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(54) **Nonwoven fabric with an acrylate interpolymer binder and a process of making the nonwoven fabric.**

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Description

The present invention concerns nonwoven fabrics, i.e., those fabrics composed of loosely assembled fibers either bound chemically, thermally, or through fiber entanglements, forming an interlocking web of fibers to make a fabric. In particular, the present invention concerns loosely assembled fibers saturated, coated, sprayed, or otherwise treated with an acrylate interpolmer, which gives a unique balance of physical properties including, but not limited to, a "soft hand", high resilience, low temperature flexibility and good dry, wet, and solvent properties.

10 Prior Art

Non-woven fabrics have distinct features and advantages over woven fabrics and can be prepared using anyone of a variety of processes. For example, chemically bonded nonwoven fabrics can be formed by impregnating, printing, or otherwise coating a loosely assembled web of fibers with a binder such as an acrylate interpolmer. Thermally bonded nonwovens can be bound by choosing fibers that will fuse onto other fibers in the web when the web is subjected to heat and/or pressure and/or sonic energy. Nonwovens produced by entangling the fibers can have strength and integrity without any thermal or chemical bonding. Entangling techniques include hydraulic methods, needle punching methods, and arrangement of spun filaments. Generally thermally bonded or entangled nonwovens will have strength and integrity but will lack resiliency. Chemically bonded nonwovens will have a degree of resilience dependent upon the resilience of the binder and the strength of interaction between the fibers.

The length and type of fibers employed depend upon the end use. For example, cotton or cellulose fibers useful in paper applications are typically less than 1 millimeter to 10 millimeters in length. Nonwoven textile fibers are generally from about 10 millimeters to 75 millimeters in length. Also a continuous filament fiber can be employed. They may be composed of synthetic fibers such as polyester, rayon, dacron, nylon, etc., or natural fibers such as cotton, wool, or the like. The nonwoven fabric can be manufactured by conventional techniques such as spinning, carding, garnetting, air laying, wet laying, or other known process.

In many end use nonwoven applications, it is desirable to produce soft fabrics having good wet, dry, and solvent properties. In chemically bonded nonwovens, the binder and the fiber type(s) are important factors in producing the soft fabric characteristics, the durability, and the wet, dry, and solvent strength properties. In some end use applications, resiliency of the nonwoven fabric is desired along with the above mentioned properties. A clothing interliner is an example of a chemically bonded nonwoven application where the balance of soft hand, durability, resilience, and strength properties is highly desirable.

Thermally bonded nonwovens, although possessing strength and durability due to the fusion of fibers in a web, will generally lack resiliency. The present invention relative to thermally bonded nonwovens can impart resiliency while maintaining or improving the "hand" characteristics of the finished material. Similarly, untreated, entangled materials will have strength and durability but lack resiliency. The present invention relative to entangled nonwovens can provided a balance of resiliency and soft "hand".

In other applications, especially those pertaining to paper or cellulose fibers, resiliency is less important, while strength, tear resistance and fold endurance are generally more important. Strongly interacting fibers, such as cellulose, limit resiliency. The present invention relative to such chemically bonded nonwovens demonstrates a balance of properties not found in the prior art.

EP-A-0 021 693 discloses a process for maleing a non-woven fabric which comprises bringing together fibers and a binder composition comprising a polymer polymerized from a monomer mixture, said composition being substantially free of crosslinking compounds.

WO 86/01519 discloses an aqueous emulsion of a thermally self-crosslinkable copolymer having a molecular weight in the range of 50 000 to 10 000 000, a second order transition temperature in the range of -50 °C to 30 °C and useful in treating textiles comprising 0.5 to 3 % by weight of itaconic acid, 2 to 12 % by weight of glycidyl methacryl acrylate, 1 to 7 % by weight of N-methylol acryl amide or N-methylol methacryl amide, 35 to 96.5 % by weight of ethyl acrylate, and at least one compatible monoethylenically unsaturated monomer.

SUMMARY OF THE INVENTION

The present invention relates to the combination of a unique acrylic latex binder and fibers thus forming a nonwoven fabric. In particular, the latex of the present invention may be applied to fibers as a coating, binder or impregnant, or otherwise deposited on the fibers. The present invention also relates to a process

of making this combination of the unique latex and fibers.

Specifically, the present invention pertains to a non-woven fibrous material comprising fibers bonding together with a binder consisting essentially of predominantly acrylate-containing polymer chains including repeated units derived from itaconic acid and up to 98.9 weight parts of an acrylate represented by the structure



wherein

- R₁ is hydrogen or methyl;
 R₂ represents C₁-C₂₀ alkyl, C₂-C₇ alkoxy alkyl, C₂-C₇ alkoxy thioalkyl, a cyano alkyl radical having 2 to 12 carbon atoms, or a mixture thereof;

said itaconic acid is present in the range from 1 to 20 weight parts; at least 40 weight parts of said acrylate in said polymer is present as an alkyl acrylate; said polymer in an aqueous emulsion form as suitable applied in the fabric at the glass transition temperature (T_g) in the range from -20 °C to -60 °C, characterized in that said polymer is present as a crosslinked polymer and said crosslinking is effected by a crosslinking monomer present in an amount in the range from 0.1 to 20 weight parts.

The polymers in these latexes have a unique and improved balance of properties. The novel polymers are low T_g, soft acrylic polymers that have a good balance of tensile strength and elongation and excellent hysteresis characteristics. They are rubbery, tough, and highly resilient, and exhibit tensile strength and elongation properties common in some "harder" acrylic polymers. The glass transition temperature (T_g) of the novel polymers is from -20 °C. to -60 °C.

The novel latexes can be prepared by polymerizing the monomers and other ingredients using a premix of the monomers which is metered into a reactor containing initiator. However, a preferred process is to prepare a premix in the usual manner but devoid of all or a substantial part of the itaconic acid, and add the itaconic acid initially to the reactor before metering the premix into the reactor.

When using the acrylic latex of the present invention with a web of fibers, a unique nonwoven is produced. In thermally bonded nonwovens or entangled nonwovens treated according to the present invention, the latex can impart durable resilience, while maintaining or improving the hand. In loosely assembled fibers bonded with the latex of the present invention, the latex can impart a unique balance of properties such as good wet, dry, and solvent strength properties, flexibility, softness, and resiliency.

The raw polymer of the latex having a tensile strength of at least 2.07 MPa (300 psi), an elongation of at least 350% and a percent hysteresis loss of less than 20%.

Furthermore, the present invention relates to process of making a non-woven fabric which comprises associating within a web, a mass of fibers, bringing into contact with the fibers a binder comprising an aqueous emulsion of a binder consisting essentially of predominantly acrylate-containing polymer chains including repeating units derived from itaconic acid and up to 98.9 weight parts of an acrylate represented by the structure



wherein

- R₁ is hydrogen or methyl;
 R₂ represents C₁-C₂₀ alkyl, C₂-C₇ alkoxy alkyl, C₂-C₇ alkoxy thioalkyl, a cyano alkyl radical having 2 to 12 carbon atoms, or a mixture thereof;

said itaconic acid is present in the range from 1 to 20 weight parts; at least 40 weight parts of said acrylate in said polymer is present as an alkyl acrylate; said polymer in an aqueous emulsion form as suitable applied in the fabric at the glass transition temperature (T_g) in the range from -20 °C to -60 °C; and drying and curing the binder treated fibers under heating conditions so that that non-woven fabric is produced, characterized in that said polymer is present as a crosslinked polymer and said crosslinking is effected by a

crosslinking monomer present in an amount in the range from 0.1 to 20 weight parts.

DETAILED DESCRIPTION OF THE INVENTION

5 The novel latexes disclosed herein can be used in conjunction with fibers to yield nonwoven articles that have unique properties. The novel polymers exhibit a unique and improved balance of properties. They have excellent low temperature flexibility and yet exhibit a good balance of tensile strength and elongation and excellent hysteresis characteristics. More specifically, the novel polymers have an improved balance of high resilience, rubberyness, toughness, low surface tack considering their softness, heat and light stability, 10 dry and wet and solvent strength, and low temperature flexibility. Certain properties of the novel polymers are comparable to those of some much harder acrylate polymers. For example, the novel polymers exhibit abrasion resistance comparable to harder acrylate polymers. Moreover, the novel polymers exhibit rubbery behavior when compared to the more plastic behavior observed with harder acrylate polymers. Prior to this invention, low T_g, soft acrylic polymers basically exhibited a poor balance of tensile strength and elongation 15 properties and inadequate hysteresis characteristics. The polymers of this invention exhibit a much improved balance of properties in this regard. Particularly, the novel polymers of this invention are low T_g, soft acrylic polymers that have a good balance of tensile strength and elongation and excellent hysteresis characteristics as shown by a low percent hysteresis loss.

20 The novel latexes disclosed herein are prepared by polymerizing itaconic acid containing 4 to 10 carbon atoms, with the above-mentioned copolymerizable acrylate monomer in the presence of an initiator and a surfactant. Optionally, a crosslinking monomer can be interpolymerized with the itaconic acid and the copolymerizable monomer(s). The total amount of all of the monomers charged to the reactor, whether batchwise, incrementally, and/or metered in, equals 100 parts by weight.

25 The amount of the itaconic acid employed is from 1 part to 20 parts by weight, and more preferably from 2 parts to 8 parts by weight. The use of itaconic acid in amounts above 8 parts by weight necessitates suitable adjustments in polymerization ingredients due to a destabilizing effect of the acid and some retardation of the polymerization. For example, in an experiment where 8 weight parts of itaconic acid was charged initially into the reactor using the same amount of surfactant and initiator that gave good results when 4 weight parts of itaconic acid was used, the resulting latex had a high residual monomer content 30 which caused some difficulty in forming an even or level film. When 20 weight parts of itaconic acid was charged initially into the reactor, a latex was formed but the residual monomer level was quite high. In such cases the polymerization conditions and ingredients can be readily adjusted to obtain latexes with acceptable amounts of residual monomers. This can be done by increasing the amounts of surfactant and/or initiator used, by increasing the temperature of polymerization, by metering in part of the unsaturated dicarboxylic acid, by stripping the latex, or combinations of the above. Excellent results have been obtained 35 using 3 to 6 parts by weight of itaconic acid.

40 The novel polymers of this invention are interpolymers of (a) itaconic acid with (b) the above-described copolymerizable acrylate monomer and (c) optionally, a crosslinking monomer(s). Hence, a polymer may be an interpolymer as simple in structure as a copolymer of 95% by weight n-butyl acrylate and 5% by weight itaconic acid. However, the novel polymers are more likely to contain interpolymerized units of more than two monomers.

45 The copolymerizable acrylate monomer used in this invention can be any unsaturated monomer capable of interpolymerizing with itaconic acid. The amount of copolymerizable monomer employed is such that the weight parts of itaconic acid, and the crosslinking monomer(s), if used, together with the weight parts of the copolymerizable monomer used total up to one hundred (100) weight parts. For example, a novel copolymer of the invention containing 4 parts by weight of itaconic acid and 2 parts by weight of a crosslinking monomer would then contain 94 parts by weight of a copolymerizable monomer. Since all the monomers are charged on a 100 weight parts total basis, and the conversions in the latex reaction typically reach substantial completion, the weight parts of monomer charged substantially equals the weight percent 50 of the interpolymerized monomer in the final polymer. If this is not the case, the use of conventional analytical techniques readily establishes the weight percent of any interpolymerized monomer in the polymer. Typically, the total amount of copolymerizable monomer charged into the reactor is at least 70 parts by weight, and more typically at least 90 parts by weight of the total weight of all monomers.

55 Examples of the copolymerizable monomers are alkyl, alkoxyalkyl, alkylthioalkyl, and cyanoalkyl acrylates and methacrylates containing 1 to 20 carbon atoms in the alkyl group; diacrylates and dimethacrylates such as ethyleneglycol dimethacrylate and diethylene glycol diacrylate; monolefins containing 2 to 10 carbon atoms such as ethylene, propylene, isobutylene, 1-hexene and 1-octene; vinyl and allyl acetates containing 4 to 20 carbon atoms such as vinyl acetate, vinyl propionate and allyl acetate; vinyl

ketones containing 4 to 20 carbon atoms such as methyl vinyl ketone; vinyl and allyl ethers containing 4 to 20 carbon atoms such as vinyl methyl ether, vinyl ethyl ether, vinyl-n-butyl ether, allyl methyl ether; vinyl aromatics containing 8 to 20 carbon atoms such as styrene, α -methyl styrene, p-n-butyl styrene, p-n-octyl styrene, vinyl toluene; vinyl nitriles containing 3 to 6 carbon atoms such as acrylonitrile and methacrylonitrile; vinyl amides containing 4 to 20 carbon atoms such as acrylamide, methacrylamide, N-methyl methacrylamide; and dienes and divinyls containing 4 to 20 carbon atoms such as butadiene, isoprene, divinyl benzene, divinyl ether; monomers of 2 to 20 carbon atoms containing a halogen group such as vinyl chloride, vinyl bromide, vinylidene chloride, vinyl benzyl chloride, vinyl benzyl bromide, vinyl chloroacetate, allyl chloroacetate, 2-chloroethyl acrylate, chloroprene; unsaturated sulfonate monomers such as sodium styrene sulfonate, vinyl sulfonate; unsaturated carboxylic ester and amide monomers containing 4 to 20 carbon atoms such as dimethyl fumarate, dibutyl itaconate, the half-ethyl ester of itaconic acid; and unsaturated monocarboxylic acids containing 3 to 5 carbon atoms such as acrylic acid, methacrylic acid.

The two conditions on the selection of the copolymerizable monomer are (1) that the glass transition temperature (T_g) of the polymer made is from -20°C. to -60°C., and more preferably from -25°C., to -50°C. and (2) that the copolymerizable monomer contains a major portion of an acrylate monomer.

The acrylate monomer employed is an alkyl, alkoxyalkyl, alkylthioalkyl, or cyanoalkyl acrylate of the formula



wherein R₁ is hydrogen or methyl, and R₂ is an alkyl radical containing 1 to 20 carbon atoms, an alkoxyalkyl or alkylthioalkyl radical containing a total of 2 to 12 carbon atoms, or a cyanoalkyl radical containing 2 to 12 carbon atoms. The alkyl structure can contain primary, secondary, or tertiary carbon configurations. Examples of such acrylates are methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, isobutyl acrylate, n-pentyl acrylate, isoamyl acrylate, n-hexyl acrylate, 2-methyl pentyl acrylate, n-octyl acrylate, 2-ethylhexyl acrylate, n-decyl acrylate, n-dodecyl acrylate, n-octadecyl acrylate; methoxymethyl acrylate, methoxyethyl acrylate, ethoxyethyl acrylate, butoxyethyl acrylate, ethoxypropyl acrylate, methylthioethyl acrylate, hexylthioethylacrylate; and α and β -cyanoethyl acrylate, α , β and α -cyanopropyl cyanobutyl, cyanohexyl, and cyanooctyl acrylate; n-butyl methacrylate, 2-ethylhexyl methacrylate, isodecyl methacrylate, octadecyl methacrylate. Mixtures of two or more acrylate monomers are readily employed.

The copolymerizable monomer used contains at least forty percent (40%) by weight of acrylates of the above formula acrylate wherein R₁ is hydrogen and R₂ is an alkyl radical containing 4 to 10 carbon atoms or an alkoxyalkyl radical containing 2 to 8 carbon atoms. Examples of the most preferred acrylates are n-butyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, and methoxyethyl acrylate, ethoxyethyl acrylate. Both an alkyl acrylate and an alkoxyalkyl acrylate can be used. Excellent results have been obtained when the acrylate monomer(s) employed is the most preferred acrylate monomer(s) and such monomer(s) comprises about seventy-five percent (75%) to one hundred percent (100%) of the copolymerizable monomer.

The two criteria on the selection of the copolymerizable monomer such that the novel polymer has a low T_g and contains a major portion of interpolymerized acrylate monomer(s) are somewhat complementary in that the use of a high level of the preferred acrylate monomer(s) as the copolymerizable monomer readily yields a novel polymer having the required T_g value. It is understood that the novel polymers of this invention can have more than one T_g value within the prescribed T_g range.

The T_g of a polymer can be easily determined using differential thermal analysis. Further, the T_g of a polymer is predictable from the interpolymerized monomers using known formulas and readily obtainable data following the procedure and teachings given in many publications. One such publication is the book Mechanical Properties of Polymers by L. E. Nielsen, Reinhold Publishing Corp. (1962) Library of Congress catalog card no. 62-18939. Chapter 2 is devoted to transitions in polymers, and the tables given on pages 16 to 24 list out the T_g values of many polymers, including acrylate polymers, based on the monomers employed.

Hence, the T_g of the novel polymers can be determined through knowledge of the types and amounts of copolymerizable monomers employed. However, from the aforementioned list of copolymerizable monomers, it is apparent that some of the monomers cannot be used in large amounts and yet make a polymer meeting the necessary criteria. For example, the "hard" copolymerizable monomers; i.e. those which would yield a homopolymer T_g value of +80°C. or above, would typically be used in amounts of from 0 percent to 25 percent by weight of the total weight of the copolymerizable monomers. Examples of

such hard monomers are the vinyl aromatics such as styrene, α -methyl styrene, vinyl toluene; vinyl nitriles such as acrylonitrile and methacrylonitrile; and monomers containing a halogen group such as vinyl chloride, vinylidene chloride, vinyl benzyl chloride. Further, certain of the copolymerizable monomers have an activity which, if the monomers were present in large amounts, could overshadow the features of the polymers of this invention. Hence, copolymerizable monomers such as the vinyl amides, the diacrylates and dimethacrylates, the unsaturated sulfonate monomers, and the unsaturated monocarboxylic acids would typically be used in amounts of from 0 percent to 5 percent by weight of the total weight of the copolymerizable monomers.

The uses of the novel polymers benefit from the presence of a crosslinking monomer in the polymer or the addition of a crosslinking agent to the novel polymer.

The crosslinking monomers used herein can be any monomer or oligomer polymerizable with the unsaturated dicarboxylic acid and copolymerizable monomer which exhibits crosslinking or which can be converted into a crosslinking site. An example of a crosslinking monomer which can be interpolymerized with the itaconic acid and copolymerizable monomer, and then converted to yield a crosslinking site is acrylamide, which, when treated with formaldehyde, forms a methylol group. The more preferred crosslinking monomers are monoethylenically unsaturated monomers containing N-methylol groups such as N-methylol acrylamide, or N-methylol derivatives of allyl carbamate which may contain one or two N-methylol groups. The N-methylol groups may be left unreacted or they may be etherized, as with C₁ to C₄ carbon alcohols. The alcohol is released on curing to regenerate the N-methylol group for cure. Alcohol etherifying agents are illustrated by methyl alcohol, ethyl alcohol, isopropyl alcohol, isobutyl alcohol, 2-ethoxyethanol, and 2-butoxy ethanol.

More particularly, the preferred crosslinking monomers are selected from N-alkylol acrylamides that contain from 4 to 18, preferably 4 to 12 carbon atoms in the alkyl group, and lower alkyl acrylamidoglycolate lower alkyl ethers containing from 7 to 20 carbon atoms. Specific examples of the particularly preferred crosslinking monomers include N-methylol acrylamide, N-methylol methacrylamide, N-butoxymethyl acrylamide, iso-butoxymethyl acrylamide and methyl acrylamidoglycolate methyl ether. Especially good results have been obtained using N-methylol acrylamide as the crosslinking monomer.

The crosslinking monomer is used in the range from 0.1 to 10 parts by weight, and more preferably from 0.5 to 5 parts by weight based on 100 parts by weight total of all monomers.

If a crosslinking monomer is not interpolymerized with the itaconic acid and the copolymerizable monomer, the novel polymer can still be crosslinked by the post-polymerization addition of a crosslinking agent to the latex or the polymer. Examples of such crosslinking agents are urea-formaldehyde resins, melamine-formaldehyde resins and partially methylolated melamine-formaldehyde resins and glyoxal resins. These crosslinking agents can be used in levels of from 0.1 part to 20 parts, and more preferably from 0.5 part to 2 parts, by weight, based on 100 parts by weight of polymer.

The novel polymers are prepared as latexes. As the novel polymers have great utility used in the form of a latex, the latexes themselves are unique and novel.

The aqueous medium in which the novel polymers are prepared may be free of traditional emulsifiers, or it may contain traditional emulsifiers. When traditional emulsifiers are used to prepare the unique latexes of this invention, the standard types of anionic and nonionic emulsifiers can be employed. Useful emulsifiers include alkali metal or ammonium salts of the sulfates of alcohols having from 8 to 18 carbon atoms such as sodium lauryl sulfate, ethanolamine lauryl sulfate, and ethylamine lauryl sulfate; alkali metal and ammonium salts of sulfonated petroleum and paraffin oils; sodium salts of sulfonic acids such as dodecane-1-sulfonic acid and octadiene-1-sulfonic acid; aralkyl sulfonates such as sodium isopropyl benzene sulfonate, sodium dodecyl benzene sulfonate and sodium isobutyl naphthalene sulfonate; alkali metal and ammonium salts of sulfonated dicarboxylic acid esters such as sodium dioctyl sulfosuccinate and disodium-N-octadecyl sulfosuccinate; alkali metal or ammonium salts of the free acid of complex organic amon-and diphosphate esters; copolymerizable surfactants such as vinyl sulfonate and the like. Nonionic emulsifiers such as octyl- or nonylphenyl polyethoxyethanol may also be used. Latexes of the invention having excellent stability are obtained using the alkali metal and ammonium salts of aromatic sulfonic acids, aralkyl sulfonates, long chain alkyl sulfonates and poly(oxyalkylene) sulfonates as emulsifiers.

The emulsifier or a mixture thereof may be added entirely at the outset of the polymerization or it may be added incrementally or metered throughout the run. Typically, some of the emulsifier is added to the reactor at the outset of the polymerization and the remainder is charged incrementally or proportionately to the reactor as the monomers are proportioned.

The polymerization of the monomers may be conducted at temperatures from 0°C up to 100°C in the presence of a compound capable of initiating the polymerizations. Initiating compounds and mixtures thereof are chosen, often in conjunction with oxidation-reduction catalysts, in an amount and type which

results in a suitable initiation rate at a chosen polymerization temperature profile. Commonly used initiators include the free radical initiators like the various peroxygen compounds such as persulfates, benzoyl peroxide, t-butyl diperphthalate, pelargonyl peroxide and 1-hydroxycyclohexyl hydroperoxide; azo compounds such as azodiisobutyronitrile and dimethylazodiisobutyrate. Particularly useful initiators are the water-soluble peroxygen compounds such as hydrogen peroxide and sodium, potassium and ammonium persulfates used by themselves or in activated systems. Typical oxidation-reduction systems include alkali metal persulfates in combination with a reducing substance such as polyhydroxyphenols, oxidizable sulfur compounds such as sodium sulfite or sodium bisulfite, reducing sugars, dimethylamino propionitrile, diazomercapto compounds, water-soluble ferricyanide compounds, or the like. Heavy metal ions may also be used to activate persulfate catalyzed polymerizations.

The amount of surfactant used is from 0.01 to 10 parts by weight, and the amount of initiator is used from 0.01 to 1.5 parts by weight, both based on 100 weight parts of the total amount of monomers.

Polymer latexes of the invention having excellent stability are obtained using an alkali metal and ammonium persulfate as the initiator. The initiator may be charged completely into the reactor at the outset of the polymerization, or incremental addition or metering of the initiator throughout the polymerization may also be employed. Addition of the initiator throughout the polymerization is often advantageous in providing a suitable rate throughout the polymerization.

The novel acrylic latexes can be made in different ways. In a one process, a premix is prepared by mixing the monomers, optionally with water, a surfactant or a mixture thereof, buffering agents, modifiers and the like. If water is used, the aqueous premix is agitated to form an emulsion. Separately added to a reactor are more water, the initiator, and optional ingredients. The premix is then metered into the reactor and the monomers are polymerized.

In a variation on the above process, part of the premix can be added to the reactor, the initiator is then added and polymerization of the initial monomers in the reactor thereto is allowed to form seed polymer particles. Thereafter, the remainder of the premix or another premix is metered into the reactor and the polymerization reaction is concluded in the usual way. In yet another variation, the premix can be fed to the reactor incrementally rather than continuously. Finally, in yet another variation of the process, all of the monomers and other ingredients can be added directly to the reactor and polymerization conducted in a known manner. This last variation is typically called a batch process. Monomers can also be added to the reactor in separate streams other than in the premix.

In a preferred embodiment of the process for preparing a latex of the invention, 2 to 8 weight parts of itaconic acid is polymerized in water with 90 to 98 weight parts of an alkyl acrylate monomer such as n-butyl acrylate and 0.5 to 5 weight parts of a crosslinking monomer such as N-methylol acrylamide, in the presence of 0.1 to 5 weight part of a suitable surfactant such as sodium lauryl sulfate and 0.01 to 1.5 weight parts of a suitable initiator such as sodium persulfate.

The itaconic acid can be added all initially into the reactor before metering of the premix is commenced, or part or all of the said acid can be metered into the reactor during polymerization. In a preferred embodiment of the process, the itaconic acid is all initially added to the reactor, and the premix containing the copolymerizable monomer(s) and crosslinking monomer(s) is metered into the reactor. The best balance of polymer physical properties was obtained when all of the itaconic acid was added initially to the reactor. However, as compared to similar polymers made using monocarboxylic acids only, polymers having an improved balance of properties are also obtained when some or all of itaconic acid is added to the premix.

As already noted, processes for preparing acrylic latexes usually involve a number of stages. A premix is typically prepared containing one or more monomers, optionally surfactant, water and ingredients such as buffering agents, chain modifiers, and the like. The premix is vigorously agitated to form an emulsion at ambient temperature. The reactor is also prepared for polymerization by addition of water, initiator, monomer (if added to the reactor), optionally buffering agents, and other ingredients. The reactor and its contents can be preheated. The premix is metered to the reactor over a period of 0.5 to 10 or more hours, preferably 1 to 4 hours. As soon as the polymerization starts, the temperature of the reactor increases. A cold water or other type of cooling jacket around the reactor can be used to control the polymerization temperature, preferably at 30 °C. to 90 °C.

The latex obtained is typically treated or processed to reduce residual monomers and the pH is adjusted to whatever value is desired. The latex is then often filtered through a cheesecloth or filter sock and stored. The stored latex has a total solids content of from 10 to 68%, and more typically from 40% to 60%.

It should be understood that although the best results were obtained when all or at least one-half or more of the itaconic acid was placed in the reactor initially, an unexpected improvement in the balance of

the physical properties of the novel polymers was also obtained when over one-half or all of the acid is placed in the premix, as long as the acid used is the itaconic acid described herein. The use of unsaturated monocarboxylic acids, such as acrylic acid and methacrylic acid, did not work to produce the unique balance of properties in the novel polymer. Further, when acrylic acid or methacrylic acid was placed initially all in the reactor, the reaction mixture gelled or coagulated, despite attempts to prevent this by adding water during the polymerization.

As already described, in a preferred process of this invention, the itaconic acid is all added initially to the reactor, unlike prior art processes in which all of the monocarboxylic acid is typically added to the premix. Addition of large amounts of the itaconic acid to the reactor initially requires adjustments in the polymerization recipe in order to obtain a latex with optimum properties. For example, placing all of the itaconic acid into the reactor without making any other changes in the polymerization recipe or process can result in a larger particle size latex. The reason for this is believed to be that the dicarboxylic acid reduces the efficiency of the initiator in the reactor and/or causes destabilization of forming particles in the reactor, which, in turn, can affect the particle size of the latex polymer.

It is known in acrylic latex technology that the amount of the surfactant in the reactor can substantially affect the particle size of the latex. Hence, by increasing the amount of surfactant used, the particle size of the latex can be reduced. Since the presence of the unsaturated dicarboxylic acid in the reactor can have the affect of increasing the particle size, an upward adjustment in the amount of surfactant (and/or initiator) used can compensate for this effect.

The novel latexes disclosed herein have typical colloidal properties. They are anionically stabilized, have a pH of from 1 to 6 as prepared, have a particle size in the range of 100 to 500nm (1000 to 5000 angstroms), and exhibit good mechanical stability when their pH is raised above neutral.

One of the most unique properties of the polymers of this invention is their excellent hysteresis characteristics. The novel polymers prepared herein have very tight hysteresis curves. The tighter a hysteresis curve, the more resilient the polymer. Also, the tighter the hysteresis curve, the less heat will be generated on stretching or working of the polymer.

The percent hysteresis loss of polymers were determined from the polymer's hysteresis curve using the following procedure. Dumbell samples of the raw polymer having 178 to 254 μm (7 to 10 mils) thickness were prepared from the latex using a draw bar. The cast films were air-dried then heated at 149°C (300°F) for 5 minutes. By raw polymer is it meant that no compounding ingredients such as fillers, pigments, plasticizers and the like were added, and no curative ingredients were added. The samples were placed in an Instron tensile testing machine and elongated to 200% elongation at a speed of 50.8cm/min (20 inches/minute). The sample was then retracted at 50.8cm/min (20 inches/minute) to its original position (making one cycle), and then elongated and retracted again until five cycles were completed. The tensile/elongation (i.e. hysteresis) curves for each cycle were recorded. The percent hysteresis loss measurements were performed in each case on the recorded data for the second cycle. The area of the figure described by the initial stretch of the polymer to 200% elongation represents the amount of work energy needed to produce the elongation (E_A). The area of the figure described when the polymer is retracted in the cycle represents the work energy exerted by the polymer in returning to its original position (E_B). A perfectly resilient polymer which exhibits no heat or other energy losses would have a hysteresis curve wherein E_A would equal E_B , i.e. the two curves would lie on top of each other. The deviation from this ideal condition is a measure of the polymer's hysteresis loss. A gummy polymer would have a very high percent hysteresis loss.

The percent hysteresis loss of the polymers was determined by the following formula:

$$\text{Percent Hysteresis Loss} = \frac{E_A - E_B}{E_A} \times 100\%.$$

The polymers of this invention exhibit a percent hysteresis loss of less than 20% as calculated from their hysteresis curves. The polymers prepared from the most preferred unsaturated dicarboxylic acids, copolymerizable monomers, and crosslinking monomers and prepared by the preferred process exhibit a percent hysteresis loss of below 15 percent.

The novel polymers have other properties which make them unique. They are soft, yet rubbery and tough. Their ultimate raw polymer tensile strength is at least 2.07 MPa (300 psi) and ultimate percent elongation is at least 350%, as measured on raw polymer films cast with a draw bar, air-dried and heated for 5 minutes at 149°C (300°F). A way of observing the good balance of tensile strength and elongation

exhibited by the polymers of this invention is to calculate their "TxE Product", which is simply the figure obtained by multiplying the polymer's ultimate tensile strength by its percent elongation at break. The figure is reported to the nearest 1000. The TxE Product a measure of the overall strength of the polymer. The TxE Product of the novel polymers is at least 140,000, and more preferably at least 200,000. The TxE Product for the novel polymers made from the most preferred monomers using the most preferred process is at least 250,000.

The following examples are presented for the purpose of illustrating the invention. The examples are not to be construed as limiting the invention in any manner, the scope of which is defined by the appended claims.

EXAMPLES

In the following experiments, except as stated otherwise, the latex was prepared by polymerizing a monomer mix of 93 to 97 parts by weight parts of the copolymerizable monomer, 2 to 4.5 weight parts of itaconic acid, and 1 to 3 weight parts of the crosslinking monomer. In comparative experiments where no acid was used, the amount of copolymerizable monomer was increased accordingly. The premix was prepared in a separate tank by mixing demineralized water, sodium lauryl sulfate as the surfactant, the crosslinking monomer, and the copolymerizable monomer. All or part of the acid was placed in the premix or the reactor, as indicated. The reactor initially contained demineralized water, sodium lauryl sulfate, and sodium persulfate. The premix was metered into the reactor over a period of about 1.5 to about 2.5 hours, during which time the temperature in the reactor was controlled at 70 °C. to 80 °C.

After commencement of the metering of the premix to the reactor, in some cases a second initiator system was added to the reactor. The second initiator system consisted of sodium persulfate, sodium lauryl sulfate, and ammonium carbonate in demineralized water. The second initiator was metered into the reactor over a period of 3.5 hours. At times, an initiator booster was merely slugged into the reactor rather than metered in. When the reaction was completed, the latex in the reactor was allowed to stand for about 1.5 hours at 75 °C. and was then cooled to 40 °C. At this point, the latex was stripped, cooled to 30 °C., its pH was adjusted with ammonia to about 4.5 pH, and it was filtered through cheesecloth and stored.

Following the above general procedures, three variations of reaction conditions were actually employed. In Variation A, the reaction temperature was 80 °C., the premix metering time was 2 hours, an initiator booster containing 0.05 weight part of sodium persulfate was added after 2 hours, and the amount of sodium lauryl sulfate used was 0.05 weight part in the reactor and 0.95 weight part in the premix. Variation B was like Variation A except that the reaction temperature was 75 °C. In Variation C, the reaction temperature was 70 °C., 0.35 weight part of sodium persulfate initiator was in the reactor, a second initiator of 0.15 part of sodium persulfate and 0.05 part of sodium lauryl sulfate was metered in over 3.5 hours, and the amount of sodium lauryl sulfate in the reactor was 0.4 weight part and in the premix was 0.6 weight part.

The raw polymer films were prepared in the following manner. First, the latex was neutralized by adjusting the pH of the latex to between 7 and 8 with ammonia. Thickener was added to the latex, as necessary, to raise its viscosity to about 500 mPa·s (cps) so that a level film could be obtained. A latex film was deposited on a polyethylene backing using a draw bar so as to yield a dry film of 178 to 254 μm (7 to 10 mils) thickness, and the latex film was dried at room temperature for about 24 hours. The polymer film was then peeled from the backing, dusted with talc if necessary for easier handling, and heated for 5 minutes at 300 °F (149 °C). The test specimens were prepared and tested using the following procedure. A dumbbell shaped test specimen was prepared from the polymer film and placed in an Instron tensile tester at a 2.54cm (1") jaw spacing. The jaws were separated at a speed of 50.8cm/min (20 inches/minute). Elongation was measured using a 1.27cm (0.5 inch) benchmark. Each data point given in the examples represents an average of three separate measurements.

EXAMPLE 1

This example demonstrates the preparation of a novel latex of the invention, the preparation of a novel polymer of the invention from the latex, and shows a comparison of the properties of the novel polymer with those of polymers containing no acid, acrylic acid, or methacrylic acid in the polymer. Only the polymer prepared from the latex containing polymerized itaconic acid is representative of the invention. The other samples were prepared and are presented for comparison purposes only. All of the latexes were prepared with 2 parts by weight of N-methylol acrylamide as the crosslinking monomer, and using the process described above as Variation B. The acid, if used, was placed all in the premix and the premix was metered into the reactor. All reaction conditions and procedures were identical in these tests except for the particular

acid used, if any. Ultimate tensile strength and percent elongation tests were performed on film samples of the raw polymers, which samples were prepared as described above. The results are given in Table A below:

	Table A	
	Acrylic Acid	Itaconic Acid
Tensile Strength, MPa (psi)	2.41(350)	4.78(693)
Elongation, %	343	380
TxE Product	120000	263000
Percent Hysteresis Loss	18.1	18.9
	No Acid	
Tensile Strength, MPa (psi)	1.43(207)	
Elongation, %	260	
TxE Product	54000	
Percent Hysteresis Loss	12.2	

It is apparent from the above data that the novel polymer of the invention made using itaconic acid (IA) has a superior balance of tensile strength and elongation and percent hysteresis loss. The polymer containing polymerized itaconic acid (IA) had a tensile strength of 4.78 MPa (693 psi) an ultimate elongation of 380%, and a TxE Product of 263000, whereas the corresponding results for acrylic acid (AA) were 2.41 MPa (350 psi), 390%, and 120000, and for methacrylic acid (MAA) were 2.27 MPa (330 psi), and 390%, and 129000 respectively. For the polymer prepared containing no acid at all, the tensile strength was only 1.43 MPa (207 psi), elongation was 260%, and the TxE Product was only 53800. The data shows that the polymer of the invention has a good balance of tensile strength and elongation and low hysteresis loss.

EXAMPLE 2

For purposes of further comparison, the properties of a novel polymer of the invention were compared to properties of some commercial polymers. The novel polymer used herein is similar to the polymer prepared in Example 1 above except that, in this case, all of the itaconic acid was placed initially into the reactor (no itaconic acid was in the premix). The commercial polymers are Hycar® 2671 (Acrylic A), Hycar® 2673 (Acrylic B), and an acrylic polymer known as Rhoplex TR934 sold by Rohm and Haas (Acrylic C). Results are given in Table B below:

Table B

	Novel Polymer	Acrylic A	Acrylic B	Acrylic C
Tensile, MPa (psi)	5.20 (755)	4.58 (665)	2.81 (407)	4.25 (617)
Elongation, %	608	610	1483	433
TxE Product	459000	406000	636000	267000
Percent Hysteresis Loss	12.8	22.0	36.4	12.5
Tg, °C	-44	-11	-15	-28

The data shows that the novel polymer of the invention gives a unique balance of good tensile strength and elongation and low hysteresis loss. The balance of tensile and elongation properties and hysteresis loss of the novel polymer were actually better than most of those properties of the "harder" acrylic polymers, yet the Tg of the novel polymer was considerably lower than such polymers.

EXAMPLE 3

This example shows the preparation and testing of polymers of the invention wherein the latexes were prepared using Variation A and all of the unsaturated dicarboxylic acid was placed in the premix. The following monomers were charged on the following weight basis: 4.5 parts of the stated acid, 1.0 part N-methylol acrylamide, and 94.5 parts n-butyl acrylate.

The film samples were prepared from the polymers and tested as described above. As a comparison, a polymer was also prepared using the monocarboxylic acid, acrylic acid, in place of itaconic acid. The acrylic acid was also placed all in the premix. Results of the tests are given in Table C below.

Table C

	AA all in Premix	IA all in Premix
Tensile, MPa (psi)	2.13 (310)	3.76 (546)
Elongation %	493	553
TxE Product	153000	317000
Percent Hysteresis Loss	23.1	19.6

The tensile strength, elongation, TxE Product, and hysteresis loss for the polymer made with acrylic acid (AA) in the premix was 2.13 MPa (310 psi), 493%, 153000, and 23.1% respectively. When itaconic acid (IA) was used all in the premix, thereby making a polymer of this invention, the tensile strength, elongation, TxE Product, and hysteresis loss was 3.76 MPa (546 psi), 553%, 317000, and 19.6% respectively. When the experiment with the itaconic acid all placed in the premix was repeated, the results were even better, with a tensile strength of 4.62 MPa (670 psi), and elongation of 573%, a TxE Product of 366000, and a percent hysteresis loss of 17.5%. All of the polymers had a Tg of about -44 °C. It is apparent that the use of itaconic acid (IA) in place of acrylic acid (AA) results in a polymer having a superior balance of tensile strength and elongation properties and low percent hysteresis loss at a low Tg.

EXAMPLE 4

An experiment was performed wherein the itaconic acid was placed all initially in the reactor. This experiment used the same monomers and parts by weight, and same polymerization and test conditions given in Example 3 above. This novel polymer had a tensile strength of 3.49 MPa (507 psi), and elongation of 753%, a TxE Product of 382000, and a percent hysteresis loss of 19.8%.

With no buffers, the latex prepared in this Example 3 had a pH of about 1.9. As mentioned before, it is believed that the use of all of the unsaturated dicarboxylic acid initially in the reactor has the effect of reducing initiation efficiency of the polymerization and/or destabilizing the forming particles, which can result in a latex which has a larger particle size than when the acid is placed in the premix. The reduction in initiation efficiency can be overcome by increasing the amount of the surfactant or initiator, or both. This was demonstrated by conducting an experiment in which the level of the surfactant used in the reactor was increased from 0.05 weight part to 0.5 weight part, with all other conditions remaining the same. By

increasing the amount of surfactant, the preparation of the novel latex was more nearly optimized. The data obtained on the film of the novel polymer prepared in this manner shows that the tensile strength of the polymer increased to 5.33 MPa (773 psi), the elongation dropped to 647%, the TxE Product increased to 500000, and the percent hysteresis loss dropped to 14.9%. This indicates a different balance of properties than obtained using the lesser amount of surfactant. This balance of properties may be preferred in some uses.

EXAMPLE 5

This example demonstrates the superior results that can be obtained by preparing the novel latexes by the preferred process wherein all or at least one-half of the unsaturated dicarboxylic acid is placed initially in the reactor. The data in Table D gives properties for films made from latexes wherein the amount of itaconic acid (IA) placed in the reactor ranged from all placed into the reactor initially to all of the itaconic acid placed in the premix. The latexes were prepared with 2 parts by weight of N-methylol acrylamide as the crosslinking monomers, and using process procedure Variation A. Results are given in Table D below.

Table D

	4 parts IA in Reactor	3 parts IA in Reactor 1 part IA in Premix	2 parts IA in Reactor 2 parts IA in Premix	1 part IA in Reactor 3 parts IA in Premix	4 parts IA in Premix
Tensile, MPa (psi)	5.20 (755)	5.84 (843)	6.13 (890)	6.44 (645)	4.77 (693)
Elongation, %	603	533	517	380	380
TXE Product	459000	449000	460000	245000	263000
Percent Hysteresis Loss	12.8	12.6	13.6	14.8	18.9

When all 4 weight parts of the itaconic acid are placed initially in the reactor, tensile strength, elongation, TXE Product, and hysteresis loss were 5.46 MPa (792 psi), 688%, 45900, and 12.8% respectively. As more of the itaconic acid was placed in the premix, the polymer properties changed, especially in the percent elongation and percent hysteresis loss. However, no matter how the novel polymers were prepared, i.e. by the process wherein all of the itaconic acid was placed in the reactor, in the

premix, or the itaconic acid was split between the two, the polymers still show a superior balance of properties as compared to similar polymers made using acrylic acid or methacrylic acid. See Table A for a comparison.

5 EXAMPLE 6

The suitability of using unsaturated dicarboxylic acid other than itaconic acid is demonstrated in this Example for comparison. The polymers were prepared using 2 parts by weight of N-methylol acrylamide as the crosslinking monomer, and using the process procedure Variation B where all 4.0 weight parts of the
10 defined acid was placed initially into the reactor. The unsaturated dicarboxylic acids employed were itaconic acid (IA), fumaric acid (FA), maleic acid (MA), and citraconic acid (CA). An attempt was also made to prepare comparative latexes and polymers which would contain no acid, acrylic acid (AA) or methacrylic acid (MAA) in place of the unsaturated dicarboxylic acid. Results are given in Table E below:

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Table E

	Itaconic Acid	Fumaric Acid	Maleic Acid	Citraconic Acid	Acrylic Acid	Methacrylic Acid	No Acid
Tensile, MPa (psi)	5.20 (755)	3.13 (454)	(440)	2.25 (327)	gelled	gelled	1.42 (207)
Elongation, %	603	427	467	637			260
TxE Product	459000	233000	2050000	208000			54000
Percent Hysteresis Loss	12.8	18.4	18.0	19.9			12.2

(note: only the itaconic acid example is according to the invention).

Both experiments wherein acrylic acid (AA) or methacrylic acid (MAA) was placed all in the reactor resulted in a gelled latex during polymerization, even though an attempt was made to prevent this by adding water to the reactor during polymerization. With itaconic acid (IA) in the reactor, the tensile strength of the novel polymer was 5.20 MPa (755 psi), elongation was 603%, the TxE Product was 459000, and the percent hysteresis loss was a low 12.8%. The use of fumaric acid (FA) in the process produced a polymer having a somewhat lower tensile strength and elongation and higher percent hysteresis low. The use of

maleic acid (MA) or citraconic acid (CA) as the unsaturated dicarboxylic acid yielded polymers having lower tensile strengths and good elongations. The TxE Products and percent hysteresis loss of these polymers was good. With no acid, the tensile strength of the polymer was only 1.42 MPa (207 psi), its elongation was only 260%, and the TxE Product was a very low 5400.

Certain of the above experiments were repeated wherein the unsaturated dicarboxylic acid was placed all in the premix (none initially in the reactor). The polymer prepared using maleic acid in the premix had a tensile strength of 2.42 MPa (351 psi), an elongation of 357%, and a TxE Product of 12600. The polymer prepared using citraconic acid in the premix had a tensile strength of 2.21 MPa (321 psi), an elongation of 553%, and a TxE Product of 17800. Both of these results are better than those obtained when using acrylic acid in the reactor (as above) or in the premix (see Table A).

EXAMPLE 7

This example demonstrates the use of other copolymerizable monomers in the preparation of the novel latexes and polymers of this invention. The procedures used were the same as those used in Example 6 wherein the itaconic acid was placed all initially into the reactor. A portion of the n-butyl acrylate in the premix was replaced with one or more of the indicated higher Tg yielding copolymerizable monomers in the amounts shown. Results are given in Table F below:

Table F

	5 PHR ST 5 PHR AN	10 PHR VAC	10 PHR MMA
Tensile, MPa (psi)	5.77 (838)	4.67 (678)	6.50 (943)
Elongation, %	670	630	560
TxE Product	562000	427000	529000
Percent Hysteresis Loss	17.8	13.8	14.5
Estimated Tg, °C	-25	-36	-29

The above results demonstrate that the novel latexes and polymers of this invention can be readily prepared using a large range of copolymerizable monomers, as long as the Tg of the final polymer is between -20 °C. and -60 °C., and an acrylate monomer is present as the major copolymerizable monomer. Of course, the presence of one or more other copolymerizable monomers, particularly "harder" monomers, can affect the physical properties of the polymers made from the corresponding latexes. For example, with 5 weight parts of styrene (ST) and 5 weight parts of acrylonitrile (AN) used in place of a corresponding amount of n-butyl acrylate, the tensile strength of the polymer was 5.77 MPa (838 psi) and elongation was 670%. Using 10 weight parts of vinyl acetate (VAC), the polymer tensile strength was 4.67 MPa (678 psi) and elongation was 630%. With 10 weight parts of methyl methacrylate (MMA), polymer tensile strength was 6.50 MPa (943 psi) and elongation was 560%. In all three cases, the TxE Products were very high and the percent hysteresis loss was within the stated range.

A very low Tg polymer was prepared using the same procedure as given above using 94 weight parts of 2-ethyl hexyl acrylate (2-EHA) as the sole copolymerizable monomer. The polymer was weak, having a tensile strength of 2.27 MPa (230 psi), an elongation of 980%, and a Tg of -65.5 °C. This polymer did not meet the necessary criteria of the novel polymers of this invention. This Example shows that a choice of copolymerizable monomer(s) which takes the Tg of the polymer outside of the stated Tg range, results in a polymer that does not have the unique balance of properties described herein.

EXAMPLE 8

This example demonstrates the use of other crosslinking monomers in the preparation of the novel latexes and polymers of the invention. The crosslinking monomer is used in each experiment at 2.0 weight parts in the premix. The itaconic acid was used at 4 parts by weight and was placed all initially in the reactor. The process procedure used was Variation B. Results are given in Table G below:

TABLE G

	NMA	NMMA	MAGME
Tensile, MPa (psi)	5.72 (830)	6.46 (937)	6.27 (910)
Elongation, %	773	360	1055
TxE Product	642000	337000	960000
Percent Hysteresis Loss	15.4	13.9	14.2

The first column of data in Table G shows data from a latex polymerization wherein N-methylol acrylamide (NMA) was used as the crosslinking monomer. The polymer prepared using N-methylol methacrylamide (NMMA) as the crosslinking monomer had a higher tensile strength 6.46 MPa (937 psi) but lower elongation (360%). When methyl acrylamidoglycolate methyl ether (MAGME) was used as the crosslinking monomer, the polymer tensile strength was 6.27 MPa (910 psi), elongation was 1055%, and an exceptionally high TxE Product was obtained.

From Table G, it is readily seen that a broad range of crosslinking monomers are suitable for use in this invention.

EXAMPLE 9

A series of latexes were prepared in which the amount of itaconic acid (IA) and the amount of N-methylol acrylamide (NMA) were varied. The copolymerizable monomer used was n-butyl acrylate at 93 to 97 parts by weight. The itaconic acid was placed all initially in the reactor. The initiator used was sodium persulfate. Process procedure C was employed. The results of the tests on the polymers are given in Table H below.

TABLE H

Run	IA (parts)	NMA (parts)	Initiator in Reactor (parts)	Tensile Strength (MPa (psi))	Elongation (%)	TxE Product
1	4	2	0.35	4.33 (715)	607	434000
2	4	2	0.35	4.32 (627)	573	359000
3	2	2	0.35	4.83 (710)	420	298000
4	3	2	0.1	4.50 (653)	577	377000
5	2	1	0.1	3.60 (523)	587	307000
6	3	1	0.35	3.69 (536)	563	302000
7	4	3	0.35	4.05 (587)	603	354000
8	3	3	0.1	4.15 (602)	500	301000

The above data shows that the novel polymers of this invention can be readily prepared using various amounts of the unsaturated dicarboxylic acid and the crosslinking monomer.

EXAMPLE 10

The MIT fold test was conducted in this example by saturating 127 μm (5 mil) flat paper with 40% add-on. Forty percent add-on means 40 weight parts of dry polymer has been added to each 100 weight parts of fibers. The saturated paper was dried on a photoprint drier at approximately 100 °C (212 °F) and then cured at 149 °C (300 °F) for 3 minutes. The cured paper was cut into 15 millimeter widths in the machine direction and mounted in a MIT tester with a load of 1 kilogram applied to the ends of the strip of paper. The paper was then flexed by the MIT tester at a 180 ° angle to first one side and then the other side. The number of folds necessary to break the paper was measured to indicate the fold endurance of the latex and paper. All testing was conducted at a relative humidity of 50% at a temperature of 22 °C (72 °F). The results of the test are set forth in Table I.

Table I

LATEX TYPE	MIT DOUBLE FOLDS 1 KILOGRAM LOAD
HYCAR® 2600 X 322 (A commercially available latex manufactured by BFG having a Tg of -15 °C used commonly in paper saturation)	240
HYCAR® 26083 (Another commercially available latex manufactured by BFG specifically made for use in paper applications having a Tg of -15 °C)	1,400
HYCAR® 1562 (A commercially available nitrile latex manufactured by BFG for paper saturation having a Tg of -26 °C)	200
Latex A of the present invention having a Tg of -29 °C.	3,500
Latex B of the present invention having a Tg of -43 °C.	1,725

Latex A included 86 weight parts of N-butyl acrylate, 6 weight parts acrylonitrile, 4 weight parts itaconic acid, 2 weight parts ethyl acrylate and 2 weight parts N-methylol acrylamide. Latex B included 92 weight parts n-butyl acrylate, 4 weight parts itaconic acid, 2 weight parts ethyl acrylate and 2 weight parts N-methylol acrylamide.

This example demonstrates that a latex of the present invention having a low Tg performs better than the indicated commercially available soft latexes employed in paper applications. Latex B performed better than the above noted commercially available latexes. Latex A was far superior to any of the above noted commercially available latexes. In fact, the number of folds achieved when using Latex A is more than double the best of the above latexes.

EXAMPLE 11

In this experiment, a Handle-O-Meter test was conducted on 31.1 g (1.1 ounce) per square yard chemically bound saturated polyester nonwoven fabric to measure softness. In the procedure, a latex was applied to an unbound carded polyester fiber web at about 30% add-on. The fabric was dried on a photoprint dryer at approximately 100 °C (212 °F) and then cured for 3 minutes at 149 °C (300 °F). Two 7.62cm x 7.62cm (3" x 3") squares were cut from the nonwoven fabric and tested using the Thwing-Albert Digital Handle-O-Meter, which measures the force necessary to advance a sample through a measured open slit width. The polyester nonwoven fabric was tested in the machine direction, cross-direction, then flipped over and again tested in the machine direction and the cross direction. All testing was conducted at 50% relative humidity and 22 °C (72 °F). The results of this experiment are set forth in Table J. The lower numbers indicate a softer hand. The averages of 8 readings are also shown.

Table J

Handle-O-Meter					
Latex Type	M.D.	C.D.	F.M.D.	F.C.D.	Avg.
Rhoplex TR934, Rohm and Haas (Tg-28)	30.4	35.0	24.8	36.2	29.0
	22.4	30.6	22.7	29.6	
HYCAR® 2671 (Tg-11)	25.0	40.8	25.9	38.4	32.0
	29.1	38.3	24.6	33.3	
Latex B (Tg-43)	20.2	27.9	18.9	28.1	26.0
	24.3	34.6	23.6	30.1	

The results indicate that the nonwoven web produced from Latex B of the present invention (EXAMPLE 10) has a softer hand than the other soft acrylic latexes designed to be employed in such nonwovens.

EXAMPLE 12

In this example, the dry, solvent and wet tensile strengths of 127 µm (5 mil) flat paper saturated with 40% add-on are demonstrated. In these tests, a 2.54cm x 7.62cm (1" x 3") piece of saturated paper was

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tested in the machine direction using the Thwing-Albert Intellect II tensile tester. Prior to testing, the samples were dried at 100°C (212°F) on a photoprint dryer and then cured for 3 minutes at 149°C (300°F). For the wet and solvent strength tests, the strips of paper were soaked for 20 minutes and tested wet. All testing was conducted at 50% relative humidity and 22°C (72°F) to eliminate temperature and air moisture as variables. Jaw separation was 5.08cm (2") and jaw speed was 2.54cm (1") per minute. The tensile strength indicated is the peak or maximum value in pounds. The elongation indicated is the elongation at peak tensile strength. The tensile energy absorption is the TEA at the peak tensile strength. The results of the test are set forth below in Table K.

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Table K

Latex Type	Dry		Wet		Solvent	
	PKLO ¹	% Elong. ²	PKLO ¹	% Elong. ²	PKLO ¹	% Elong. ²
HYCAR 26171 Tg of -44 (manufactured by BFGoodrich Co.)	6.16 (13.6)	4.4	0.402 3.53(7.8)	7.6	0.370 3.22(7.1)	2.3
						0.094
HYCAR 26171 Tg of -44 (laboratory made).	6.11 (13.5)	4.0	0.362 4.08(9.0)	9.3	0.494 3.26(7.2)	2.4
						0.104
Present invention; 4.5 weight parts itaconic acid in premix, 93.5 nBA and 2 weight parts nMA.	8.06 (17.8)	5.7	0.668 5.30(11.7)	9.1	0.614 3.38(8.8)	2.6
						0.124
Present invention; 4.5 weight parts itaconic acid in reactor, 93.5 weight parts nBA and 2 weights nMA.	8.74 (19.3)	5.5	0.684 5.53(12.2)	9.3	0.651 5.12(11.3)	3.5
						0.226
Present invention; 4.5 weight parts itaconic acid in reactor, 93.5 weight parts nBA, and 2 weight parts of nMA (smaller particle size).	8.01 (17.7)	5.4	0.632 4.66(10.3)	7.8	0.573 4.48(9.9)	3.5
						0.172

Table K (continued)

Latex Type	Dry		Wet		Solvent	
	PKLO ¹	% Elong. ²	PKLO ¹	% Elong. ²	PKLO ¹	% Elong. ²
Present invention; 94 weight parts nBA, 4 weight parts itaconic acid in reactor and 2 weight parts NMA.	8.83 (19.5)	5.1	0.6916.34 (14.0)	7.6	0.4836.43 (14.2)	3.6
						0.287
Present invention, as above except 1 weight part itaconic acid in premix and 3 weight parts itaconic acid in reactor.	9.74 (21.5)	5.1	0.6365.35 (12.7)	7.8	0.6186.23 (13.9)	0.286

As above, except 2 weight parts itaconic acid in premix with 2 weight parts itaconic acid in reactor.	9.15 (20.2)	5.0	0.6366.43 (14.2)	8.3	0.618	---

Table K (continued)

Latex Type	Dry		Wet		Solvent	
	PKLO ¹	% Elong. ²	PKLO ¹	% Elong. ²	PKLO ¹	% Elong. ²
as above, except all parts of itaconic acid are in the premix.	8.87 (19.6)	5.7	0.6635.30 (11.7)	8.0	0.4836.45 (12.1)	3.5
Latex B	9.28 (20.5)	5.6	0.7046.43 (14.2)	7.9	0.6176.37 (14.1)	3.7
						0.228
						0.283

¹ Peak Load in Kg(lbs).

² Percent Elongation at Peak Load

³ Tensile Energy Absorption at Peak Load

nBA is n-butyl acrylate

NMA is n-methylol acrylamide

The latex of the present invention having all weight parts of itaconic acid in the reactor produced the highest wet, dry, and solvent strengths. In particular, the last five experiments indicate that all the latexes of the present invention using a dicarboxylic acid are an improvement over the commercially available acrylic latexes having the same Tg, and similar composition except with respect to the acid used.

EXAMPLE 13

The same dry, wet, and solvent strength tests as in Example 12 were conducted on chemically bonded polyester nonwoven fabric having 30% add-on. The untreated fiber mat having an unbonded density of 37.3g/m² (1.1 oz. per sq. yd.) was cut into 2.54cm x 7.62cm (1" x 3") rectangles and tested in the cross machine direction using the Thwing-Albert Intellect II tensile tester. Drying, curing, and testing were identical to those in Example 11. The results for the polyester nonwoven fabric are set forth in Table L.

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Table L

Latex Type	Dry		Wet		Solvent	
	PKLG ¹	% Elong. ²	PKLG ¹	% Elong. ²	PKLG ¹	% Elong. ²
Hycar 26171 Tg of -44	168	28	132	35	35	19
Hycar 26171 Tg of -44 (laboratory made)	170	38	147	29	31	32
Present invention; Tg of -444.5 weight parts itaconic acid in premix, with 93.5 nBA and 2 weight parts NMA.	319	54	228	43	67	17
Present invention; 4.5 weight parts itaconic acid in reactor, 93.5 weight parts nBA and 2 weights NMA.	263	58	184	54	71	23
Present invention; 4.5 weight parts itaconic acid in reactor, 93.5 weight parts nBA, and 2 weight parts NMA (smaller particle size).	277	57	135	48	49	21
			123.6			7.5
			156.6			12.0
			34.9			6.6
			35.3			5.3
			38.9			5.3
			77.4			7.6
			64.6			12.0
			54.6			7.5

Table L (continued)

Latex Type	Dry		Wet		Solvent	
	PKLG ¹	% Elong. ² TEA ³	PKLG ¹	% Elong. ² TEA ³	PKLG ¹	% Elong. ² TEA ³
Present invention; 94 weight parts nBA, 4 weight parts itaconic acid in reactor and 2 weight parts NMA.	393	42 100.5	252	27 51.6	87	13 5.2
Present invention, as above except 1 weight part itaconic acid in premix and 3 weight parts itaconic acid in the reactor.	256	33 65.8	243	34 65.1	68	12 5.6
As above, except 2 weight parts itaconic acid in premix with 2 weight parts itaconic acid in reactor.	263	60 123.8	177	46 64.1	54	17 6.1

As above, except all parts of itaconic acid are in premix.

1 Peak Load in Grams
2 Percent Elongation at Peak Load
3 Tensile Energy Absorption at Peak Load

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properties are obtained with all the itaconic acid being in the reactor while the best wet properties are obtained with all the itaconic acid in the premix. The solvent strength data in the last five examples indicates that the best solvent strengths were obtained with the itaconic acid in the reactor. Thus, again the balance of properties is best achieved when all weight parts of itaconic acid are introduced in the reactor.

EXAMPLE 14

This example demonstrates the tear strength of a 40% add-on saturated 127 μm (5 mil) flat paper. In this example, 6.35cm (2-1/2") square samples of 1-ply paper were tested on the Thwing-Albert Elmendorf tear tester. The paper was dried and cured under the same conditions set forth in Example 7.

The paper was tested first in the machine direction and then in the cross direction for its tear strength. The results are set forth below in Table M.

Table M

Latex Type	Machine Direction	Cross Direction
Latex B	88	88
Latex A	72	96
Latex C	112	128
Hycar 26083 BFG commercially available latex Tg -15.	84	84
Hycar 26000 x 322 (commercially available BFG manufactured acrylic latex) Tg -18	76	84
Hycar 1562 (commercially available BFG nitrile latex) Tg -25.	116	140

Latexes A and B are set forth in Example 10. Latex C comprises 82 weight parts 2 ethylhexyl acrylate, 10 weight parts n-butyl acrylate, 2 weight parts ethyl acrylate, 4 weight parts itaconic acid and 2 weight parts N-methylol acrylamide (Tg of -60°C).

The three Hycar latexes were selected because they are recommended for use in paper saturations. The nitrile latex was developed specifically to give good tear strength. As the results indicate, the Elmendorf tear of the present invention (Latexes A, B, and C) are about as good or better than the commercially available acrylic latexes. Though the nitrile latex product has excellent tear strength, it has several shortcomings such as poor wet strength and poor resistance to oxidation. The latexes of the present invention do not have these draw backs.

EXAMPLE 15

This example demonstrates the delamination resistance or internal bond of 40% add-on saturated 5 mil flat paper (the same paper used in Example 10). A sheet of 20 cm long saturated paper (20 cm long in machine direction) was sandwiched between 2 sheets of heat sensitive tape. The sandwich was heated and pressurized at 153°C - 155.5°C (308°F - 312°F) with a hand iron. Samples were cut into 1.5 cm by 20 cm. After ironing, the samples are positioned in a delamination press for 30 seconds at 135°C (275°F) and 186.2 kPa (27 psig). The samples were then tested on the Thwing-Albert Intellect II. Jaw separation was one inch and jaw speed was 25 cm/min. The test conditions were at 50% relative humidity and 22.2°C (72°F). The results are set forth below in Table N.

<u>Table N</u>	<u>Latex Type</u>	<u>Machine Direction</u>	<u>Cross Direction</u>	<u>Mean Delamination Resistance (oz.)</u>
	Latex B	88	88	9.32 264,2g
	Latex A	72	96	13.23 375, g
	Latex C	112	128	10.92 309,6g
	Hycar 26083 (BFG commercially available latex) Tg -15.	84	84	13.23 375,0g
	Hycar 26000 x 322 (commercially available BFG manufactured acrylic latex) Tg -18	76	84	10.56 299,4g
	Hycar 1562 (commercially available BFG nitrile latex) Tg -25.	116	140	10.31 292,3g

As this data indicates, the delamination resistance of the three samples of the present invention are very comparable to the Hycar latexes designed for paper use.

EXAMPLE 16

This example demonstrates the durability to dry cleaning and washing of a nonwoven fabric treated with the latex of the present invention. All the samples were saturated with different levels of latex add-on and dried at approximately 100°C (212°F) on a photoprint dryer and cured for 3 minutes at 149°C (300°F) in an air circulating oven. The washability test was a modified AATCC #61-1980-II-A test using a Launder-O-Meter for 1 cycle (1 cycle represents approximately 5 machine washings). The entangled nonwoven fabric chosen was Dupont's Sontara® 8103 fabric. The results are reported in Table O.

Table O

% Latex Add-On	Comments
Control - 0% 4% 10% 18%	All samples OK - no fabric damage, treated samples were still resilient indicating minimal or no loss of polymer. All samples, including control sample, had a slightly softer hand after testing.

The dry cleaning test was a modified AATCC #86-1761 test on a Launder-O-Meter for one 30 minute cycle. The results of this test is set forth in Table P.

Table P

% Latex Add-On	Comments
Control - 0% 3.9% 9.0% 17%	All samples OK - no fabric damage, treated samples were still resilient. All samples including control had a slightly softer hand.

These tests show that the latex treated Sontara® nonwoven of this invention was durable to the wash and dry clean tests used.

EXAMPLE 17

This example demonstrates the resiliency of latex treated Sontara® nonwoven fabric of this invention at different levels of latex add-on after 20% elongation and 30% elongation. In the resiliency testing 2.54cm x 15.24cm (1" x 6") samples were cut in cross machine direction and 15.24cm (6") is the cross machine direction) and the samples were stretched to the indicated elongation and released. Each sample was measured after five minutes. The permanent deformation is calculated as:

$$\frac{(\text{length after stretch and relaxation} - \text{original length})}{\text{Original Length}}$$

The results are set forth in Tables Q and R.

Table Q

20% Elongation

<u>Add On</u>	<u>Permanent Deformation (1 cycle)</u>	<u>Perm. Def. (2 cycles)</u>	<u>Permanent Change Between 1 & 2 cycles</u>
0%	6.3%	10.4%	4.1%
4%	3.1%	4.2%	1.1%
10%	2.1%	3.1%	1.0%
18%	2.1%	2.1%	0%

Table R**30% Elongation**

<u>Add On</u>	<u>Permanent Deformation (1 cycle)</u>	<u>Perm. Def. (2 cycles)</u>	<u>Permanent Change Between 1 & 2 cycles</u>
0%	15.6%	17.7%	2.1%
4%	6.3%	8.3%	2.0%
10%	5.2%	6.3%	1.1%
18%	5.2%	6.3%	1.1%

This example shows that a significant level of resiliency can be imparted to an entangled synthetic fiber nonwoven fabric using the latex of this invention.

Furthermore, when the 10% pick-up sample was stretched to 20% of its elongation 10 times and each stretch was held for 10 seconds and then relaxed 5 minutes between stretches, the permanent deformation after one stretch was 2.1%, after two stretches 3.1%, and after ten stretches 4.2%. This shows that the change in permanent deformation after 10 stretches is smaller than that after 1 or 2 stretches.

EXAMPLE 18

This example demonstrates the resistance to heat aging which can cause latex treated nonwoven fabrics to discolor. Yellowing or other discoloration is not desirable in many end use applications of nonwoven fabrics.

Samples of polyester nonwoven fabric having an unbounded density of 37.3 g/ml (1.1 oz per sq. yd.) with about 30% add-on with latex A, latex B (see Example 6), Hycar® 2671 and RHOPLEX® Tr 934 (made by Rohm & Haas Co.) were tested. Each sample was air dried and cured at 149° C (300° F) for 3 minutes before testing. The results of the example are set forth in Table S as present reflectance of incident light passed through a 2.54cm by 2.54cm (1" by 1") nonwoven samples and reflected back from the standard reference. The samples were heated for the time indicated. The standard reference white ceramic plaque was calibrated to 78% reflectance. The lower values indicate a lower reflectance.

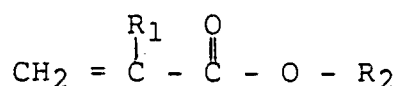
Table S
% Photovolt Reflectance

<u>Latex</u>	<u>Time (in minutes)</u>					
	<u>0</u>	<u>10</u>	<u>20</u>	<u>30</u>	<u>40</u>	<u>60</u>
Latex A	82.9	80.7	80.2	80.8	80.4	79.3
Latex B	82.3	82.3	81.5	81.9	82	81.9
Hycar 2671	81.1	82.2	81.6	80.6	79.3	79.2
RHOPLEX TR 934	81.9	82.1	80.8	82	81.5	80.7

The results of this experiment indicate that the novel latex saturated nonwoven fabric possesses comparable resistance to discoloration after heat aging with commercially available latexes designed for use with nonwoven fabrics. It has thus been demonstrated that the products of the present invention resulting from the treatment of fibers used in the examples with the novel latexes have a superior balance of properties which is unique. This balance of properties is demonstrated by high fold endurance, soft hand, good dry, wet, and solvent tensile properties, good tear resistance, good delamination resistance, a high degree of permanent deformation resistance and good color aging properties. None of conventional latex polymers tested demonstrated this unique balance.

Claims

1. A non-woven fibrous material comprising fibers bonding together with a binder consisting essentially of predominantly acrylate-containing polymer chains including repeated units derived from itaconic acid and up to 98.9 weight parts of an acrylate represented by the structure



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wherein

R₁ is hydrogen or methyl;

10 R₂ represents C₁-C₂₀ alkyl, C₂-C₇ alkoxy alkyl, C₂-C₇ alkoxy thioalkyl, a cyano alkyl radical having 2 to 12 carbon atoms, or a mixture thereof;

15 said itaconic acid is present in the range from 1 to 20 weight parts; at least 40 weight parts of said acrylate in said polymer is present as an alkyl acrylate; said polymer in an aqueous emulsion form as suitable applied in the fabric at the glass transition temperature (T_g) in the range from -20 °C to -60 °C, characterized in that said polymer is present as a crosslinked polymer and said crosslinking is effected by a crosslinking monomer present in an amount in the range from 0.1 to 20 weight parts.

2. The non-woven fibrous material of claim 1 wherein said crosslinking monomer is selected from the group consisting of N-methylol acrylamide and bis-(N-methylol)allyl carbamate, N-methylol acrylamide etherified with a C₁-C₄ alkanol and bis-(N-methylol)allyl carbamate etherified with a C₁-C₄ alkanol.

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3. The non-woven fibrous material of claim 1 wherein said polymer chains include repeating units of a copolymerized monomer selected the group consisting of alkyl acrylates; diacrylate and dimethacrylate monomers; C₂-C₁₀ monoolefins; C₂-C₁₀ vinyl and allyl acetates; C₄-C₂₀ vinyl ketones; C₄-C₂₀ allyl ethers; C₈-C₂₀ vinyl aromatics; C₃-C₆ vinyl nitriles; C₄-C₂₀ vinyl amides; C₄-C₂₀ dienes and divinyls; C₂-C₂₀ monomers containing a halogen; unsaturated sulfonate monomers; C₄-C₂₀ unsaturated carboxylic ester and unsaturated amides; and C₃-C₅ unsaturated monocarboxylic acids.

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4. The non-woven fibrous material of claims 1 or 3 wherein said copolymerized monomer is n-butyl acrylate and said itaconic acid is present in an amount in the range of from 2 to 8 weight parts.

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5. The non-woven fabric of claims 1 or 2 wherein said crosslinking monomer is N-methylol acrylamide present in the range of from 0.5 to 10 weight parts.

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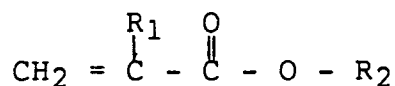
6. The non-woven fibrous material of claim 1 wherein said material is a non-woven fabric coated with a non-self-supporting film of a polymer.

7. The non-woven fabric of claim 1 wherein said polymer has a T_g of from -25 °C to -50 °C.

8. A process of making a non-woven fabric which comprises associating within a web, a mass of fibers, bringing into contact with the fibers a binder comprising an aqueous emulsion of a binder consisting essentially of predominantly acrylate-containing polymer chains including repeating units derived from itaconic acid and up to 98.9 weight parts of an acrylate represented by the structure

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45



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wherein

R₁ is hydrogen or methyl;

R₂ represents C₁-C₂₀ alkyl, C₂-C₇ alkoxy alkyl, C₂-C₇ alkoxy thioalkyl, a cyano alkyl radical having 2 to 12 carbon atoms, or a mixture thereof;

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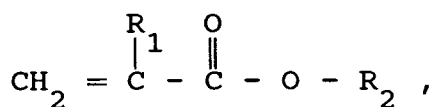
said itaconic acid is present in the range from 1 to 20 weight parts; at least 40 weight parts of said acrylate in said polymer is present as an alkyl acrylate; said polymer in an aqueous emulsion form as suitable applied in the fabric at the glass transition temperature (T_g) in the range from -20 °C to -60 °C; and drying and curing the binder treated fibers under heating conditions so that that non-woven fabric is produced,

characterized in that said polymer is present as a crosslinked polymer and said crosslinking is effected by a crosslinking monomer present in an amount in the range from 0.1 to 20 weight parts.

9. The process of claim 8 wherein said crosslinking monomer is selected from the group consisting of N-methylol acrylamide, and bis-(N-methylol)allyl carbamate, N-methylol acrylamide etherified with a C₁-C₄ alkanol and bis-(N-methylol)allyl carbamate etherified with a C₁-C₄ alkanol.
10. The process of claim 8 wherein said polymer chains include repeating units of a copolymerized monomer selected from the group consisting of an alkyl acrylate; diacrylate and dimethacrylate monomers; C₂-C₁₀ monoolefins; C₂-C₁₀ vinyl and allyl acetates; C₄-C₂₀ vinyl ketones, C₄-C₂₀ allyl ethers; C₈-C₂₀ vinyl aromatics; C₃-C₆ vinyl nitriles; C₄-C₂₀ vinyl amides; C₄-C₂₀ dienes and divinyls; C₂-C₂₀ monomers containing a halogen; unsaturated sulfonate monomers; C₄-C₂₀ unsaturated carboxylic acid and unsaturated amides; and C₃-C₅ unsaturated monocarboxylic acids.
11. The process of claim 8 or 10 wherein said copolymerized monomer is n-butyl acrylate and said itaconic acid is present in an amount in the range from 2 to 8 parts by weight.
12. The process of claim 8 wherein said crosslinking monomer is N-methylol acrylamide present in the range from 0.5 to 10 weight parts.
13. The process of claim 8 wherein said associating step includes the step of metering the latex into the reactor, a premix which comprises said copolymerizable monomer and up to one half of said itaconic acid, wherein said reactor contains at least one half of said itaconic acid, adding said crosslinking agent to said itaconic acid and subsequently conducting polymerization in the reactor at a temperature from 0 °C to 100 °C.
14. The process of claim 13 wherein all of said itaconic acid is added initially to the reactor and said premix is devoid from the itaconic acid.

Patentansprüche

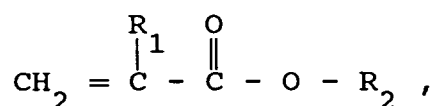
1. Faseriges Faservlies-Material, umfassend Fasern, die mit einem Bindemittel zusammen verbunden werden, das im wesentlichen aus vorherrschend Acrylat enthaltenden Polymerketten, einschließlich sich wiederholenden Struktureinheiten, die sich von Itaconsäure ableiten, und bis zu 98,9 Gewichtsteilen eines Acrylats besteht, dargestellt durch die Struktur



worin

- R₁ Wasserstoff oder Methyl ist;
R₂ C₁-C₂₀-Alkyl, C₂-C₇-Alkoxyalkyl, C₂-C₇-Alkoxythioalkyl, ein Cyanoalkyl-Rest mit 2 bis 12 Kohlenstoffatomen oder deren Mischung ist;
wobei Itaconsäure in einem Bereich von 1 bis 20 Gewichtsteilen vorliegt; wenigstens 40 Gewichtsteile des Acrylats in dem Polymer als ein Alkylacrylat vorliegen; das Polymer sich in einer wäßrigen Emulsion bei geeigneter Anwendung in dem Vlies bei einer Glasübergangstemperatur (T_g) im Bereich von von -20 °C bis -60 °C bildet, dadurch gekennzeichnet, daß das Polymer als vernetztes Polymer vorliegt und daß die Vernetzung durch ein vernetzendes Monomer erfolgt, das in einer Menge von 0,1 bis 20 Gewichtsteilen vorliegt.
2. Faseriges Faservlies-Material gemäß Anspruch 1, worin das vernetzende Monomer ausgewählt ist aus der Gruppe, bestehend aus N-Methylolacrylamid und Bis-(N-methylol)allylcarbamate, N-Methylolacrylamid, das mit einem C₁-C₄-Alkanol verethert ist und Bis-(N-methylol)allylcarbamate, das mit einem C₁-C₄-Alkanol verethert ist.

3. Faseriges Faservlies-Material gemäß Anspruch 1, worin die Polymerketten Repetiereinheiten eines copolymerisierten Monomers umfassen, das ausgewählt ist aus der Gruppe, bestehend aus Alkylacrylaten, Diacrylat- und Dimethacrylat-Monomeren, C₂-C₁₀-Monoolefinen, C₂-C₁₀-Vinyl- und Allylacetaten, C₄-C₂₀-Vinylketonen, C₄-C₂₀-Allylethern, C₈-C₂₀-Vinylaromaten, C₃-C₆-Vinylnitrilen, C₄-C₂₀-Vinylamiden, C₄-C₂₀-Dienen und Divinylen, C₂-C₂₀-Monomeren, die ein Halogen enthalten, ungesättigten Sulfonat-Monomeren, ungesättigten C₄-C₂₀-Carboxylester und ungesättigten Amiden und ungesättigten C₃-C₅- Monocarbonsäuren.
4. Faseriges Faservlies-Material gemäß Anspruch 1 oder 3, worin das copolymerisierte Monomer n-Butylacrylat ist und die Itaconsäure in einer Menge von 2 bis 8 Gewichtsteilen vorliegt.
5. Faseriges Faservlies-Material gemäß Anspruch 1 oder 2, worin das vernetzende Monomer N-Methylolacrylamid ist, das im Bereich von 0,5 bis 10 Gewichtsteilen vorliegt.
6. Faseriges Faservlies-Material gemäß Anspruch 1, worin das Material ein Faservlies ist, das mit einem nichtselbsttragenden Film eines Polymers beschichtet ist.
7. Faservlies gemäß Anspruch 1, worin das Polymer eine T_g von -25 °C bis -50 °C hat.
8. Verfahren zur Herstellung eines Faservlieses, umfassend das Verbinden einer Masse von Fasern in einem Gewebe, das in-Kontakt-Bringen eines Bindemittels mit den Fasern, das eine wäßrige Emulsion eines Bindemittels umfaßt, das im wesentlichen aus vorherrschend Acrylat enthaltenden Polymerketten, einschließlich sich wiederholenden Struktureinheiten, die sich von Itaconsäure ableiten, und bis zu 98,9 Gewichtsteilen eines Acrylats besteht, dargestellt durch die Struktur



worin

R₁ Wasserstoff oder Methyl ist;

R₂ C₁-C₂₀-Alkyl, C₂-C₇-Alkoxyalkyl, C₂-C₇-Alkoxythioalkyl, ein Cyanoalkyl-Rest mit 2 bis 12 Kohlenstoffatomen oder deren Mischung ist;

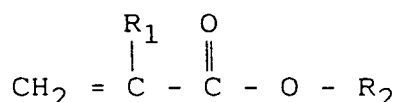
wobei Itaconsäure in einem Bereich von 1 bis 20 Gewichtsteilen vorliegt; wenigstens 40 Gewichtsteile des Acrylats in dem Polymer als ein Alkylacrylat vorliegen; das Polymer sich in einer wäßrigen Emulsion bei geeigneter Anwendung in dem Vlies bei einer Glasübergangstemperatur (T_g) im Bereich von von -20 °C bis -60 °C bildet, und Trocknen und Härten der mit dem Bindemittel behandelten Fasern unter Erwärmungsbedingungen, so daß das Faservlies hergestellt wird, dadurch gekennzeichnet, daß das Polymer als vernetztes Polymer vorliegt und daß die Vernetzung durch ein vernetzendes Monomer erfolgt, das in einer Menge von 0,1 bis 20 Gewichtsteilen vorliegt.

9. Verfahren gemäß Anspruch 8, worin das vernetzende Monomer ausgewählt ist aus der Gruppe, bestehend aus N-Methylolacrylamid und Bis-(N-methylol)allylcarbamate, N-Methylolacrylamid, das mit einem C₁-C₄-Alkanol verethert ist und Bis-(N-methylol)allylcarbamate, das mit einem C₁-C₄-Alkanol verethert ist.
10. Verfahren gemäß Anspruch 8, worin die Polymerketten Repetiereinheiten eines copolymerisierten Monomers umfassen ausgewählt aus der Gruppe, bestehend aus Alkylacrylaten, Diacrylat- und Dimethacrylat-Monomeren, C₂-C₁₀-Monoolefinen, C₂-C₁₀-Vinyl- und Allylacetaten, C₄-C₂₀-Vinylketonen, C₄-C₂₀-Allylethern, C₈-C₂₀-Vinylaromaten, C₃-C₆-Vinylnitrilen, C₄-C₂₀-Vinylamiden, C₄-C₂₀-Dienen und Divinylen, C₂-C₂₀-Monomeren, die ein Halogen enthalten, ungesättigten Sulfonat-Monomeren, ungesättigten C₄-C₂₀-Carboxylester und ungesättigten Amiden und ungesättigten C₃-C₅-Monocarbonsäuren.
11. Verfahren gemäß Anspruch 8 oder 10, worin das copolymerisierte Monomer n-Butylacrylat ist und die Itaconsäure in einer Menge von 2 bis 8 Gewichtsteilen vorliegt.

12. Verfahren gemäß Anspruch 8, worin das vernetzende Monomer N-Methylolacrylamid ist, das im Bereich von 0,5 bis 10 Gewichtsteilen vorliegt.
13. Verfahren gemäß Anspruch 8, worin die Verbindungsstufe die Stufe des Eingebens des Latex in den Reaktor, einer Premix-Masse, die das copolymerisierbare Monomer und bis zur Hälfte der Itaconsäure umfaßt, worin der Reaktor wenigstens eine Hälfte der Itaconsäure enthält, Zugabe des Vernetzungsmittels zur Itaconsäure und anschließendes Durchführen der Polymerisation in dem Reaktor bei einer Temperatur von 0 °C bis 100 °C umfaßt.
14. Verfahren gemäß Anspruch 13, worin die gesamte Itaconsäure zu Beginn dem Reaktor zugegeben wird und die Premix-Masse frei von der Itaconsäure ist.

Revendications

1. Matériau fibreux non tissé, constitué de fibres liées les unes aux autres par un liant composé essentiellement de chaînes polymères contenant en majorité des groupes acrylates comprenant des motifs répétitifs dérivés de l'acide itaconique, et jusqu'à 98,9 parties en poids d'un acrylate représenté par la structure



dans laquelle

R₁ est un hydrogène ou le radical méthyle,

R₂ est un radical alkyle en C₁-C₂₀, alcoxyalkyle en C₂-C₇, alcoxythioalkyle en C₂-C₇, un radical cyanoalkyle ayant de 2 à 12 atomes de carbone ou un de leurs mélanges ;

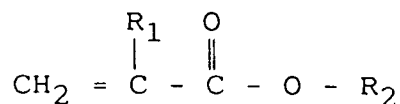
l'acide itaconique est présent dans l'intervalle de 1 à 20 parties en poids ; au moins 40 parties en poids de l'acrylate se trouvant dans le polymère sont présents sous forme d'un acrylate d'alkyle ; le polymère, sous forme d'une émulsion aqueuse, étant appliqué comme il convient dans l'étoffe à une température de transition vitreuse (T_g) comprise dans l'intervalle de -20 à -60 °C, caractérisé en ce que le polymère est présent sous forme d'unpolymère réticulé, et que la réticulation est effectuée par un monomère de réticulation présent en une quantité comprise dans l'intervalle de 0,1 à 20 parties en poids.

2. Matériau fibreux non tissé selon la revendication 1, dans lequel le monomère de réticulation est choisi parmi l'ensemble comprenant le N-méthylolacrylamide et le carbamate de bis-(N-méthylol)allyle, le N-méthylolacrylamide étherifié par un alcool en C₁-C₄ et le carbamate de bis-(N-méthylol)allyle étherifié avec un alcool en C₁-C₄.
3. Matériau fibreux non tissé selon la revendication 1, dans lequel les chaînes polymères comprennent des motifs répétitifs d'un monomère copolymérisé choisi parmi l'ensemble comprenant les acrylates d'alkyle, les monomères diacrylates et diméthacrylates ; les monooléfines en C₂-C₁₀, les acétates de vinyle et d'allyle en C₂-C₁₀, les vinylcétones en C₄-C₂₀, les oxydes d'allyle en C₄-C₂₀, les vinylaromatiques en C₈-C₂₀, les vinylnitriles en C₃-C₆, les vinylamides en C₄-C₂₀, les diènes et divinyles en C₄-C₂₀ ; les monomères en C₂-C₂₀ contenant un halogène ; les monomères sulfonates insaturés ; les esters d'acides carboxyliques insaturés et les amides insaturés en C₄-C₂₀ ; et les acides monocarboxyliques insaturés en C₃-C₅.
4. Matériau fibreux non tissé selon la revendication 1 ou 3, dans lequel le monomère copolymérisé est l'acrylate de n-butyle, et l'acide itaconique est présent en une quantité comprise dans l'intervalle de 2 à 8 parties en poids.
5. Etoffe non tissée selon la revendication 1 ou 2, dans laquelle monomère de réticulation est le N-méthylolacrylamide, présent en une quantité comprise dans l'intervalle de 0,5 à 10 parties en poids.

6. Matériau fibreux non tissé selon la revendication 1, dans lequel le matériau est une étoffe non tissée revêtue d'un film non autoporteur d'un polymère.

7. Etoffe non tissée selon la revendication 1, dans laquelle le polymère a une T_g de -25 à -50 °C.

8. Procédé pour fabriquer une étoffe non tissée, qui consiste à associer, dans un tissu, une masse de fibres, à mettre en contact avec les fibres un liant comprenant une émulsion aqueuse d'un liant constitué essentiellement de chaînes polymères contenant en majorité des groupes acrylates, comprenant des motifs répétitifs dérivés de l'acide itaconique, et jusqu'à 98,9 parties en poids d'un acrylate représenté par la structure



dans laquelle

R_1 est un hydrogène ou le radical méthyle,

R_2 est un radical alkyle en $\text{C}_1\text{-C}_{20}$, alcoxyalkyle en $\text{C}_2\text{-C}_7$, alcoxythioalkyle en $\text{C}_2\text{-C}_7$, un radical cyanoalkyle ayant de 2 à 12 atomes de carbone ou un de leurs mélanges;

l'acide itaconique est présent dans l'intervalle de 1 à 20 parties en poids ; au moins 40 parties en poids de l'acrylate se trouvant dans le polymère sont présents sous forme d'un acrylate d'alkyle ; le polymère, sous forme d'une émulsion aqueuse, étant appliqué comme il convient dans l'étoffe à une température de transition vitreuse (T_g) comprise dans l'intervalle de -20 à -60 °C ; et à sécher et durcir les fibres traitées par le liant, dans des conditions de chauffage telles qu'il y ait production de l'étoffe non tissée, caractérisé en ce que le polymère est présent sous forme d'un polymère réticulé, et que la réticulation est effectuée par un monomère de réticulation présent en une quantité comprise dans l'intervalle de 0,1 à 20 parties en poids.

9. Procédé selon la revendication 8, dans lequel le monomère de réticulation est choisi parmi l'ensemble comprenant le N-méthylolacrylamide et le carbamate de bis-(N-méthylol)allyle, le N-méthylolacrylamide étherifié par un alcool en $\text{C}_1\text{-C}_4$ et le carbamate de bis-(N-méthylol)allyle étherifié avec un alcool en $\text{C}_1\text{-C}_4$.

10. Procédé selon la revendication 8, dans lequel les chaînes polymères comprennent des motifs répétitifs d'un monomère copolymérisé choisi parmi l'ensemble comprenant les acrylates d'alkyle, les monomères diacrylates et diméthacrylates ; les monooléfines en $\text{C}_2\text{-C}_{10}$, les acétates de vinyle et d'allyle en $\text{C}_2\text{-C}_{10}$, les vinylicétones en $\text{C}_4\text{-C}_{20}$, les oxydes d'allyle en $\text{C}_4\text{-C}_{20}$, les vinylaromatiques en $\text{C}_8\text{-C}_{20}$, les vinylnitriles en $\text{C}_3\text{-C}_6$, les vinylamides en $\text{C}_4\text{-C}_{20}$, les diènes et divinyles en $\text{C}_4\text{-C}_{20}$; les monomères en $\text{C}_2\text{-C}_{20}$ contenant un halogène ; les monomères sulfonates insaturés ; les esters d'acides carboxyliques insaturés et les amides insaturés en $\text{C}_4\text{-C}_{20}$; et les acides monocarboxyliques insaturés en $\text{C}_3\text{-C}_5$.

11. Procédé selon la revendication 8 ou 10, dans lequel le monomère copolymérisé est l'acrylate de n-butyle, et l'acide itaconique est présent en une quantité comprise dans l'intervalle de 2 à 8 parties en poids.

12. Procédé selon la revendication 8, dans lequel le monomère de réticulation est le N-méthylolacrylamide, présent en une quantité comprise dans l'intervalle de 0,5 à 10 parties en poids.

13. Procédé selon la revendication 8, dans lequel l'étape d'association comprend l'étape consistant à doser le latex dans le réacteur, un prémix comprenant le monomère copolymérisable et jusqu'à la moitié de l'acide itaconique, le réacteur contenant au moins une moitié de l'acide itaconique, à ajouter l'agent de réticulation à l'acide itaconique puis à mettre en oeuvre la polymérisation dans le réacteur à une température de 0 à 100 °C.

14. Procédé selon la revendication 13, dans lequel la totalité de l'acide itaconique est introduite initialement dans le réacteur, le prémix ne contenant pas d'acide itaconique.