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(54) CROSSLINKABLE STABILIZED COMPOSITION FOR A NONWOVEN SUBSTRATE AND PROCESS FOR PREPARING THE SAME

VERNETZBARE STABILISIERTE ZUSAMMENSETZUNG FÜR EIN VLIESSTOFFSUBSTRAT UND VERFAHREN ZUR HERSTELLUNG DAVON

COMPOSITION STABILISÉE RÉTICULABLE POUR SUBSTRAT NON TISSÉ ET SON PROCÉDÉ DE PRÉPARATION

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(56) References cited:
EP-A1- 2 199 333
WO-A1-2013/085764
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Description

BACKGROUND

[0001] The invention relates in general to a composition for a nonwoven substrate. The invention also relates to a process for preparing the same.

[0002] Polymer dispersions may be applied to nonwoven substrates to improve the dry and wet tensile strength exhibited by the substrate. Such substrates may be utilized in products such as, for example, wet and dry wipes.

[0003] However, during the manufacturing of such products formaldehyde may be produced as an undesirable by-product due to the use of certain crosslinking agents. Additionally, formaldehyde may be present in the polymer dispersion due to the use of certain radical initiators used in forming the polymers. Formaldehyde may also be present due to the use of certain preservatives. The presence of formaldehyde in the dispersion and/or the substrate is undesirable for the manufacturer of the nonwoven product and the end use consumer. Efforts to use polymer dispersions that have a low level of formaldehyde and that do not contain crosslinking agents that produce formaldehyde have typically resulted in nonwoven products that exhibit an insufficient wet tensile strength and dispersions that do not have sufficient stability.

[0004] Thus, a need exists for a composition that overcomes the aforementioned deficiencies. A process for making such a composition would also be desirable.

[0005] WO 2013/085764 describes crosslinkable, formaldehyde-free binders for treating nonwovens, comprising an aqueous dispersion of vinyl acetate-ethylene copolymer and a polyvinyl alcohol as a dispersion stabilizer.

BRIEF SUMMARY

[0006] Embodiments of a crosslinkable stabilized composition for a nonwoven substrate are described below. According to a first aspect of the present invention, the composition comprises an aqueous dispersion of vinyl acetate-ethylene copolymers, a polyvinyl alcohol dispersion stabilizer, and a copolymer comprising maleic anhydride units or a copolymer comprising maleic acid units. The composition exhibits a free formaldehyde content of 5 ppm or less. In some embodiments, the composition exhibits a viscosity of 4000 mPa-s or less when measured at 23°C and using a no. LV-3 spindle at 60 revolutions per minute. In one such embodiment, the composition exhibits a viscosity of 200 to 4000 mPa-s when measured at 23°C and using a no. LV-3 spindle at 60 revolutions per minute.

[0007] In other embodiments, the viscosity exhibited by the composition does not undergo a change of more than 60% after 75 days at 20°C. In some of these embodiments, the viscosity exhibited by the composition does not undergo a change of more than 25% after 75 days at 20°C.

[0008] In some embodiments, the copolymer comprises ethylene units.

[0009] In an embodiment, the copolymer comprises ethylene maleic anhydride polymers.

[0010] In some embodiments, the composition does not comprise N-methylol acrylamide.

[0011] In other embodiments, the composition comprises the copolymer in an amount of 0.5 wt% or more based on the total weight of monomers in the aqueous dispersion.

[0012] In some embodiments, the polyvinyl alcohol dispersion stabilizer comprises a partially hydrolysed polyvinyl acetate having an average degree of hydrolysis of 80 to 96 mol%.

[0013] Embodiments of a process for preparing a crosslinkable stabilized composition for a nonwoven substrate are also described below. According to a second aspect of the present invention, the process comprises providing a copolymer comprising maleic anhydride units or a copolymer comprising maleic acid units. Vinyl acetate and ethylene are provided. The vinyl acetate and ethylene are copolymerized in the presence of a polyvinyl alcohol dispersion stablizer to form vinyl acetate-ethylene copolymers. A composition comprising the vinyl acetate-ethylene copolymers and that has a formaldehyde level of 5 ppm or less is formed.

[0014] In some embodiments, the vinyl acetate-ethylene copolymers are provided in an aqueous dispersion that is formed by emulsion polymerization. In an embodiment, the copolymer is mixed with the aqueous dispersion to form the composition.

[0015] In other embodiments, the copolymer is mixed with the polyvinyl alcohol dispersion stablizer prior to forming the vinyl acetate-ethylene copolymers.

[0016] In an embodiment, the copolymer is provided in an amount of 0.5 wt% or more based on total weight of monomers in the aqueous dispersion. In this embodiment, the copolymer is provided in an amount of 0.5 to 5 wt% based on total weight of monomers in the aqueous dispersion.

[0017] In some embodiments, the composition exhibits a viscosity of 50 to 4000 mPa-s when measured at 23°C and using a no. LV-3 spindle at 60 revolutions per minute.

[0018] In other embodiments, a nonwoven product is provided. According to a third aspect of the present invention, the nonwoven product comprises a nonwoven substrate treated with the crosslinkable stabilized composition described above.

[0019] In this embodiment, the nonwoven product exhibits a wet tensile strength that is 25% or more of a dry tensile strength exhibited and a formaldehyde content of 1.5 ppm or less. In an embodiment, the copolymer and vinyl acetate-ethylene copolymers are crosslinked.

DETAILED DESCRIPTION

[0020] It is to be understood that the invention may assume various alternative orientations and step sequences, except where expressly specified to the contrary. It is also to be understood that the specific materials and methods described in the following specification are simply exemplary embodiments of the invention as defined by the appended claims. Hence, specific properties, conditions, or other physical characteristics relating to the embodiments disclosed are not to be considered as limiting, unless expressly stated otherwise.

[0021] In an embodiment, a crosslinkable stabilized composition is provided. The composition has a low level of free formaldehyde. The composition may be applied to a nonwoven substrate. After the composition is applied, the nonwoven substrate is typically allowed to dry and cure. It is preferred that a full cure occurs, which is achieved when the nonwoven substrate reaches a temperature that results in maximum crosslinking. Once dried and cured, the nonwoven substrate has a high level of wet and dry tensile strength and low levels of free formaldehyde. These properties make it useful in products such as, for example, wet or dry wipes. However, the composition may be applied to substrates utilized in other applications.

[0022] The composition comprises an aqueous dispersion. The aqueous dispersion comprises polymers dispersed in water and will be discussed primarily with respect to copolymers. However, the aqueous dispersion may comprise homopolymers or a mixture of homopolymers and copolymers. In certain embodiments, the polymers may be utilized as a binder in a product comprising a nonwoven substrate.

[0023] The aqueous dispersion comprises vinyl acetate-ethylene (VAE) copolymers. In some embodiments, the VAE copolymers in the composition provide the nonwoven substrate with desirable dry tensile strength, stretch, and/or elongation properties. The aqueous dispersion including the VAE copolymers may be formed by way of a polymerization process by copolymerizing vinyl acetate monomers, ethylene, and, optionally, additional monomers in water. In such embodiments, the vinyl acetate monomer content in the VAE copolymers is an amount from 66 to 100% by weight, preferably 68% to 95% by weight, more preferably 68% to 93% by weight, and most preferably 68% to 92% by weight, based in each case on the total weight of the comonomers in the aqueous dispersion. The ethylene content in the VAE copolymers is an amount of 1% or more by weight. Preferably, ethylene is in the VAE copolymers in an amount of 1 to 32% by weight. In some embodiments, ethylene is in the VAE copolymers in an amount of 5 to 32%. In all cases, the % by weight of ethylene is based on the total weight of the comonomers in the aqueous dispersion.

[0024] Optionally, in some embodiments, the range of available properties for the polymers in the aqueous dispersion may be extended by copolymerizing additional monomers with vinyl acetate, or with vinyl acetate and ethylene. Typically, suitable additional monomers (comonomers) are monomers with a single polymerizable olefinic group. Examples of such comonomers are vinyl esters of carboxylic acids having 3 to 18 C atoms. Preferred vinyl esters are vinyl propionate, vinyl butyrate, vinyl 2-ethylhexanoate, vinyl laurate, 1-methyl vinyl acetate, vinyl pivalate, and vinyl esters of a-branched monocarboxylic acids having 9 to 11 C atoms, examples being VEOVA9™ or VEOVA10™ esters (available from Hexion, Columbus, OH). Other suitable comonomers include esters of acrylic acid or methacrylic acid with unbranched or branched alcohols having 1 to 15 C atoms. Exemplary methacrylic esters or acrylic esters include methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate and norbornyl acrylate. Other suitable comonomers include vinyl halides such as vinyl chloride, or olefins such as propylene. In general, the further comonomers are copolymerized in an amount of 0.5 to 30 wt%, preferably 0.5 to 20 wt%, based on the total amount of comonomers in the copolymer.

[0025] Optionally, 0.05% to 10% by weight, based on the total amount of vinyl acetate and ethylene monomers in the aqueous dispersion, of additional monomers (auxiliary monomers) may additionally be copolymerized in forming the aqueous dispersion. Auxiliary monomers may include a polymerizable olefinic group and at least one additional functional group, which may be an additional polymerizable olefinic group to provide crosslinking. Other functional groups may include reactive groups such as carboxylic or sulfonic acid groups.

[0026] Examples of auxiliary monomers are ethylenically unsaturated monocarboxylic and dicarboxylic acids, typically acrylic acid, methacrylic acid, fumaric acid and maleic acid; ethylenically unsaturated carboxamides and carbonitriles, typically acrylamide and acrylonitrile; and monoesters and diesters of fumaric acid and maleic acid, such as the diethyl and diisopropyl esters, and also maleic anhydride, ethylenically unsaturated sulphonic acids and their salts, typically vinyl sulphonic acid, 2-acrylamido-2-methylpropanesulphonic acid. Other examples are pre-crosslinking comonomers such as polyethylenically unsaturated comonomers, examples being divinyl adipate, diallyl maleate, allyl methacrylate or triallyl cyanurate. Also suitable are epoxy-functional comonomers such as glycidyl methacrylate and glycidyl acrylate. Other examples are silicon-functional comonomers, such as acryloyloxypropyltri(alkoxy)- and methacryloyloxypropyltri(alkoxy) silanes, vinyltrialkoxysilanes and vinylmethyldialkoxysilanes, alkoxy groups that may be present being, for example, methoxy, ethoxy and ethoxypropylene glycol ether radicals. Additional monomers comprise hydroxyl or CO groups, examples being methacrylic and acrylic hydroxyalkyl esters such as hydroxyethyl, hydroxypropyl or hydroxybutyl acrylate or methacrylate, and compounds such as diacetoneacrylamide and acetylacetoxyethyl acrylate or methacrylate.

[0027] The choice of monomers or the choice of the proportions by weight of the monomers is preferably made in such a way that, in general, that the VAE copolymers exhibit a glass transition temperature, T_g, of from -30 to +40°C results. The glass transition temperature (Tg) of the VAE copolymers can be determined in a known way by means of differential scanning calorimetry (DSC) with a heating rate of 20°C per minute according to ASTM D3418-82 as onset temperature. The Tg may also be calculated approximately in advance by means of the Fox equation. According to Fox T.G., Bull. Am. Physics Soc. 1, 3, page 123 (1956), it holds that: $1/Tg = x1/Tg1 + x2/Tg2 + \ldots + xn/Tgn$, where xn is the mass fraction (% by weight/100) of the monomer n and Tgn is the glass transition temperature, in degrees Kelvin, of the homopolymer of the monomer n. Tg values for homopolymers are listed in Polymer Handbook, 2nd Edition, J. Wiley & Sons, New York (1975).

[0028] As noted above, the aqueous dispersion including the VAE copolymers are formed by a polymerization process. In some embodiments, the polymerization can proceed under a conventional emulsion polymerization procedure. Examples of such procedures are described in the Encyclopedia of Polymer Science and Engineering, Vol. 8 (1987), John Wiley & Sons, pages 659 to 677 and in EP 1916275 A1. In certain embodiments, the polymerization process takes place in a pressure reactor at a temperature of 50°C to 120°C. The pressure reactor can be utilized to form a mixture of water, vinyl acetate monomers, and ethylene. The mixture may also comprise additional monomers and components that will be utilized to yield the aqueous dispersion of VAE copolymers.

[0029] For example, in some embodiments, the aqueous dispersion of VAE copolymers is formed by adding an amount of initiator to the mixture. The initiator may be a redox initiator combination such as those that are customary for emulsion polymerization. However, it is preferred that the VAE copolymers be formed by initiating the polymerization with an initiator that does not contain formaldehyde-producing moieties. Examples of suitable oxidation initiators are the sodium, potassium, and ammonium salts of peroxodisulfuric acid, hydrogen peroxide, t-butyl peroxide, t-butyl hydroperoxide, potassium peroxodiphosphate, tert-butyl peroxopivalate, cumene hydroperoxide, isopropylbenzene monohydroperoxide. The stated initiators are used in general in an amount of 0.01 to 2.0% by weight, based on the total weight of the monomers.

[0030] Preferably, when utilizing an initiator to form the aqueous dispersion, a reducing agent is also utilized to form the aqueous mixture and control the reaction rate. Suitable reducing agents are the sulfites and bisulfites of the alkali metals and of ammonium, such as, for example, sodium sulfite, the derivatives of sulfoxylic acid such as zinc sulfoxylates or alkali metal formaldehyde sulfoxylates, such as, for example, sodium hydroxymethanesulfinate (Brüggolit), and (iso)ascorbic acid. In some embodiments, it is preferred to use sodium erythorbate, which is the sodium salt of (iso)ascorbic acid, as the reducing agent. The amount of reducing agent is preferably 0.015 to 3% by weight, based on the total weight of the monomers.

[0031] The stated oxidizing agents, more particularly salts of peroxodisulfuric acid, may also be used on their own as thermal initiators.

[0032] In some embodiments, the aqueous dispersion of VAE copolymers is formed in the presence of one or more surfactants. However, the addition of a surfactant is not necessary for forming the aqueous dispersion described above. In fact, in certain embodiments, it may not be preferred to add a surfactant to the polymerization. However, in some embodiments, it may be advantageous to make concomitant use of small amounts of surfactants, typically from 1 to 4% by weight, based on the total weight of the monomers utilized in the polymerization. Alternatively, one or more surfactants may be added to the aqueous dispersion after polymerization. When provided, the one or more surfactants may be used to stabilize the aqueous dispersion of VAE copolymers. In other embodiments, the one or more surfactants may be added to improve the absorbency of the nonwoven substrate or form an aqueous dispersion of VAE copolymers with a bimodal particle size distribution and lower the viscosity of the aqueous dispersion.

[0033] It is preferred that any surfactants utilized do not contain alkyl phenol ethoxylate structures and are not endocrine disruptors. Suitable surfactants may be either anionic, cationic, or nonionic surfactants. Examples of suitable anionic emulsifiers are alkyl sulfates whose chain length is from 8 to 18 carbon atoms, alkyl or alkylaryl ether sulfate having from 8 to 18 carbon atoms in the hydrophobic radical and up to 40 ethylene oxide units, alkyl- or alkylarylsulfonates having from 8 to 18 carbon atoms, esters and half-esters of sulfosuccinic acid with monohydric alcohols or alkylphenols.

[0034] Suitable nonionic surfactants include, for example, alkyl polyglycol ethers or alkylaryl polyglycol ethers having from 8 to 40 ethylene oxide units. Preferred surfactants include nonionic, ethoxylated emulsifiers with a branched or linear alkyl radical or are in the form of ethylene oxide-propylene oxide block copolymers.

[0035] Advantageously, the composition may include an aqueous dispersion of VAE copolymers that exhibit a particle size and polydispersity typical of a PVOH or surfactant stabilized aqueous dispersion. For example, the aqueous dispersion may comprise VAE copolymers that exhibit a mean particle size of 0.3 to 5 microns on a volume basis. Preferably, the VAE copolymers exhibit a mean particle size of 0.5 to 2 microns on a volume basis. In addition, the span of the particle size distribution may be 1.1 to 2.0, preferably 1.1 to 1.8. The span is defined as $(D_{v90}-D_{v10})/D_{v50}$ where D_{v90}, D_{v10} and D_{v50} are the values of the particle diameters below which 90, 10 and 50 percent of the distribution's volume lies.

The particle size can be measured by methods known in the art such as, for example, by laser light scattering using a Horiba LA-920 particle size analyzer.

[0036] The aqueous dispersion of VAE copolymers may also exhibit a high solids content. For example, the aqueous dispersion may include a solids content of 50 wt% or more based on the total weight of the aqueous dispersion. In some embodiments, the composition may have a solids content of 50 to 75 wt% based on the total weight of the aqueous dispersion. Preferably, the aqueous dispersion has a solids content of 50 to 60 wt% based on the total weight of the aqueous dispersion. The solids content of the dispersion can be calculated by known methods.

[0037] The composition also comprises a polyvinyl alcohol (PVOH) dispersion stabilizer. The PVOH dispersion stabilizer is provided to stabilize the dispersion by helping to prevent the VAE copolymers from coalescing. In an embodiment, the PVOH dispersion stabilizer is present in the composition at a level of 1 to 10 parts per 100 parts of polymer by weight. Preferably, the PVOH dispersion stabilizer is present in the composition at a level of 2 to 8 parts, or preferably 4 to 6 parts, in each case present per 100 parts of polymer by weight.

[0038] The PVOH dispersion stabilizer may comprise polyvinyl alcohols known in the art, which are suitable for use in forming the aqueous dispersion of VAE copolymers. Suitable polyvinyl alcohols include those that are partially hydrolysed or fully hydrolysed polyvinyl acetates or mixtures thereof having an average degree of hydrolysis of 80 to 99.9 mol%. Suitable polyvinyl alcohols may also include ultra-low viscosity (3-4 cP for a 4% aqueous solution), low viscosity (5-6 cP for a 4% aqueous solution), medium viscosity (22-30 cP for a 4% aqueous solution) and high viscosity (45-72 cP for a 4% aqueous solution) varieties. Ultra-low viscosity polyvinyl alcohols have a mass-average degree of polymerization of 150-300 and a weight average molecular weight of 13,000-23,000. Low viscosity polyvinyl alcohols have a mass-average degree of polymerization of 350-650 and a weight average molecular weight of 31,000-50,000. Medium viscosity polyvinyl alcohols have a mass-average degree of polymerization of 1000-1500 and a weight average molecular weight of 85,000-124,000. High viscosity polyvinyl alcohols have a mass-average degree of polymerization of 1600-2200 and a weight average molecular weight of 146,000-186,000. Preferably, the viscosity of the PVOH dispersion stabilizer is ultra-low, low or medium.

[0039] The weight average molecular weight and degree of polymerization of polyvinyl alcohol can be determined by using size exclusion chromatography / gel permeation chromatography measurement techniques. The viscosity of polyvinyl alcohol can be measured on a 4% solids aqueous solution of the polyvinyl alcohol using a Brookfield viscometer. Viscosity of a polyvinyl alcohol may be described herein with reference to a 4% aqueous polyvinyl alcohol solution at 20°C.

[0040] In certain embodiments, the PVOH dispersion stabilizer may comprise partially hydrolysed polyvinyl acetates or mixtures thereof having an average degree of hydrolysis of 80 to 96 mol%. Particular preference is given to partially hydrolysed polyvinyl acetate having an average degree of hydrolysis of 86 to 90 mol%, typically in each case having a mass-average degree of polymerization of 150 to 2200. To adjust the viscosity of the resulting polymer dispersion it may be advantageous to use mixtures of polyvinyl alcohols with different degrees of polymerization, in which case the degrees of polymerization of the individual components may be smaller or greater than the mass-average degree of polymerization, of, for example, 150 to 2200, of the mixture.

[0041] In certain embodiments, the PVOH dispersion stabilizer may comprise fully hydrolysed polyvinyl acetates, i.e., those having an average degree of hydrolysis of 96.1 to 99.9 mol%, typically in each case having an average degree of hydrolysis of 97.5 to 99.5 mol%, alone or in mixtures with partially hydrolysed polyvinyl acetates. The fully hydrolysed polyvinyl acetates mentioned above may have a mass-average degree of polymerization of 150 to 2200.

[0042] Alternatively, or in addition, in some embodiments, it may be useful to employ modified polyvinyl alcohols. For example, in some embodiments, the PVOH dispersion stabilizer may comprise a polyvinyl alcohol comprising one or more functional groups, such as, for example, one or more acetoacetyl groups. In other embodiments, the polyvinyl alcohol may comprise comonomer units. Examples of such polyvinyl alcohols include vinyl laurate-modified and VERSATIC™ acid vinyl ester-modified polyvinyl alcohols, which is available from Hexion Chemicals Company under the trade name VEOVA™ for example VEOVA™ 9 and VEOVA™ 10. Also suitable are ethylene-modified polyvinyl alcohols, which are known, for example, under the trade name EXCEVAL™ polymer, which is available from Kuraray America, Inc. The ethylene-modified polyvinyl alcohols mentioned above can be used either alone or in combination with standard unsubstituted polyvinyl alcohols. Preferred ethylene-modified polyvinyl alcohols have an ethylene fraction of up to 12 mol%, for example 1 to 7 mol%, preferably 2 to 6 mol%, and more preferably 2 to 4 mol%. Suitable ethylene-modified polyvinyl alcohols may have a mass-average degree of polymerization in each case of from 500 to 5000, preferably 2000 to 4500, and more preferably 3000 to 4000, based on molecular weight data obtained via aqueous gel permeation chromatography. Preferably, the ethylene-modified polyvinyl alcohol has an average degree of hydrolysis that is greater than 92 mol%, preferably 94.5 to 99.9 mol%, and more preferably 98.1 to 99.5 mol%. In some embodiments, it may be advantageous to use mixtures of different ethylene-modified polyvinyl alcohols. Such mixtures can be utilized alone or as part of a mixture that also comprises partially hydrolysed and/or fully hydrolysed unmodified polyvinyl alcohols.

[0043] The composition comprises a copolymer that is utilized as a crosslinker. In particular and after curing, the copolymer is crosslinked with the PVOH dispersion stabilizer and VAE copolymers. In certain embodiments, the copolymer comprises maleic anhydride units. In these embodiments, the copolymer may comprise 20 mole% maleic anhydride units or more. In some embodiments, the copolymer comprises 40 mole% or more of maleic anhydride units. In these embodiments, the copolymer may comprise up to 70 mole% of maleic anhydride units, which in all cases is based on the total monomer units of the copolymer.

[0044] When dissolved in water, maleic anhydride units are converted to maleic acid units. As such, an aqueous solution of a maleic anhydride copolymer is equivalent to an aqueous solution of a maleic acid copolymer. Thus, in some embodiments, the copolymer comprises maleic anhydride units or maleic acid units. By utilizing such a copolymer, crosslinking that enables the nonwoven substrate to exhibit a desirable tensile strength and does not generate formaldehyde can be achieved.

[0045] Preferably, the copolymer does not contain moieties that generate formaldehyde. In some embodiments, the copolymer may comprise units of styrene, vinyl ethers, vinyl acetate, (meth)acrylates and/or other unsaturated hydrocarbons such as propylene or butylene. However, in certain embodiments, it is preferred that the copolymer comprises ethylene units. In certain embodiments, the copolymer comprises ethylene maleic anhydride. An ethylene maleic anhydride copolymer may be preferred in some embodiments because of its water solubility and advantageous crosslinking functionality per weight of polymer. An ethylene maleic anhydride copolymer may be particularly preferred when the products utilizing the composition are intended for use in food contact applications. In embodiments where ethylene maleic anhydride copolymers are utilized, it is preferred that the ratio of maleic anhydride units to ethylene units is about 1:1 on a mole basis.

[0046] The composition exhibits a free formaldehyde content of 5 ppm or less. In order to achieve such low levels of formaldehyde content it is preferred that the composition does not comprise N-methylol acrylamide. N-methylol acrylamide contains unreacted formaldehyde and contributes to the formaldehyde level in an aqueous dispersion. Furthermore, depending on the test method used to measure the formaldehyde in a nonwoven substrate, N-methylol acrylamide can contribute even higher levels of formaldehyde to a nonwoven substrate. Thus, in certain embodiments, the aqueous dispersion does not comprise N-methylol acrylamide. However, in some embodiments, the aqueous dispersion can be prepared with low levels of formaldehyde if low levels of N-methylol acrylamide, especially commercially available mixtures of N-methylol acrylamide and acrylamide that are low in formaldehyde content, are used to prepare the dispersion. In such embodiments, it is preferred that the aqueous dispersion exhibits a formaldehyde content that is below 15 ppm, preferably below 10 ppm, and more preferably below 5 ppm. Alternatively, other N-methylol functional monomers that do not contain formaldehyde may be utilized in the aqueous dispersion. In embodiments where N-methylol functional monomers are utilized, the level of these monomers in the aqueous dispersion should be less than 1%, and preferably 0.5% or less, of the total monomer content in the aqueous dispersion.

[0047] Suitable N-methylol-functional monomers for making the VAE copolymers are, for example, N-methylolacrylamide (NMA), N-methylolmethacrylamide, allyl N-methylolcarbamate, the alkyl ethers, such as isobutyl ether, or esters of N-methylolacrylamide, of N-methylol-methacrylamide or of allyl N-methylolcarbamate. If it is desired to add an N-methylol functional monomer, N-methylolacrylamide and N-methylol-methacrylamide are preferred.

[0048] In some embodiments, the N-methylol-functional monomers may be provided as a mixture that includes other monomers. For example, NMA may be provided as a 48% aqueous solution of NMA and acrylamide in a 1:1 molar ratio, available commercially under the tradename CYLINK® NMA-LF monomer (Solvay, Bristol, PA). In some embodiments the NMA-LF level is selected so that the formaldehyde level of the aqueous dispersion is below 10 ppm, preferably below 5 ppm. It should also be noted that the NMA and acrylamide need not be provided as a mixture, but they can be added separately to a fed to the reactor during polymerization. Suitable amounts of NMA, relative to the total of NMA plus acrylamide, are in a range of 20 mol% to 80 mol%, or in a range of 30 mol% to 70 mol%, or 40 mol% to 60 mol%.

[0049] Preferably, when a copolymer comprising maleic anhydride units or a copolymer comprising maleic acid units is provided, vinyl acetate and ethylene are also provided. The vinyl acetate and ethylene are copolymerized in the presence of a PVOH dispersion stablizer.

[0050] The desired monomers and ethylene are directed into the reactor. All of the monomers may form an initial charge, or all of the monomers may form a feed, or portions of the monomers may form an initial charge and the remainder may form a feed after the polymerization has been initiated. The feeds may be separate (spatially and chronologically), or all or some of the components may be fed together into the reactor. In certain embodiments, a first amount of vinyl acetate monomers are directed to the reactor as an initial charge and a second amount of vinyl acetate monomers are fed to the reactor in a second amount.

[0051] Also, the desired copolymer, PVOH dispersion stablizer, and, if utilized, surfactant are directed into the reactor. In some embodiments, the copolymer may be added to the reactor when the PVOH dispersion stablizer or, if utilized, the surfactant is added to the reactor. All of the PVOH dispersion stablizer may form an initial charge, or all of the dispersion stablizer may form a feed, or portions of the dispersion stablizer may form an initial charge and the remainder may form a feed after the polymerization has been initiated. Similarly, when a surfactant is utilized, all of the surfactant may form an initial charge, or all of the surfactant may form a feed, or portions of the surfactant may form an initial charge and the remainder may form a feed after the polymerization has been initiated.

[0052] It has been surprisingly discovered that the time in which the copolymer is added impacts the wet tensile strength exhibited by the nonwoven product. Thus, in certain embodiments, the copolymer can be directed to the reactor at a desired predetermined time. For example, in an embodiment, the copolymer may be added to the reactor prior to initiating the polymerization. In this embodiment, all of the copolymer may be added to the reactor prior to initiating the polymerization, or all of the copolymer may form a feed, or portions of the copolymer may form an initial feed and the remainder may form a feed after the polymerization has been initiated. In these embodiments, the copolymer may be fed into the reactor before the first amount of the vinyl acetate monomers are provided as an initial charge. Thus, in these embodiments, the copolymer is fed into the reactor prior to forming the VAE copolymers.

[0053] In some embodiments, the copolymer is added to the reactor after initiating the polymerization. The copolymer may be added to the other components of the composition after VAE copolymers have been formed. In fact, in certain embodiments, the composition is formed by adding the copolymer to the other components of the composition after polymerization. In one such embodiment, the copolymer may be mixed with the aqueous dispersion of VAE copolymers in the reactor or in another vessel as part of a post-polymerization addition process.

[0054] The copolymer is added at a predetermined amount to form the composition. In some embodiments, the copolymer is added in an amount of 0.5 wt% or more. In other embodiments, the copolymer is added in an amount of 5 wt% or less. Preferably, the copolymer is added in an amount of 0.5 to 5 wt%. More preferably, the copolymer is added in an amount of 1 to 3 wt%. In each case, the wt% of the copolymer added is based on the total weight of the monomers in the aqueous dispersion.

[0055] In some embodiments, undesirable materials such as residual monomers may be removed by employing known methods of post-polymerization. Residual monomers may include, for example, unreacted vinyl acetate monomers. Preferably, for example, after post-polymerization, the unreacted vinyl acetate monomer content in the composition is below 1000 ppm. In certain embodiments, unreacted vinyl acetate monomers may be removed before the copolymer is added to the reactor. Unreacted vinyl acetate monomers can be removed by processes known in the art such as, for example, a stripping process. In other embodiments, post-polymerization may be initiated with a redox catalyst. Volatile residual monomers may also be removed by distillation, preferably under reduced pressure, and optionally with inert entraining gases such as air, nitrogen or steam being passed through or over the aqueous dispersion. After removing the residual monomers and other undesirables, the aqueous dispersion of VAE copolymers may be ready for use in the composition. Typically, biocides, defoamers, and potentially other additives may be added to the composition.

[0056] Preferably, the composition has a high solids content. For example, the VAE copolymers, PVOH dispersion stabilizer, and copolymer together typically comprise from 45 to 65 wt % of the composition. More typically, the composition has a solids content in the range from 50 to 60 wt%, or from 50 to 55 wt%. The solids content of the composition can be calculated by known methods.

[0057] Preferably, the composition is formed such that it exhibits a free formaldehyde content that is minimized. For example, the composition exhibits a free formaldehyde content of 5 ppm or less. The free formaldehyde content of the composition can be determined using liquid chromatography according to ASTM D5910-05.

[0058] Also, it is preferred that the composition exhibits a desirable viscosity. Preferably, the composition exhibits a Brookfield viscosity of 4000 mPa-s or less when measured at 23°C and using a no. LV-3 spindle at 60 revolutions per minute (rpm). In some embodiments, the composition may exhibit a Brookfield viscosity in the range of 50 to 4000 mPa-s when measured at 23°C and using a no. LV-3 spindle at 60 rpm. Preferably, the composition exhibits a viscosity in the range of 50 to 2000 mPa-s when measured at 23°C and using a no. LV-3 spindle at 60 rpm. More preferably, the composition exhibits a viscosity in the range of 300 to 1000 mPa-s when measured at 23°C and using a no. LV-3 spindle at 60 rpm. The viscosity of the composition can be determined utilizing commercially available viscometers such as those available from Brookfield.

[0059] Preferably, the composition is stable, which is illustrated by the relatively small change in the Brookfield viscosity exhibited by the composition over an extended period of time. In some embodiments, the Brookfield viscosity exhibited by the composition does not undergo a change of more than 60% after 75 days at 20°C. Preferably, the Brookfield viscosity exhibited by the composition does not undergo a change of more than 25% after 75 days at 20°C. More preferably, any change in the Brookfield viscosity exhibited by the composition is 10% or less after 75 days at 20°C. The Brookfield viscosity exhibited by the composition after 75 days can be determined at 23°C, using a no. LV-3 spindle at 60 rpm, and a commercially available viscometer as described above.

[0060] After forming the composition, the composition may be applied to a nonwoven substrate via any of several application methods, including but not limited to spraying, saturation, foaming and printing.

[0061] The nonwoven substrate comprises a fibrous material. The fibrous material used in the nonwoven substrate can be a natural fiber such as, for example, cellulose fiber, a synthetic fiber including but not limited to one or more of polyester, polyethylene, polypropylene and polyvinyl alcohol, or viscose fiber, or a combination of any of these, or a blend of natural and synthetic fibers. The fibrous nonwoven substrate can be produced with various methods including but not limited to airlaid, wet laid, carding, and hydroentanglement.

[0062] After applying the composition to the substrate, the substrate can be dried using a commercially available drying appratus such as, for example, an oven or utilizing another method. Drying can occur at a predetermined temperature and for a predeterimined time. Drying temperatures and times known in the art are suitable when utilizing the composition. Preferred drying temperatures and times are those that achieve maximum crosslinking, which in some embodiments may be 150°C for 2 minutes or more.

[0063] Once dried, the nonwoven product exhibits a desirable wet tensile strength. However, the specific wet tensile strength exhibited by a nonwoven product will vary between embodiments depending on, for example, the composition of the substrate and the amount of composition applied to the substrate. For example, an airlaid substrate containing 88% cellulose fibers and 12% bicomponent fibers comprising polyester with a polyethylene sheath having the composition applied at a 20% add-on, which is based on the dry composition on dry substrate by weight basis, may exhibit a wet tensile strength of 600 g/ 5 cm or more. In fact, in such an example, the nonwoven product may exhibit a wet tensile strength of 600 to 2000 g/5 cm. Methods and devices for determining the wet tensile strength known in the art are suitable for determining the tensile strength of the nonwoven product. For example, the wet tensile strength can be determined by testing in accordance with ASTM D5035-95 using a commercially available tensile tester such as an Instron model 1122.

[0064] Similarly, once dried, the nonwoven product exhibits a desirable dry tensile strength. However, the specific dry tensile strength exhibited by a nonwoven product will vary between embodiments depending on, for example, the composition of the substrate and the amount of composition applied to the substrate. For example, an airlaid substrate containing 88% cellulose fibers and 12% bicomponent fibers comprising polyester with a polyethylene sheath having the composition applied at a 20% add-on, which is based on the dry composition on dry substrate by weight basis, may exhibit a dry tensile strength of greater than 2500 g/ 5 cm. In this example, the nonwoven product may exhibit a dry tensile strength of 2500 to 6000 g/ 5 cm. Methods and devices for determining the dry tensile strength known in the art are suitable for determining the tensile strength of the nonwoven product. For example, the dry tensile strength can be determined by testing in accordance with ASTM D5035-95 using a commercially available tensile tester such as an Instron model 1122.

[0065] Preferably, once dried, the wet tensile strength exhibited by the nonwoven product is within a desirable range of the dry tensile strength exhibited. For example, in an embodiment and once dried, the nonwoven product exhibits a wet tensile strength that is 25% or more of the dry tensile strength exhibited. In some embodiments, the nonwoven product exhibits a wet tensile strength that is 25 to 60% of the dry tensile strength exhibited by the nonwoven product. Preferably, the nonwoven product exhibits a wet tensile strength that is more than 25% of the dry tensile strength exhibited by the nonwoven product. In some embodiments, it may be preferred that the nonwoven product exhibits a wet tensile strength that is 30% or more of the dry tensile strength exhibited. In these embodiments, once dried, the nonwoven product may exhibit a wet tensile strength that is 30 to 60% of the dry tensile strength exhibited. In some embodiments, once dried, the nonwoven product may exhibit a wet tensile strength that is 40% or more. In these embodiments, once dried, the nonwoven product may exhibit a wet tensile strength that is 40 to 60% of the dry tensile strength exhibited .

[0066] Additionally, the nonwoven product exhibits a formaldehyde content of 1.5 ppm or less. The formaldehyde content of the nonwoven product can be measured utilizing commercially available extraction methods such as, for example, extraction with deionized water at various pH values in accordance with ASTM D5910-96.

Examples

[0067] Examples, which are within the scope of the invention, are described below. Comparative Examples, which are not within the scope of the invention, are also described below. These examples are presented solely for the purpose of further illustrating and disclosing the embodiments of the composition and method of making the same.

Preparation and Evaluation of Composition

Formaldehyde Content:

[0068] Determination of free formaldehyde content was done using ASTM D5910-96. Viscosity:
Determination was made with a Brookfield viscometer (model DV-1) at 23°C by use of no. LV-3 spindle at 60 revolutions per minute (rpm).

Solids Content:

[0069] Determination was made using a Cenco digital moisture balance (made by the CSC Scientific company) and a 125 watt infra-red lamp. A 2-5 gram sample was placed on a pan in the Cenco moisture balance and run under the automated program.

Example 1

[0070] A mixture was formed in a pressure reactor having a capacity of one gallon by initially charging the reactor with

300.0 grams of deionized water, 486.9 grams of a 20% aqueous solution of Selvol® 205, which is a poly(vinyl alcohol) with average hydrolysis level of 88% and 4% aqueous solution Brookfield that has a viscosity of 5.2-6.2 cP and is available from Sekisui, 162.5 grams of a 10% aqueous solution of ZeMac® E60, which is an alternating copolymer of ethylene and maleic anhydride with a number average molecular weight of 30,000 and is available from Vertellus, and 2.1 grams of a 5% aqueous solution of ferrous ammonium sulfate. The pH of this mixture was 3.0. The reactor was purged with nitrogen, and 1100.0 grams of vinyl acetate was then added to the reactor with agitation (200 rpm). The reactor was purged with ethylene, the agitation was increased to 1000 rpm, and 245 grams of ethylene was added to the reactor. The temperature was increased to 32°C, and 7.3 grams of a 4.75% aqueous sodium erythorbate solution was added to the reactor. The reactor contents were allowed to equilibrate. A 1.50% aqueous solution of hydrogen peroxide and a 4.75% aqueous solution of sodium erythorbate were both continuously fed to the reactor at a rate of 0.20 g/min. After the polymerization initiated, which was indicated by a 1°C rise in temperature, an additional 278.0 grams of vinyl acetate was continuously metered to the reactor over 90 minutes at a rate of 3.09 grams/minute, and the reactor temperature was increased to 85°C over 60 minutes. During the polymerization, the flow rates of the hydrogen peroxide and sodium erythorbate feeds were maintained at an approximately 1:1 ratio and the flows were adjusted so that the 85°C reaction temperature was maintained. The polymerization was conducted for approximately 3.5 hours until no further heat of polymerization was released and the vinyl acetate level was below 1.5%. After 3.5 hours, the hydrogen peroxide and sodium erythorbate feeds were stopped, the reactor was cooled to 50°C, and the reaction mixture was transferred to a degasser to remove unreacted ethylene. A mixture of 1.5 grams of Foamaster® VF defoamer, which is available from BASF, and 10.0 grams of water were added to inhibit foam formation during transfer. To reduce unreacted vinyl acetate monomer below 0.1%, 25.0 grams of an 8.0% aqueous sodium erythorbate solution and 20.0 grams of an 8.0% aqueous *tert*-butyl hydroperoxide solution were both added continuously to the degasser contents over 15 minutes. The composition of Example 1 had solid content of 53.7%, a pH of 3.9, and a Brookfield viscosity of 654 mPa-s. The residual vinyl acetate level in the composition was < 1000 ppm and the composition had a measured grit level, after passing through a 100 mesh (149 μm) screen, of 25 ppm. The composition of Example 1 was formed so that the copolymer of ethylene and maleic anhydride was present in an amount of 1 wt%, the wt% of copolymer being based on the total weight of the monomers in the composition.

Example 2

[0071] A mixture was formed in a pressure reactor having a capacity of one gallon by initially charging the reactor with 200.0 grams of deionized water, 486.9 grams of a 20% aqueous solution of Selvol® 205, and 324.6 grams of a 10% aqueous solution of ZeMac® E60. The pH of this mixture was adjusted to 3.4 with 24.5 grams of a 10% aqueous solution of sodium hydroxide, and 2.1 grams of a 5% aqueous solution of ferrous ammonium sulfate was added. The reactor was purged with nitrogen, and 1100.0 grams of vinyl acetate was then added to the reactor with agitation (200 rpm). The reactor was purged with ethylene, the agitation was increased to 1000 rpm, and 245 grams of ethylene was added to the reactor. The temperature was increased to 32°C, and 7.3 grams of a 4.75% aqueous sodium erythorbate solution was added to the reactor. The reactor contents were allowed to equilibrate. A 1.50% aqueous solution of hydrogen peroxide and a 4.75% aqueous solution of sodium erythorbate were both continuously fed to the reactor at a rate of 0.20 grams/minute. After the polymerization initiated, indicated by a 1°C rise in temperature, an additional 278.0 grams of vinyl acetate was continuously metered to the reactor over 90 minutes at a rate of 3.09 grams/minute, and the reactor temperature was increased to 85°C over 60 minutes. During the polymerization, the flow rates of the hydrogen peroxide and sodium erythorbate feeds were maintained at an approximately 1:1 ratio and the flows were adjusted so that the 85°C reaction temperature was maintained. The polymerization was carried on until no further heat of polymerization was released and the vinyl acetate level was below 1.5%, approximately 3.5 hours. After 3.5 hours, the hydrogen peroxide and sodium erythorbate feeds were stopped, the reactor was cooled to 50°C, and the reaction mixture was transferred to a degasser to remove unreacted ethylene. A mixture of 1.5 grams of Foamaster® VF defoamer and 10.0 grams of water were added to inhibit foam formation during transfer. To reduce unreacted vinyl acetate monomer below 0.1%, 25.0 grams of an 8.0% aqueous sodium erythorbate solution and 20.0 grams of an 8.0% aqueous *tert*-butyl hydroperoxide solution were both added continuously over 15 minutes. The composition of Example 2 had solid content of 51.2%, a pH of 3.8, and a Brookfield viscosity of 1308 mPa-s. The residual vinyl acetate level of the composition was < 1000 ppm and the composition had a measured grit level, after passing through a 100 mesh (149 μm) screen, of 26 ppm. The composition of Example 2 was formed so that the copolymer of ethylene and maleic anhydride was present in an amount of 2 wt%, the wt% of copolymer being based on the total weight of the monomers in the composition.

Preparation of Examples 3, 4, and 5

[0072] A mixture was formed in a pressure reactor having a capacity of one gallon by initially charging the reactor with 430.0 grams of deionized water and 487.5 grams of a 20% aqueous solution of Selvol® 205. The pH of this mixture was adjusted to 3.2 with 4.4 grams of a 50% aqueous solution of phosphoric acid, and 2.1 grams of a 5% aqueous solution of ferrous ammonium sulfate was added. The reactor was purged with nitrogen, and 1144.0 grams of vinyl acetate was then added to the reactor with agitation (200 rpm). The reactor was purged with ethylene, the agitation was increased to 1000 rpm, and 195 grams of ethylene was added to the reactor. The temperature was increased to 32°C, and 7.3 grams of a 4.75% aqueous sodium erythorbate solution was added to the reactor. The reactor contents were allowed to equilibrate. A 1.50% aqueous solution of hydrogen peroxide and a 4.75% aqueous solution of sodium erythorbate were both continuously fed to the reactor at a rate of 0.20 grams/minute. After the polymerization was initiated, which was indicated by a 1°C rise in temperature, an additional 286.0 grams of vinyl acetate was continuously metered to the reactor over 90 minutes at a rate of 3.18 grams/minute, and the reactor temperature was increased to 85°C over 50 minutes. During the polymerization, the flow rates of the hydrogen peroxide and sodium erythorbate feeds were maintained at an approximately 1:1 ratio and the flows were adjusted so that the 85°C reactor temperature was maintained. The polymerization was carried on for approximately 3.5 hours until no further heat of polymerization was released and the vinyl acetate level was below 1.5%. After 3.5 hours, the hydrogen peroxide and sodium erythorbate feeds were stopped, the reactor was cooled to 50°C, and the reaction mixture was transferred to a degasser to remove unreacted ethylene. A mixture of 1.5 grams of Foamaster® VF defoamer and 10.0 grams of water were added to inhibit foam formation during transfer. To reduce unreacted vinyl acetate monomer below 0.1%, 25.0 grams of an 8.0% aqueous sodium erythorbate solution and 20.0 grams of an 8.0% aqueous tert-butyl hydroperoxide solution were both added continuously over 15 minutes. The aqueous dispersion of VAE copolymers obtained had solid content of 52.0%, a pH of 5.0 and a Brookfield viscosity (60 rpm) of 248 mPa-s. The residual vinyl acetate level was < 1000 ppm. The measured grit level, after passing through a 100 mesh (149 μm) screen, was 37 ppm.

Examples 3, 4, and 5

[0073] Compositions, which are referred to below as Examples 3, 4, and 5, were formed by mixing samples of the aqueous dispersion of VAE copolymers with different amounts of a 10% aqueous solution of poly(ethylene-co-maleic anhydride). The composition of Example 3 comprised the aqueous dispersion of VAE copolymers and an amount of the 10% aqueous solution of poly(ethylene-co-maleic anhydride) so that the copolymer was present in an amount of 1 wt%. The composition of Example 4 comprised the aqueous dispersion of VAE copolymers and an amount of the 10% aqueous solution of poly(ethylene-co-maleic anhydride) so that the copolymer was present in an amount of 2 wt%. The composition of Example 5 comprised the aqueous dispersion of VAE copolymers and an amount of the 10% aqueous solution of poly(ethylene-co-maleic anhydride) so that the copolymer was present in an amount of 3 wt%. In each of Examples 3-5, the wt% of the poly(ethylene-co-maleic anhydride) is based on the total weight of the monomers in the composition.

[0074] A comparative example, Comparative Example 1, will be referred to below, which is a sample of the aqueous dispersion of VAE copolymers utilized to form the compositions of Examples 3-5 that does not contain any copolymer comprising maleic anhydride units or copolymer comprising maleic acid units.

[0075] Table 1, provided below, lists the free formaldehyde content of certain Examples and Comparative Examples 1-2, which is commercially available composition comprising vinyl acetate-ethylene-acrylamide-N-methylol acrylamide polymers having a glass transition temperature (onset) in the range of 7-13°C. The composition is sold under the name Vinnapas® 192 available from Wacker Chemical Corporation.

Table 1

Composition	Formaldehyde (ppm)
Example 2	3.5
Example 4	1.3
Comparative Example 1	3.98
Comparative Example 2	49.7

[0076] As shown in Table 1, the compositions of Examples 2 and 4 each exhibit a free formaldehyde content of less than 5 ppm. In stark contrast, the composition of Comparative Example 2 exhibits a free formaldehyde content of more than 45 ppm.

[0077] Additionally, the stability of Examples 1-4 was measured by way of measuring the change in the Brookfield viscosity exhibited by each composition after 75 days, at 20°C, using a no. LV-3 spindle at 60 rpm, and a Brookfield viscometer (model DV-1). The change the Brookfield viscosity exhibited by the compositions of Examples 1-4 is shown below in Table 2.

Table 2

Composition	Change in Viscosity (%)
Example 1	8
Example 2	5
Example 3	25
Example 4	53

[0078] As shown in Table 2, each of the compositions of Examples 1-4 does not undergo a change in Brookfield viscosity of more than 60% after 75 days at 20°C. In fact, the Brookfield viscosity exhibited by the compositions of Examples 1-3 does not undergo a change of more than 25% after 75 days at 20°C. More preferably, the change in Brookfield viscosity exhibited by the compositions of Examples 1-2 was less than 10% after 75 days at 20°C.

Comparative Example 3

[0079] A mixture was formed in a pressure reactor having a capacity of one gallon by way of an initial charge of 385.0 grams of deionized water, 9.0 grams of a surfactant stabilizer sold under the name Aerosol® MA80I, which is an 80% aqueous solution of sodium di(1,3-dimethylbutyl) sulfosuccinate and available from Solvay USA, and 390.0 grams of a 10% aqueous solution of ZeMac® E60. The pH of the mixture was adjusted to 3.2 with 23.6 grams of a 10% aqueous solution of sodium hydroxide, and 2.0 grams of a 5% aqueous solution of ferrous ammonium sulfate was added. The reactor was purged with nitrogen, and 263.0 grams of vinyl acetate was then added to the reactor with agitation (200 rpm). The reactor was purged with ethylene, the agitation was increased to 900 rpm, and 195 grams of ethylene was added to the reactor. The temperature was increased to 55°C. The reactor contents were allowed to equilibrate. An aqueous mixture of sodium persulfate (4.50%) and sodium bicarbonate (2.00%) along with a 2.03% aqueous solution of sodium erythorbate were both continuously fed to the reactor at a rate of 0.40 grams/minute. After the polymerization initiated, indicated by a 1°C rise in temperature, an additional 1492.0 grams of vinyl acetate and 500.0 grams of a solution consisting of 383.1 grams of deionized water, 19.5 grams of AMPS® 2403, which is a 50 % aqueous solution of sodium 2-acrylamide-2 methylpropanesulfonate and available from Lubrizol Corporation, and 97.4 grams of Rhodasurf® TLA3040, which is a 40% aqueous solution of an ethoxylated tridecyl alcohol with ca. 30 units of ethylene oxide and available from Solvay USA, were both continuously metered to the reactor over 120 minutes at rates of 12.43 grams/minute and 4.17 grams/minute, respectively. In addition, the reactor temperature was increased to 85°C over 30 minutes. During the polymerization, the flow rates of the sodium persulfate and sodium erythorbate feeds were maintained at an approximately 1:1 ratio and the flows were adjusted so that the 85°C reaction temperature was maintained. The polymerization was carried on until no further heat of polymerization was released and the vinyl acetate level was below 1.5%, approximately 3.25 hours. After 3.25 hours, the sodium persulfate/sodium bicarbonate and sodium erythorbate feeds were stopped, the reaction was cooled to 50°C and the reaction mixture was transferred to a degasser to remove unreacted ethylene. A mixture of 1.0 g of Rhodoline® 670 defoamer, which is available from Solvay USA, and 10.0 grams of water were added to inhibit foam formation during the transfer. To reduce unreacted vinyl acetate monomer below 0.1%, 2.0 grams sodium erythorbate dissolved in 20.0 grams of deionized water and 2.5 grams of tert-butyl hydroperoxide dissolved in 30.0 grams of deionized water were both added to the dispersion. The aqueous dispersion of VAE copolymers obtained had solid content of 54.8 %, a pH of 3.4 and a Brookfield viscosity (60 rpm) of 390 mPa-s. The residual vinyl acetate level was < 1000 ppm. The measured grit level, after passing through a 100 mesh (149 μm) screen, was 48 ppm.

Comparative Example 4

[0080] Comparative Example 4 was formed in a manner similar to Comparative Example 3, except that the 10% aqueous solution of ZeMac® E60 was not added to the reactor prior to forming an aqueous dispersion of VAE copolymers. Instead, for Comparative Example 4, a sample of the aqueous dispersion of VAE copolymers was mixed with an amount of a 10% aqueous solution of poly(ethylene-co-maleic anhydride) so that the copolymer was present in an amount of 2 wt%, which is based on the total weight of the monomers in the composition.

Preparation and Evaluation of Nonwoven Products

[0081] Nonwoven products were then formed by treating a nonwoven substrate with one of the compositions of Examples 1-5 and Comparative Examples 1-4. The nonwoven products formed utilizing the composition of Examples 1-5 are referred to below as Examples 1A-5A and the nonwoven products formed utilizing Comparative Examples 1-4 are referred to below as Comparative Examples 1A-4A.

[0082] To form Examples 1A-5A and Comparative Examples 1A-4A, the composition of a particular Example or Comparative Example was sprayed on an airlaid substrate containing 88% cellulose fibers and 12% bicomponent fibers comprising polyester with a polyethylene sheath. Each composition was applied to the airlaid substrate at a 20% add-on, which is based on the dry composition on dry substrate by weight basis. After the spray application, the nonwoven products were cured in the oven at 150°C for 2.5 minutes and allowed to condition at 72°F and 50% humidity for 24 hours.

[0083] Each Example and Comparative Example was tested for wet tensile strength by submerging the nonwoven product in water and 1% surfactant mixture before being tested in the cross-direction using an Instron model 1122. Also, each Example and Comparative Example was tested for dry tensile strength in the cross-direction using an Instron model 1122. Table 3, provided below, lists the dry tensile strength and wet tensile strength of each Example and Comparative Example. The dry tensile strength and wet tensile strength are each reported in Table 3 in g/ 5 cm. The relationship between the wet tensile strength and the dry tensile strength is reported as a percentage in a separate column labelled "Wet/Dry." The free formaldehyde content of certain Examples and Comparative Examples is also provided in Table 3.

Table 3

Nonwoven Product	Composition applied to nonwoven substrate	Dry Tensile Strength	Wet Tensile Strength	Wet/Dry	Formaldehyde (ppm)
Comparative Example 1A	Comparative Example 1	4011	572	14	1.4
Comparative Example 2A	Comparative Example 2	4500	1950	43	14.8
Comparative Example 3A	Comparative Example 3	3407	864	25	--
Comparative Example 4A	Comparative Example 4	2975	548	18	--
Example 1A	Example 1	3619	1360	38	--
Example 2A	Example 2	4068	1872	46	1.4
Example 3A	Example 3	3827	1048	27	--
Example 4A	Example 4	3531	1384	39	1.3
Example 5A	Example 5	3868	1689	44	--

[0084] As shown in Table 3, the compositions of Examples 2A and 4A each exhibit a free formaldehyde content of less than 1.5 ppm. In stark contrast, the composition of Comparative Example 2A exhibits a free formaldehyde content of more than 10 ppm. Furthermore, as illustrated in Table 3, treating a nonwoven substrate with the compositions of Examples 1-5 enables the resulting nonwoven product to exhibit a desirable dry tensile strength and wet tensile strength. Thus, all of the nonwoven products of Examples 1A-5A had a wet tensile strength that was more than 25% of the dry tensile strength exhibited thereby. In fact, the composition of Example 2 enabled the nonwoven product of Example 2A to exhibit a wet tensile strength that was 96% of the wet tensile strength exhibited by the nonwoven product of Comparative Example 2A.

[0085] Further, Examples 2A and 4A and Comparative Examples 3A-4A illustrate the impact of utilizing the polyvinyl alcohol dispersion stabilizer in forming the composition that is utilized in the nonwoven product. For example, Example 2A and Comparative Example 3A were each formed utilizing a composition where the copolymer was present in an amount of 2 wt%, which is based on the total weight of the monomers in the composition. However, the composition of Example 2 utilized a polyvinyl alcohol dispersion stabilizer, whereas, in the composition of Comparative Example 3, the aqueous dispersion of VAE copolymers was surfactant stabilized. As illustrated in Table 3, the use of the polyvinyl alcohol dispersion stabilizer of the the nonwoven product of Example 2A exhibited a wet tensile strength that was over 200% greater than the wet tensile strength exhibited by the nonwoven product of Comparative Example 3A. A similar result is observed when comparing Example 4A with Comparative Example 4A, which each included the use of compositions where the copolymer was mixed with the aqueous dispersion of VAE copolymers to form the composition.

[0086] From the foregoing detailed description, it will be apparent that various modifications, additions, and other alternative embodiments are possible without departing from the scope of the claims.

[0087] The embodiments discussed herein were chosen and described to provide the best illustration of the principles of the invention and its practical application to thereby enable one of ordinary skill in the art to use the invention in various embodiments and with various modifications as are suited to the particular use contemplated. As should be appreciated, all such modifications and variations are within the scope of the invention.

Claims

1. A crosslinkable stabilized composition for a nonwoven substrate, comprising:
an aqueous dispersion of vinyl acetate-ethylene copolymers, a polyvinyl alcohol dispersion stabilizer, and a copolymer comprising maleic anhydride units or a copolymer comprising maleic acid units, wherein the composition exhibits a free formaldehyde content of 5 ppm or less.

2. The crosslinkable stabilized composition of claim 1, wherein the composition exhibits a viscosity of 4000 mPa-s or less when measured at 23°C and using a no. LV-3 spindle at 60 revolutions per minute.

3. The crosslinkable stabilized composition of claim 1, wherein the copolymer further comprises ethylene units.

4. The crosslinkable stabilized composition of claim 1, wherein the composition does not comprise N-methylol acrylamide.

5. The crosslinkable stabilized composition of claim 1, wherein composition comprises the copolymer in an amount of 0.5 wt% or more based on the total weight of monomers in the aqueous dispersion.

6. The crosslinkable stabilized composition of claim 1, wherein the polyvinyl alcohol dispersion stabilizer comprises a partially hydrolysed polyvinyl acetate having an average degree of hydrolysis of 80 to 96 mol%.

7. The crosslinkable stabilized composition of claim 2, wherein the composition exhibits a viscosity of 200 to 4000 mPa-s when measured at 23°C and using a no. LV-3 spindle at 60 revolutions per minute.

8. The crosslinkable stabilized composition of claim 2, wherein the viscosity exhibited by the composition does not undergo a change of more than 60% after 75 days at 20°C.

9. The crosslinkable stabilized composition of claim 3, wherein the copolymer comprises ethylene maleic anhydride polymers.

10. The crosslinkable stabilized composition of claim 8, wherein the viscosity exhibited by the composition does not undergo a change of more than 25% after 75 days at 20°C.

11. Process for preparing a crosslinkable stabilized composition for a nonwoven substrate, comprising:

    providing a copolymer comprising maleic anhydride units or a copolymer comprising maleic acid units;
    providing vinyl acetate and ethylene;
    polymerizing vinyl acetate and ethylene in the presence of a polyvinyl alcohol dispersion stablizer to form vinyl acetate-ethylene copolymers; and
    forming a composition comprising the vinyl acetate-ethylene copolymers and that has a formaldehyde level of 5 ppm or less.

12. The process of claim 11, wherein the vinyl acetate-ethylene copolymers are provided in an aqueous dispersion that is formed by emulsion polymerization.

13. The process of claim 11, wherein the copolymer is mixed with the polyvinyl alcohol dispersion stablizer prior to forming the vinyl acetate-ethylene copolymers.

14. The process of claim 11, wherein the copolymer is provided in an amount of 0.5 wt% or more based on total weight of monomers in the aqueous dispersion.

15. The process of claim 11, wherein the composition exhibits a viscosity of 50 to 4000 mPa-s when measured at 23°C and using a no. LV-3 spindle at 60 revolutions per minute.

16. The process of claim 11, wherein the copolymer further comprises ethylene units.

17. The process of claim 12, further comprising mixing the copolymer with the aqueous dispersion to form the composition.

18. The process of claim 14, wherein the copolymer is provided in an amount of 0.5 to 5 wt% based on total weight of monomers in the aqueous dispersion.

19. A nonwoven product, comprising:
a nonwoven substrate treated with the composition of claim 1, wherein the nonwoven product exhibits a wet tensile strength that is 25% or more of a dry tensile strength exhibited and a formaldehyde content of 1.5 ppm or less.

20. The nonwoven product of claim 19, wherein the copolymer and vinyl acetate-ethylene copolymers are crosslinked.

Patentansprüche

1. Vernetzbare stabilisierte Zusammensetzung für ein Vliessubstrat, umfassend:
eine wässrige Dispersion von Vinylacetat-Ethylen-Copolymeren, einen Polyvinylalkohol-Dispersionsstabilisator und ein Maleinsäureanhydrid-Einheiten enthaltendes Copolymer oder ein Maleinsäure-Einheiten enthaltendes Copolymer, wobei die Zusammensetzung einen Gehalt an freiem Formaldehyd von 5 ppm oder weniger aufweist.

2. Vernetzbare stabilisierte Zusammensetzung nach Anspruch 1, wobei die Zusammensetzung eine Viskosität von 4000 MPa-s oder weniger bei Messung bei 23 °C und unter Verwendung einer Spindel Nr. LV-3 bei 60 Umdrehungen pro Minute aufweist.

3. Vernetzbare stabilisierte Zusammensetzung nach Anspruch 1, wobei das Copolymer ferner Ethylen-Einheiten umfasst.

4. Vernetzbare stabilisierte Zusammensetzung nach Anspruch 1, wobei die Zusammensetzung kein N-Methylolacrylamid umfasst.

5. Vernetzbare stabilisierte Zusammensetzung nach Anspruch 1, wobei die Zusammensetzung das Copolymer in einer Menge von 0,5 Gew.-% oder mehr, bezogen auf das Gesamtgewicht der Monomere in der wässrigen Dispersion, umfasst.

6. Vernetzbare stabilisierte Zusammensetzung nach Anspruch 1, wobei der Polyvinylalkohol-Dispersionsstabilisator ein teilhydrolysiertes Polyvinylacetat mit einem durchschnittlichen Hydrolysegrad von 80 bis 96 Mol-% umfasst.

7. Vernetzbare stabilisierte Zusammensetzung nach Anspruch 2, wobei die Zusammensetzung eine Viskosität von 200 bis 4000 MPa-s bei Messung bei 23 °C und unter Verwendung einer Spindel Nr. LV-3 bei 60 Umdrehungen pro Minute aufweist.

8. Vernetzbare stabilisierte Zusammensetzung nach Anspruch 2, wobei sich die Viskosität, die die Zusammensetzung zeigt, nach 75 Tagen bei 20 °C um nicht mehr als 60 % ändert.

9. Vernetzbare stabilisierte Zusammensetzung nach Anspruch 3, wobei das Copolymer Ethylen-Maleinsäureanhydrid-Polymere umfasst.

10. Vernetzbare stabilisierte Zusammensetzung nach Anspruch 8, wobei sich die Viskosität, die die Zusammensetzung zeigt, nach 75 Tagen bei 20 °C um nicht mehr als 25 % ändert.

11. Verfahren zur Herstellung einer vernetzbaren stabilisierten Zusammensetzung für ein Vliessubstrat, umfassend:

Bereitstellen eines Copolymers, das Maleinsäureanhydrid-Einheiten umfasst, oder eines Copolymers, das Maleinsäure-Einheiten umfasst;
Bereitstellen von Vinylacetat und Ethylen;
Polymerisieren von Vinylacetat und Ethylen in Gegenwart eines Polyvinylalkohol-Dispersionsstabilisators zu Vinylacetat-Ethylen-Copolymeren; und
Bilden einer Zusammensetzung, die die Vinylacetat-Ethylen-Copolymere umfasst und die einen Formaldehydgehalt von 5 ppm oder weniger aufweist.

12. Verfahren nach Anspruch 11, wobei die Vinylacetat-Ethylen-Copolymere in einer wässrigen Dispersion bereitgestellt werden, die durch Emulsionspolymerisation gebildet wird.

13. Verfahren nach Anspruch 11, wobei das Copolymer vor der Bildung der Vinylacetat-Ethylen-Copolymere mit dem Polyvinylalkohol-Dispersionsstabilisator gemischt wird.

14. Verfahren nach Anspruch 11, wobei das Copolymer in einer Menge von 0,5 Gew.-% oder mehr, bezogen auf das Gesamtgewicht der Monomere in der wässrigen Dispersion, bereitgestellt wird.

15. Verfahren nach Anspruch 11, wobei die Zusammensetzung eine Viskosität von 50 bis 4000 MPa-s oder weniger bei Messung bei 23 °C und unter Verwendung einer Spindel Nr. LV-3 bei 60 Umdrehungen pro Minute aufweist.

16. Verfahren nach Anspruch 11, wobei das Copolymer ferner Ethylen-Einheiten umfasst.

17. Verfahren nach Anspruch 12, ferner umfassend das Mischen des Copolymers mit der wässrigen Dispersion zur Bildung der Zusammensetzung.

18. Verfahren nach Anspruch 14, wobei das Copolymer in einer Menge von 0,5 bis 5 Gew.-%, bezogen auf das Gesamtgewicht der Monomere in der wässrigen Dispersion, bereitgestellt wird.

19. Vliesprodukt, umfassend:
ein mit der Zusammensetzung nach Anspruch 1 behandeltes Vliessubstrat, wobei das Vliesprodukt eine Nasszugfestigkeit, die 25 % oder mehr einer gezeigten Trockenzugfestigkeit beträgt, und einen Formaldehydgehalt von 1,5 ppm oder weniger aufweist.

20. Vliesprodukt nach Anspruch 19, wobei das Copolymer und Vinylacetat-Ethylen-Copolymere vernetzt sind.

Revendications

1. Composition stabilisée réticulable pour un substrat non tissé, comprenant :
une dispersion aqueuse de copolymères d'acétate de vinyle-éthylène, un stabilisant de dispersion de poly(alcool vinylique), et un copolymère comprenant des motifs d'anhydride maléique ou un copolymère comprenant des motifs d'acide maléique, dans laquelle la composition présente une teneur en formaldéhyde libre de 5 ppm ou moins.

2. Composition stabilisée réticulable selon la revendication 1, dans laquelle la composition présente une viscosité de 4 000 mPa-s ou moins lorsqu'elle est mesurée à 23 °C et en utilisant une broche n° LV-3 à 60 tours par minute.

3. Composition stabilisée réticulable selon la revendication 1, dans laquelle le copolymère comprend en outre des motifs d'éthylène.

4. Composition stabilisée réticulable selon la revendication 1, dans laquelle la composition ne comprend pas de N-méthylol acrylamide.

5. Composition stabilisée réticulable selon la revendication 1, dans laquelle la composition comprend le copolymère en une quantité de 0,5 % en poids ou plus par rapport au poids total de monomères dans la dispersion aqueuse.

6. Composition stabilisée réticulable selon la revendication 1, dans laquelle le stabilisant de dispersion de poly(alcool vinylique) comprend un poly(acétate de vinyle) partiellement hydrolysé ayant un degré moyen d'hydrolyse de 80 à 96 % en moles.

7. Composition stabilisée réticulable selon la revendication 2, dans laquelle la composition présente une viscosité de 200 à 4 000 mPa-s lorsqu'elle est mesurée à 23 °C et en utilisant une broche n° LV-3 à 60 tours par minute.

8. Composition stabilisée réticulable selon la revendication 2, dans laquelle la viscosité présentée par la composition ne subit pas un changement de plus de 60 % après 75 jours à 20 °C.

9. Composition stabilisée réticulable selon la revendication 3, dans laquelle le copolymère comprend des polymères d'éthylène anhydride maléique.

10. Composition stabilisée réticulable selon la revendication 8, dans laquelle la viscosité présentée par la composition ne subit pas un changement de plus de 25 % après 75 jours à 20 °C.

11. Procédé de préparation d'une composition stabilisée réticulable pour un substrat non tissé, comprenant :

la fourniture d'un copolymère comprenant des motifs d'anhydride maléique ou d'un copolymère comprenant des motifs d'acide maléique ;
la fourniture d'acétate de vinyle et d'éthylène ;
la polymérisation d'acétate de vinyle et d'éthylène en présence d'un stabilisant de dispersion de poly(alcool vinylique) pour former des copolymères d'acétate de vinyle-éthylène ; et
la formation d'une composition comprenant les copolymères d'acétate de vinyle-éthylène et qui présente un taux de formaldéhyde de 5 ppm ou moins.

12. Procédé selon la revendication 11, dans lequel les copolymères d'acétate de vinyle-éthylène sont fournis dans une dispersion aqueuse qui est formée par polymérisation en émulsion.

13. Procédé selon la revendication 11, dans lequel le copolymère est mélangé avec le stabilisant de dispersion de poly(alcool vinylique) avant de former les copolymères d'acétate de vinyle-éthylène.

14. Procédé selon la revendication 11, dans lequel le copolymère est fourni en une quantité de 0,5 % en poids ou plus par rapport au poids total des monomères dans la dispersion aqueuse.

15. Procédé selon la revendication 11, dans lequel la composition présente une viscosité de 50 à 4 000 mPa-s lorsqu'elle est mesurée à 23 °C et en utilisant une broche n° LV-3 à 60 tours par minute.

16. Procédé selon la revendication 11, dans lequel le copolymère comprend en outre des motifs d'éthylène.

17. Procédé selon la revendication 12, comprenant en outre le mélange du copolymère avec la dispersion aqueuse pour former la composition.

18. Procédé selon la revendication 14, dans lequel le copolymère est fourni en une quantité de 0,5 à 5 % en poids par rapport au poids total de monomères dans la dispersion aqueuse.

19. Produit non tissé, comprenant :

un substrat non tissé traité par la composition selon la revendication 1, dans lequel le produit non tissé présente une résistance à la traction à l'état humide qui est de 25 % ou plus d'une résistance à la traction à l'état sec présentée et une teneur en formaldéhyde de 1,5 ppm ou moins.

20. Produit non tissé selon la revendication 19, dans lequel le copolymère et les copolymères d'acétate de vinyle-éthylène sont réticulés.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 2013085764 A **[0005]**
- EP 1916275 A1 **[0028]**

Non-patent literature cited in the description

- **FOX T.G**. *Bull. Am. Physics Soc*, 1956, vol. 1 (3), 123 **[0027]**
- Polymer Handbook. J. Wiley & Sons, 1975 **[0027]**
- Encyclopedia of Polymer Science and Engineering. John Wiley & Sons, 1987, vol. 8, 659-677 **[0028]**