosity correlations obtained from light scattering [Strauss and Wineman, *J. Am. Chem. Soc.*, 80, 2366 (1958)] modified by use of the Zimm plot method [Stacey, "Light-Scattering in Physical Chemistry," Butterworths, London (1956)] the average weight value of $n$ is above about 500 and preferred from about 500 to about 100,000 with from about 1,000 to about 30,000 being especially preferred.

The term "ammoniacal nitrogen" refers to that nitrogen which is present in the form of ammonium ions and is capable of being removed by the hydrogen form of a strong cation exchange resin, i.e., the hydrogen form of a sulfonate polystyrene resin. The term "non-ammoniacal nitrogen" or "-nuclear nitrogen" refers to nitrogen incapable of being removed in the manner of true ammonium nitrogen.

The ammonium polyphosphates can be prepared exhibiting many different crystalline forms as evidenced by their X-ray diffraction patterns and, in general, any of such forms can be used (although Forms 1 and 2, infra, are preferred), as well as the non-crystalline of amorphous form. Crystalline forms illustrative of ammonium polyphosphates suitable for use include the following:

X-Ray Diffraction Data (a)

| Form 1Td Line(b) | d,A. | Form 2 Line(b) | d,A. | Form 3 Line(b) | d,A. | Form 4 Line(b) | d,A. |
|---|---|---|---|---|---|---|---|
| 1 | 6.06 | 1 | 5.70 | 1 | 6.65 | 1 | 5.70 |
| 2 | 5.47 | 2 | 6.06 | 2 | 5.68 |  | 5.60 |
| 3 | 3.83 | 3 | 3.08 | 3 | 5.40 | 3 | 3.42 |
| 4 | 3.50 | 4 | 2.93 | 4 | 3.52 | 4 | 7.00 |
| 5 | 3.24 | 5 | 3.37 | 5 | 3.80 | 6.10 |  |

(a) CuKα Radiation

(b) Five strongest lines in order of decreasing intensity

In general, the ammonium polyphosphates can be used in any size which permits their admixture with the ethylene/vinyl chloride interpolymers. In particular, ammonium polyphosphates having a particle size fine enough to pass through an 80 mesh screen (USSS) are preferred, with a particle size at least fine enough to pass through a 200 mesh screen being especially preferred.

The substantially water-insoluble ammonium polyphosphate flame-retardant component of the bonding agent compositions useful in the present invention can be prepared by many and various methods. In general, a phosphate containing material, such as monoammonium orthophosphate, diammonium orthophosphate, condensed phosphoric acid, orthophosphoric acid and the like, is thermally condensed with an ammoniating and condensing agent, such as urea, ammonium carbonate, biuret, sulfamide, sulfamic acid, ammonium sulfamate, guanyl urea, methyl urea, formamide amino urea, 1-3-diamino urea, biurea and the like. In particular, for example, monoammonium orthophosphate and urea can be thermally condensed to prepare substantially water-insoluble ammonium polyphosphates by heat treating a melt formed from substantially equimolar quantities at a temperature of about 250° C for a period of about 3 hours.

The ethylene/vinyl chloride interpolymers useful in the preparation of the flame retardant, bonded nonwoven fibrous products 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 one to three 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 acids, aconitic acid, itaconic acid, citraconic acid, and alkali metal and ammonium salts thereof, acrylyl and methacrylyl esters of hydroxyalkanoic acids having from two to about six carbon atoms in the alkanoic acid moieties, acrylylamides and methacrylylamides of aminoalkanoic acids having from two to about six carbons in the aminoalkanoic acid, hydroxyethyl and hydroxypropyl esters of acrylic, methacrylic, maleic, and fumaric acids, vinyl esters of alkanoic acids having from one to six carbon atoms such as vinyl acetate, vinyl propionate, and lower alkyl (one to six carbon atoms) sulfonic acid, vinyl esters of phenylsulfonic acids, and alkylphenylsulfonic acids and acrylyl and methacrylyl esters of hydroxyalkylsulfonic acids having from one to six carbon atoms in said alkyl moieties, and hydroxyalkylsulfonamides having from one to six 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 3percent 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 of the ethylene, vinyl chloride, and acrylamide with aqueous base or acid in an amount chemically equivalent to from about 0.1 percent 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 citraconic 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-hydroxyproprionate, 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 nonwoven fibrous products of this invention are ethylene/vinyl chloride/acrylamide, ethylene/vinyl chloride/hydroxyethylacrylate, ethylene/vinyl chloride/acrylamide/N-isopropylacrylamide, ethylene/vinyl chloride/arylamide/N-ethylmethacrylamide, ethylene/vinyl chloride/acrylamide/diammonium itaconate, ethylene/vinyl chloride/acrylamide/monobutyl acid maleate, ethylene/vinyl chloride/acrylamide/N-methacrylyl propionamide, ethylene/vinyl chloride/acrylamide/sodium acrylate and ethylene/vinyl chloride/acrylamide/sodium methacrylate.

The flame retardant, bonded nonwoven fibrous products of this invention can be formed of either natural or synthetic fibers or any combination thereof with the selection of the fiber merely depending upon the specific end use intended for the bonded nonwoven fibrous product. Among the fibers that can be used in accordance with this invention are natural fibers, for example, wood, jute, sisal, hemp, cotton, cotton linters, silk, mohair, cashmere, asbestos, wool and glass, and synthetic fibers, for example, rayon cellulose esters such as cellulose acetate, polyvinyl chloride, polyvinyl acetate, polyacrylonitrile and copolymers thereof, polyethylene, polypropylene and the like, polyesters such as ethylene glycolterephthalate polymers, and polyamides of the nylon type.

In many applications, the flame retardant, bonded nonwoven fibrous products of this invention are prepared from a plurality of natural fibers, or a plurality of synthetic fibers, or a combination of natural and synthetic fibers. Combinations of wood fiber and cotton fiber can be advantageously employed in end products such as shoe liners and the like. In general, the wood fiber comprises the major amount of the fiber content of such bonded nonwoven fibrous products. Combinations of glass fiber and asbestos fiber are generally employed in insulating applications. Combinations of glass fiber and wood fiber are also useful in certain drapery applications. The weight ratio of glass fiber to cellulosic fiber in such bonded nonwoven fibrous products is usually from about 1:10 to about 10:1.

In wearing apparel applications, a combination of wood fibers and nylon fibers or a combination of wood fibers and rayon fibers can be advantageously employed. Combinations of wood fiber and nylon fiber as well as combinations of wood fiber and polyester fiber are also widely employed in various applications where reinforced sheeting is required. In such combinations of natural and synthetic fibers, the weight ratio of natural fiber to synthetic fiber is generally from about 1:20 to about 20:1 and preferably from about 1:1 to about 3:1.

The nonwoven fibrous materials useful in the preparation of the flame retardant, bonded nonwoven fibrous products of this invention can be prepared by any method known to the art. Thus, the nonwoven fibrous material can be made of fibers deposited in a random manner as well as fibers oriented or aligned along a particular axis. Nonwoven fibrous materials in the form of two-dimensional webs can be prepared by the following methods. Oriented webs are produced using conventional web-style machines, such as openers, pickers, cards, or garnetts. Cross-laid webs are made in a manner similar to oriented webs, except that the fibers are carefully placed at right angles to the machine direction to improve cross-wise strength.

Random webs are produced in air-lay machines, and the nonwoven fibrous material has equal strength in all directions. In the air-lay method, continuous filaments are fed through a cutter or breaker which discharges the fibers into the discharge side of a blower. Suitable conduits are provided to guide the fibers to a collecting screen or air-pervious structure for collecting the fibers in the form desired. The screen may be in the form of an endless traveling belt passing through the lower portion of a tower into the upper portion of which the blown fibers are introduced by the conduit. A suction box may be placed beneath the traveling screen to assist in the deposition of the fibers thereon. Instead of using a traveling flat screen, a stationary formed screen may be used. For example, the screen may take the form of a hat shaped cone, such as that used in the felt hat-making industry. Alternatively it may have any other form which is suitable to produce the desired shape of the bonded nonwoven fibrous product such as a rectangular tray. As is the case with the endless traveling belt, suction may also be applied beneath the stationary screen to assist deposition of the fibers thereon.

Random webs are also produced by the direct spray method from a solution or molten mass of the fiber material. This is the conventional procedure for the formation of glass fibers or mineral wool fibers, as well as those of nylon or thermoplastic materials, adapted to be dissolved in a suitable solvent or to be melted. The solution or melt is directed to suitable nozzles or jet-forming orifices and a high pressure fluid stream, such air, nitrogen or steam, is directed against the stream or streams of filament-forming material to disrupt them and coagulate them as fibers in the vicinity of the orifices. Electrostatic spinning methods can also be employed for this purpose. As in the case of the use of blowers, the disrupted and dispersed fibers can be directed to the top of the settling tower and allowed to settle with the aid of suction devices upon a suitable traveling or stationary screen at the bottom of the tower. This procedure is particularly adapted to the production of fibers of siliceous materials such as glass or mineral wool, as well as to thermoplastic resin fibers.

Wet random webs are formed from a slurry of dispersed fiber on paper making or modified paper making machines. Spun-bonded webs are made of randomly oriented continuous filament fibers bonded at the cross-over point. The method includes extrusion of the continuous filament fibers, drawing to orient the fiber, some fiber entanglement by liquids or air, and bonding at the cross-over points.

The flame retardant, bonded nonwoven fibrous products of this invention are generally prepared by a method which comprises consolidating the loose fibers into nonwoven fibrous material having the structural configuration of the desired bonded nonwoven fibrous product, dispersing the bonding agent composition comprising an ethylene/vinyl chloride interpolymer and a phosphorus and nitrogen flame retardant within the nonwoven fibrous material, and heating the impregnated nonwoven fibrous material to a temperature sufficient to coalescence and fuse the interpolymer, and optionally heating to a temperature sufficient to cross-link the interpolymer if a sulfur cross-slinking agent is employed.

Another method for the preparation of the flame retardant, bonded nonwoven fibrous products of this invention which is particularly useful when the nonwoven fibrous material is formed by the air-lay method in an air-lay machine comprises contacting the fibers with the bonding agent composition comprising ethylene/vinyl chloride interpolymer and phosphorus and nitrogen flame retardant in the form of dispersion of powder as they fall through the settling chamber to their point of deposition. This is advantageously carried out by spraying the bonding agent composition dispersion or powder into the settling chamber at some intermediate point between the top and the bottom thereof. By spraying the fibers as they descend to the point of collection, it is possible to effect a thorough distribution of the bonding agent composition among the fibers before they are collected into the nonwoven fibrous material. In the production of certain fibrous products wherein a hot molten mass of a polymer such as nylon or a fused siliceous mass or glass is disrupted by jets of heated air or steam, the bonding agent composition in the form of dispersion or powder can be sprayed directly on the fibers while still hot so that immediately after deposition the bonding agent is set and it bonds and interlocks the fibers in proper relationship.

The bonding agent compositions can be applied to the fibers of the nonwoven fibrous material by an means known in the art. The bonding agent compositions are usually applied to the fibers of the nonwoven fibrous material by application to the surface thereof, or by submersion of the nonwoven fibrous material in a liquid, thickened or foamed dispersion so that the bonding agent composition penetrates into the interior of the nonwoven fibrous material. Where the nonwoven fibrous material is a two-dimensional fabric in the form of a fleece or web, the bonding agent compositions are usually applied in the form of an aqueous dispersion. In a typical application, the fabric is impregnated with the bonding agent compositions by dipping or immersing the fabric in the dispersion to provide sufficient wet pickup of the bonding agent. The wetted, nonwoven fibrous material in the form of a fleece or web can be passed between a pair of pressure rolls to effect substantially uniform impregnation and also to control the amount of the bonding agent applied. The impregnated nonwoven fibrous material is dried by conventional means known to the art in order to remove all or a portion of the water and to effect coalescence and fusion of the bonding agent composition within the nonwoven fibrous material. The drying temperature and drying time are dependent upon the size, shape and cross-section of the impregnated, nonwoven fibrous material. In general, the drying temperature is controlled so that no appreciable deterioration or degradation of the fibers or bonding agent composition occurs.

When the bonding agent compositions are used in the form of a dispersion, the dispersion generally contains from about 5 percent to about 90 percent of ethylene/vinyl chloride interpolymer by weight and from about 0.1 percent to about 300 percent of ammonium polyphosphate based on the interpolymer. Such dispersions preferably contain from about 10 percent to about 60 percent by weight of interpolymer and from about 1 percent to about 30 percent of ammonium polyphosphate for ease of application by means of dipping, soaking, spraying and the like.

The amount of ethylene/vinyl chloride interpolymer based on the weight of the fiber component of the bonded nonwoven fibrous product can vary widely depending upon the characteristics desired in the final product and the specific end use. The flame retardant, bonded nonwoven fibrous products of this invention generally contain from about 2 percent to about 200 percent of interpolymer based on the weight of the fibers.

For the production of preforms intended to be converted into shaped articles, it is preferred to employ from about 2 percent to about 10 percent of the ethylene/vinyl chloride interpolymer based on the weight of the fibers. In the production of insulation materials, the amount of ethylene/vinyl chloride interpolymer employed generally falls in the lower part of the above range if the bonding agent is applied primarily adjacent to the surface or surfaces of the product or if it is applied in conjunction with other binders.

When the ethylene/vinyl chloride interpolymer is to serve mainly to bond the fibers together to form a flame retardant bonded nonwoven fibrous product in which the maximum porosity is retained in conjunction with a minimum change of fiber hand and drape characteristics as well as an increase in tensile strength, there is preferably employed from about 10 percent to about 70 percent weight of interpolymer solids based on fiber content. The lower portion of this range generally gives the maximum porosity and provides a minimum change in the fiber hand and drape characteristics although in the higher portion of this range porosity is mainly retained and the fiber hand and drape characteristics are still evident. The flame retardant, bonded nonwoven fibrous products thus obtained are advantageously used for many sanitary purposes, such as table napkins, bibs, tablecloths, disposable diapers and disposable sheets. When this amount of interpolymer is used there is relatively little or no "window paning," i.e., the interstices between fibers are left open leaving a highly porous bulky product. If desired, the density of the product can be modified by the application of various amounts of pressure prior to, or in many cases, after the saturated nonwoven fibrous material has been heated for bonding.

Flame retardant, bonded nonwoven fibrous products containing from about 30 percent to about 150 percent by weight of ethylene/vinyl chloride interpolymer based on the weight of the fiber generally find use in the garment industry to provide interlining fabrics for coats, dresses, collars, cuffs, and the like, and to provide outer wearing apparel fabrics, such as blouses, skirts, shirts, dresses, and the like. Flame retardant, bonded nonwoven fibrous products containing the interpolymer in this range are also useful as curtain and drapery materials. In addition to the general household and apparel uses mentioned above, the flame retardant, bonded nonwoven fibrous products of this invention in which 10 to 100 percent by weight of interpolymer based on the weight of fiber is employed find many light industrial uses as wiping cloths, filters and lining materials for packaging.

The amount of ammonium polyphosphate based on the weight of the fiber component of the flame retardant, bonded nonwoven fibrous product of this invention will vary from about 1 percent to about 30 percent by weight, and preferably from about 3 percent to about 20 percent by weight.

If desired the bonding agent compositions useful in this invention can also contain a wetting agent or foaming agent. They can contain a defoamer when the ingredients of the aqueous dispersion have a tendency to give rise to foaming and when such foaming is undesirable. The conventional wetting agents such as the sodium salt of dioctylsuccinic acid can be used and the conventional foaming and defoaming agents can be employed such as sodium soaps including sodium oleate for foaming and octyl alcohol or certain silicone antifoaming agents for defoaming.

In some instances, the properties of the flame retardant, bonded nonwoven fibrous products are greatly enhanced by a heat cure of the interpolymer to effect cross-linking. Ethylene/vinyl chloride interpolymers can be cross-linked with various sulfur containing compounds as is disclosed in U.S. Pat. No. 3,356,658. The interpolymers are cross-linked by subjecting the bonded nonwoven fibrous product, after the drying operation, or as a final portion of the drying stage itself, to a curing operation as disclosed in U.S. Pat. No. 3,356,658.

The interpolymers useful in 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 derivates 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 phosphate, 2-butyl octyl diphenyl phosphate, tridecyl diphenyl phosphate, tetradecyl diphenyl phosphate, octadecyl diphenyl phosphate, 2-ethylbutyl dicresyl phosphate, n-octyl dicresyl phosphate, isooctyl dicresyl phosphate, 2-ethylhexyl dicresyl phosphate, nonyl dicresyl phosphate, decyl dicresyl phosphate, 2-n-propylheptyl dicresyl phosphate, 2-butyloctyl dicresyl phosphate, tridecyl dicresyl phosphate, tetradecyl dicresyl phosphate, octadecyl dicresyl phosphate, trichloroethyl phosphate and tri-(dimethylphenyl) phosphate;

The flame retardant, bonded nonwoven fibrous products of this invention are 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 retardant, bonded nonwoven fibrous products of this invention are suitable for use in a wide variety of end applications, many of which have been noted above and including, for example, paperboard, toweling, wrapping, 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 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/acrylamide 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 non-ionic 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. No. 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 preparation of a 21/76/3 ethylene/vinyl chloride/acrylamide interpolymer latex.

Reaction Vessel Initial Charge

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

The above ingredients are charged to a suitable reaction vessel and heated to 30° C with stirring to give a reaction pressure of 850 psig. 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 1,330 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 auto-clave. A total of about 3,500 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

Preweighed samples of Hollingsworth and Vose nonwoven fabric composite comprising 75 weight percent cellulosic fiber and 25 weight percent nylon fiber are immersed in aqueous dispersions of bonding agent compositions comprising an ethylene/vinyl chloride interpolymer and an ammonium polyphosphate. The aqueous dispersions contain 13.5 weight percent interpolymer solids and 5 weight percent ammonium polyphosphate of crystalline form 1. The impregnated fabrics are passed through a size press, weighed, dried for about two minutes at a temperature of about 118° C. and weighed. The bonded nonwoven fabrics are subjected to calendering through a single nip for smoothness and tested for flame retardancy in accordance with TAPPI T461 vertical flammability test. The ethylene/vinyl chloride/acryl-amide interpolymer contains 76 weight percent ethylene, 21 weight percent vinyl chloride and 3 weight percent acrylamide. The nonwoven fabric samples are 2.75 in. by 8.25 in. Results and further details are given in the Table below.

TABLE

| Ammonium polyphosphate(a) in test fabric, percent | After glow, sec. | Char length, in. |
|---|---|---|
| 0 (control) | entire sheet consumed | entire sheet consumed |
| 4.6 | none | 3¼ |
| 7.6 | none | 2¼ |
| 10.4 | none | 2 |

(a) Based on the weight of the fiber.

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

**1**. Flame retardant, bonded nonwoven fibrous product comprising nonwoven fibrous material bonded with a bonding agent composition comprising an ammonium polyphosphate of the formula $H_{(n-m)+2}(NH_4)_mP_nO_{3n+1}$ wherein $n$ is an integer having an average value greater than 10, $m/n$ has an average value between 0.7 and about 1.1, and $m$ has an average value equal to $n+2$ 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 a 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 one to three 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 one to six carbon atoms in said alkyl groups, acrylyl and methacrylyl esters of hydroxyalkanoic acids having from two to six carbon atoms in said alkanoic acids, acrylylamide and methacrylylamides of aminoalkanoic acids having from two to six carbon atoms in said aminoalkanoic acid, hydroxyethyl and hydroxypropyl esters of acrylic, methacrylic, maleic, and fumaric acids, vinyl esters of alkanoic acids having from one to six carbon atoms and alkyl sulfonic acid having from one to six carbon atoms, phenylsulfonic acids, and acrylyl and methacrylyl esters of hydroxyalkylsulfonic acid having from one to six carbon atoms in said alkyl moieties and hydroxyalkylsulfonamides having from one to six 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**. Product of claim **1** wherein the average value of $n$ of said ammonium polyphosphate is from about 20 to about 400 as determined by the end group titration method.

**3**. Product of claim **1** wherein said ammonium polyphosphate is present in amounts of from about 1 to about 30 weight percent based upon the fibers.

**4**. Product of claim **1** wherein said ammonium polyphosphate is present in amounts of from about 3 to about 15 weight percent based upon the fibers.

**5**. Product of claim **1** wherein the nonwoven fibrous material is made of natural fiber.

**6**. Product of claim **5** wherein the fibers are cellulosic fibers or glass fibers.

**7**. Product of claim **1** wherein the nonwoven fibrous material is made of synthetic fiber.

**8**. Product of claim **7** wherein the fibers are polyester fibers or polyamide fibers.

**9**. Product of claim **1** wherein the nonwoven fibrous material is a combination of natural fiber and synthetic fiber.

**10**. Product of claim **1** wherein the nonwoven fibrous material is in the form of a two-dimensional web.

**11**. Product 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.

**12**. Product 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.

**13**. Product of claim **1** wherein the bonding agent is (II).

**14**. Product of claim **1** wherein the polar component of the interpolymer is a combination of acrylamide and an additional polar monomer.

**15**. Product of claim **1** wherein the ethylene/vinyl chloride interpolymer is a quaternary polymer containing from about 15 to about 70 percent ethylene, from about 30 to about 85 weight percent vinyl chloride, from about 1 percent to about 5 percent acrylamide, and from about 0.1 to about 3 percent by weight of bishydroxypropyl fumarate.

**16**. Product of claim **1** wherein the nonwoven fibrous material is a combination of natural and synthetic fibers and 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.

**17**. Product of claim **16** wherein the natural fibers are cellulosic fibers.

**18**. Product of claim **17** wherein the cellulosic fibers are wood fibers.

**19**. Product of claim **16** wherein the synthetic fibers are polyamides or polyesters.

**20**. Product of claim **16** wherein the natural fibers are cellulosic fibers and the synthetic fibers are polyamides or polyesters.

**21**. Product of claim **16** wherein the combination of fibers comprises at least 50 percent by weight of fibers selected from the group consisting of cellulosic fibers, polyamide fibers, vinyl acetate fibers, fibers of polymers and copolymers of acrylonitrile, poly-(ethylene glycol-terephthalate) fibers and mixtures thereof.

**22**. Product of claim **1** wherein the nonwoven fibrous material is composed of wood fibers and 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.

**23**. Product of claim **1** wherein the nonwoven fibrous material is a combination of polyamide fibers and wood fibers and 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 acylamide.

**24**. Method for the preparation of a flame retardant, bonded nonwoven fibrous product which comprises consolidating a mass of fibers into a nonwoven fibrous material, dispersing a bonding agent composition within the material, and heating the resultant material at a temperature sufficient to effect coalescence and fusion of the bonding agent within said material, wherein the bonding agent composition is as defined in claim **1**.

**25**. Method of claim **24** wherein the bonding agent is dispersed in the material by contacting the material with an aqueous dispersion of the bonding agent composition.

**26**. Method of claim **24** wherein the nonwoven fibrous material is in the form of a two-dimensional sheet.

**27**. Method of claim **24** wherein the material is contacted with the bonding agent in a settling chamber.

**28**. Method of claim **24** wherein the nonwoven fibrous material is a combination of natural and synthetic fibers and 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.

* * * * *

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# UNITED STATES PATENT OFFICE
# CERTIFICATE OF CORRECTION

Patent No. 3,658,579 Dated April 25, 1972

Inventor(s) A. F. Ottinger et al

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

In column 1, line 75, "n+b 2" should read "n+2".

In column 2, the X-Ray Diffraction Data$^{(a)}$, lines 67-75 should be:

X-Ray Diffraction Data$^{(a)}$

| Form 1 | | Form 2 | | Form 3 | | Form 4 | |
|---|---|---|---|---|---|---|---|
| Line$^{(b)}$ | d, Å | Line$^{(b)}$ | d, Å | Line$^{(b)}$ | d, Å | Line$^{(b)}$ | d, Å |
| 1 | 6.06 | 1 | 5.70 | 1 | 6.65 | 1 | 5.70 |
| 2 | 5.47 | 2 | 6.06 | 2 | 5.68 | 2 | 5.60 |
| 3 | 3.83 | 3 | 3.08 | 3 | 5.40 | 3 | 3.42 |
| 4 | 3.50 | 4 | 2.93 | 4 | 3.52 | 4 | 7.00 |
| 5 | 3.24 | 5 | 3.37 | 5 | 3.80 | 5 | 6.10 |

(a) CuK$\alpha$ Radiation
(b) Five strongest lines in order of decreasing intensity

Column 3, line 1, cancel "(b) Five strongest lines in order of decreasing intensity".

Signed and sealed this 27th day of March 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents