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Greif et al.

[54] NONWOVEN PRODUCTS

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161/70, 82, 170, 150; 156/62.2, 62.4, 306

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[57] ABSTRACT

This invention is directed to producing polymeric binding agents in fibrous form for nonwoven fabrics and for nonwoven fabrics incorporating such polymeric binding agents in fibrous form, the fibrous form polymeric binding agents being obtained by introducing an anionic latex in fine thread-like form into a precipitating aqueous solution of a water-soluble cationic polymer, and thereby forming a fibrous precipitate of the anionic latex in the cationic solution. The nonwoven fabrics produced are characterized by their unusually high strength.

10 Claims, No Drawings

NONWOVEN PRODUCTS

This invention relates to improved nonwoven products and fabrics characterized by their unusually high strength and durability. In a further aspect, the inven-5 tion also relates to a process of preparing a polymeric binding agent in fibrous form intended for use in the production of the improved nonwoven products of this invention.

The forming of bonded nonwoven fabrics by means 10 of conventional dry processing includes the impregnating, printing, spraying, coating or otherwise depositing of an adhesive bonding agent (ordinarily a polymeric material) onto a fibrous base web comprising relatively lengthy fibers ranging from about one-half inch to two- 15 and-one-half inches, or more, composed of materials such as synthetic or natural fibers. Also known are wetlaid processes wherein an aqueous slurry or suspension of fibers together with a selected binding agent and any desired optional ingredients are utilized in forming a 20 web on a wire screen, such as is ordinarily used in a paper making process. It can be understood that such properties of nonwovens as softness, durability, dry tensile strength and wet tensile strength (i.e. the strength of the nonwoven after being substantially satu- 25 rated with water), are of primary importance and are highly dependent on the selected binding agent and the process utilized in the formation of the nonwoven. While a large number of variations in processes and binding agents are available to the practitioner, none of 30 these heretofore known processes or binding agents results in an entirely satisfactory nonwoven product which exhibits the optimum combination of requisite properties. Thus, while certain processes and binding agents of the prior art may lead to a product having ad- 35 equate dry strength, the product ordinarily will be lacking in other desirable properties.

A recently proposed wet-laid process for forming nonwovens describes the preparation and use of polymeric binding agents in fibrous form, which form of the 40binding agent will tend to have beneficial effects upon many properties of the final product. The fibrous binding agent itself is proposed to be obtained by a process of mixing a latex of a carboxyl-group containing polymer together with an aqueous solution of a cationic ⁴⁵ polymeric material at a pH of 6 to 9. After a period of time, no more than 60 minutes, the pH of the mixture is adjusted to 2 to 4, whereupon the very fine polymeric particles which are originally formed are allegedly converted into fibrous particles. In repeated attempts at 50 carrying out this proposed process, particular difficulty was encountered in obtaining a fibrous precipitate, i.e. a precipitate composed of particles having a slender, thread-like structure. Each attempt at forming the fibrous precipitate according to the proposed process resulted in a precipitate of agglomerated particles. Close examination of the resultant precipitate with the aid of a microscope confirmed the formation of pear-shaped agglomerates measuring approximately 50-100 microns, rather than the desired slender, thread-like structures.

Accordingly, the primary object of this invention is to provide a new and improved polymeric binder in fibrous form for use in nonwoven products. Another object of this invention is to provide a new and improved nonwoven product characterized by its improved durability and dry and wet strength as compared to typical

nonwovens formed by means of conventional, known processes.

By the term "nonwoven products" herein we mean bonded nonwoven sheet material comprising a bonded self-supporting fibrous base web; a representative example of a nonwoven product being a nonwoven fabric.

By the term "fibrous" herein with reference to the polymeric binding agent we mean thread-like particles having a length which is at least several times larger than the diameter of the precipitated polymer.

In accordance with this invention, it has been found that superior polymeric binding agents in fibrous form may be prepared by a controlled, instantaneous precipitation wherein an anionic latex is brought into intimate contact with an aqueous solution of a cationic polymer under critical, specified conditions. The precipitated binder particles are instantaneously obtained in distinctly fibrous form and are particularly intended for use in the production of nonwoven products by means of a wet-laid process. The resultant nonwovens utilizing the fibrous binder display a number of substantially improved desired properties and particularly exhibit unusual strength and durability as compared to comparable nonwovens formed by conventional processes.

With respect to the preparation of the fibrous binding agent, it is first necessary to prepare an aqueous solution of water-soluble cationic polymer which is to be used in precipitating the anionic latex. Among the classes of water-soluble polymers useful herein as included:

- a. acid salts of aminoalkyl esters of carboxylic acid polymers as described in U.S. Pat. No. 3,372,149 issued Mar. 5, 1968, including homopolymers and copolymers of these carboxylic acids with methyl vinyl ether, vinyl acetate, acrylamide, methacrylamide, lower alkyl esters of acrylic and methacrylic acid, etc.
- b. high molecular weight polysulfur amidoamines as described in U.S. Pat. No. 3,464,969 issued Sept.
 2, 1969. These compounds are the reaction product of a low molecular weight polyamide with a sulfur containing reagent such as a sulfur halide or sulfur acid and thereafter, if desired, chain extended by reaction with an epihalohydrin.
- c. copolymers of β -hydroxyalkyl ethylenically unsaturated ester with vinyl tertiary amine as described in U.S. Pat. No. 3,227,672 issued Jan. 4, 1966.

Representative other water-soluble cationic polymers suitable for use in precipitating the anionic latex may be selected from such classes of polymers as polyamine polymers, polyalkylenimine polymers, amine modified acrylamide polymers, quaternary amine-containing polymers, and the like. Starches which have been modified to contain cationic groups may also be utilized in preparing the precipitating solution.

The concentration of the cationic polymer in the precipitating solution will ordinarily be from about 0.3 to 4.5 percent and preferably from about 0.4 to 1.5 percent, by weight. Precipitating solutions containing less than about 0.3 percent of the cationic polymer will tend to precipitate the anionic latex in minute granular form. Solutions of the cationic polymer which contain more than about 5 percent of the cationic polymer will tend to precipitate the anionic latex in an agglomerate form.

By the term "anionic latex" as used herein we mean an aqueous latex or emulsion of a polymer having an anionic or neutral polymeric backbone. In preparing the latex or emulsion of an anionic polymer one may employ either an anionic surfactant or a non-ionic surfactant or a combination of an anionic and non-ionic surfactant. In preparing the latex or emulsion of a neutral polymer one may employ an anionic surfactant or 5 a combination of an anionic and non-ionic surfactant. Typical anionic surfactants which are useful in preparing these polymers include sodium alkyl sulfates, sodium alkyl aryl sulfonates, sodium naphthalene sulfonates, etc.

Since the relative softness or hardness of the polymeric binder will affect its adhesive or binding properties as well as the properties of the nonwoven which is formed therewith, it is important that the polymers of the anionic latices used herein fall within a specified 15 range in this respect. The polymers of the anionic latices used in the process of this invention should display a glass transition temperature (Tg) of from about $t\pm 25^{\circ}$ to -52° C. Tg is a measure of a polymer's softness or hardness, wherein higher temperatures indicate a relatively harder polymer and lower temperatures indicate a softer polymer. Moreover, the polymers of the anionic latices used herein should have a molecular weight as characterized by an intrinsic viscosity in acetone at 30°C. of at least 0.25.

Illustrative of the polymers useful in the preparation of the anionic latex herein are homo- and copolymers of such monomers as vinyl acetate, vinyl chloride, vinyl esters of alpha-branched saturated aliphatic monocarboxylic acids, vinylidene chloride, alkyl acrylates and 30methacrylates, butadiene, acrylonitrile, and styrene, etc., provided the polymers have a Tg within the range specified hereinabove. If desired, a crosslinking or functional monomer, i.e. a monomer having a functional group such as N-methylol, carboxyl or sulfoxyl 35 group, may also be copolymerized with the above mentioned monomers. Examples of such functional monomers are N-methylol acrylamide, ethylenically unsaturated mono- and dicarboxylic acids such as acrylic and methacrylic acids, maleic acid, etc. The concentration ⁴⁰ of these functional crosslinking monomers is preferably less than about 8 percent, based on the weight of the total polymer. In addition to the surfactant employed in preparing the latex, the latices may also contain such 45 optional additives as plasticizers, defoamers, dispersing agents, antioxidants, and any other conventional additives commonly used in commercial anionic latex formulations.

The anionic latex which is utilized in forming the fibrous precipitate is employed in a solids concentration of about 5 to 45 percent, by weight. Latices having a solids concentration exceeding about 50 percent solids, by weight, are functional and may be employed by the results achieved therewith are less desirable. Experiments using concentrations of anionic latex between 10 and 40 percent solids, by weight, have shown that the use of the higher solids concentrations yields a fibrous precipitate in which the fibers have a relatively larger diameter.

The process for preparing the polymeric binding agent in fibrous form according to the present invention consists in introducing the anionic latex in fine thread-like form into the precipitating aqueous solution of a water-soluble cationic polymer, which is stirred at moderate speeds, and thereby forming a fibrous precipitate of the anionic latex in the cationic solution. To accomplish this the anionic latex may conveniently be introduced by means of tubing having a very small orifice or preferably an assembly of orifices through which the latex is discharged into the cationic polymer solution. It is preferred that the diameter of the orifices through which the latex is discharged fall within a range of from about 0.01 to 0.05 inches. While orifices which fall outside of the preferred range can also be used, their undesirable effect upon the form of the polymeric precipitate discourages their use. The orifice or orifice assem-

10 bly of the tubing equipment can either be submerged below the surface of the cationic polymer solution or, if desired, raised to a point just above the surface of the cationic polymer solution so that the anionic latex, in effect, is sprayed onto the precipitating solution. From 15 a practical viewpoint, the latter variation is preferred

since the submerged procedure may lead to clogging of the openings when the precipitating is interrupted.

The forming of the fibrous precipitate can be carried out at temperatures ranging from about 40° to 180°F 20 with the preferred temperatures being from about 40° to 120°F. Most conveniently, the reaction is carried out at room temperature. Generally, the use of temperatures above about 120°F. in combination with the softer polymers is not desirable because of the poor 25 form of the resultant precipitate.

The reactants which are employed to form the fibrous precipitate, i.e. the anionic latex and the precipitating solution, are generally employed at their existing pH values, and the reaction therewith is carried out at the existing pH providing the pH of the reaction media does not exceed about pH 7.5.

A well defined fibrous precipitate is formed instantaneously on contact of the latex with the precipitating solution. No waiting period or pH adjustments are required. Chiefly for practical purposes relating to agitation and the like, the precipitated solids which are accumulated in the precipitating solution should preferably not exceed about 18%, by weight.

When the addition of the latex to the precipitating solution is completed, the solids are ordinarily separated from the supernatant liquid, washed with water, and subsequently suspended in clean water in anticipation of their use as a binding agent in forming the nonwoven product. If desired, the thus precipitated binding agent may be employed directly in forming the nonwoven, without washing.

The actual forming of the nonwoven may be carried out by admixing the selected fiber together with the prepared fibrous binding agent in water. Illustrative of the fibers which can be used herein either alone or in combination with one another are fibers from such natural materials as wool and cotton hemp, and synthetic cellulose fibers such as regenerated cellulose and rayon. Other fibers include fibers from nylon, polyesters i.e. "Dacron", acrylics i.e. "Orlon", polyolefins, polyurethanes, asbestos, and glass, as well as ceramic and metallic fibers. In general, the fibrous polymeric binding agent on a dry solids basis should be from about 10 to 80 percent or more, by weight, of the dry finished nonwoven product. The upper limit on binder concentration is not particularly critical and is at the direction of the practitioner with respect to the desired properties of the finished product.

The suspended material is then formed into a nonwoven sheet by feeding or depositing the mixture onto a wire screen, such as is employed in a conventional papermaking process, and removing the excess water. The resultant wet, self-supporting web is then dried by any means such as air oven, drying can, or the like. Ordinarily, drying is effected at temperatures of from about 210° to 280°F for periods of 2 to 8 minutes. If the latex used in forming the fibrous binding agent is a 5 heat-activated, so-called "self-reactive" type, i.e. crosslinks upon exposure to heat, or if a crosslinking agent which is heat-activated, such as is well known in the art, is optionally added to the latex, an additional step of curing at temperatures of from about 280° to 380°F for 10 a period of 3 to 5 minutes may be required. It can be easily understood that the drying and curing periods may be combined into one step if desired, and other time-temperature relationships can be employed, keeping in mind that the upper temperature limits are gov- 15 erned by the nature of the fibers and the fibrous binding agent.

The softness and flexibility of ths nonwovens described herein can be enhanced by the addition of small amounts of external plasticizers, and such plasticizers 20 as, for example, dibutyl phthalate and tricresyl phosphate, may be added, if desired, to the latex before it is added to the precipitating solution or added to the fiber suspension at any time before it is fed onto the wire screen. Other optional ingredients as, for example, 25 dyes, pigments, preservaties, etc. may likewise be added to the fiber suspension before the suspension is fed onto the wire screen, if desired.

The nonwoven products formed with the fibrous binders of this invention are particularly characterized ³⁰ by their outstanding strength and durability. In testing these products, test pro-cedures established by the Technical Association of the Pulp and Paper Industry (TAPPI) were followed. The Finch edge tear test was determined by means of TAPPI test T470 M-54, ³⁵ wherein higher readings indicate a proportionately stronger fabric. The percent elongation was determined by means of TAPPI test T457 M-46. The dry tensile strength was determined by means of TAPPI test T404 ts-66, and the Mullen burst strength was determined by means of TAPPI test T403 ts-63.

The following examples will further illustrate the embodiment of our invention. The concentration of the monomer components of the copolymers is given in parts by weight.

EXAMPLE I

This example illustrates the novel process of this invention in the formation of a representative nonwoven as well as the improved properties thereof.

A cationic precipitating solution was prepared by dissolving 10 grams of the nitrate salt of poly(2aminoethyl acrylate: 2-hydroxypropyl acrylate) (62.5:37.5) in 1 liter of water with stirring which was 55 continued at a moderate rate (about 120 rpm) throughout the precipitating step. A tubing device comprising copper tubing (14 inch diameter) shaped in the form of a circle about 3 inches in diameter and having 26 small openings (0.025 inch diameter) was fixed so as to posi-60 tion the openings to be about 1 inch from the surface of the precipitating solution. An aqueous anionic latex of an ethyl acrylate:butyl acrylate:vinyl acetate: Nmethylol acrylamide (60:30:10:3) polymer having a Tg of about -21° C. (700 millimeters, 20 percent solids, by weight) was forced through the tubing device and out 65 of the multiple openings by means of air pressure. The addition of the entire quantity of the latex required

about 12 minutes and resulted in a fibrous precipitate, which after washing and drying, weighed 142 grams. The precipitated polymer fibers measured, on the average, about 6 microns in diameter ad up to 500 microns in length. The pH of the supernatant liquid at the conclusion of the latex addition was found to be 2.8. In preparation for its use as a binding agent in the nonwoven, the precipitate was suspended in water in a concentration of about 5 percent, by weight.

Thereafter, 20 millileters of the suspension containing the fibrous precipitate (1 gram, dry weight) was added to a suspension of 2 grams of rayon fibers (1.5 denier, 0.375 inch length) in 1600 milliliters of water with moderate agitation. The resultant well-mixed suspension was poured into the head box of a standard Noble & Wood laboratory sheet making apparatus to form an 8 by 8 inch fibrous web. Excess water was removed by vacuum and the nonwoven was dried by means of a drying can at 210°F. for a period of 8 minutes. The finished nonwoven sheet measured about 0.011 inches in thickness and possessed a desirably flexible, soft hand.

The superior strength characteristics of this nonwoven are indicated in Table I, following, wherein testing results obtained with the above-identified TAPPI tests are summarized. A comparable nonwoven which had been prepared with no binder as well as a comparable nonwoven which had been prepared with an identical polymeric binder which, however, was precipitated according to prior art techniques and did not possess a fibrous form were tested in similar manner for comparison purposes.

TABLE I

	Nonwoven Fabric Formed With:		
	No	Non-Fibrous	Fibrous
Test Procedure	Binder	Binder	Binder
Finch Edge Tear (lb./square inch)	0.03	0.08	8.7
Percent Elongation	0.6	0.7	10.2
Dry Tensile Strength		•	
(lbs./square inch)	0.02	0.03	4.6
Mullen Burst Strength (lb.square			
inch)	2.6	2.9	34 7

Thus, it is seen that in all of the above tests, the nonwoven fabric of this invention surpasses, by far, the val-⁴⁵ ues obtained with the nonwoven fabric prepared with no binder as well as the nonwoven fabric prepared with the identical binder in non-fibrous form.

In a repetition of the above procedure, the cationic precipitating solution was employed in a concentration of 0.5 percent, by weight. About 350 milliliters of the identical anionic latex which, however, had a solids concentration of 40 percent, by weight, was forced through the tubing device. A nonwoven was prepared as described above, employing 1 gram of the resultant fibrous precipitate and 2 grams of the rayon fibers, which exhibited a soft, flexible hand as well as strength characteristics comparable to the nonwoven of this invention described above.

EXAMPLE II

This example illustrates the process of this invention utilizing a polymeric fibrous binding agent prepared from another anionic latex.

The procedure of Example I was repeated except that the latex used therein was replaced with an aqueous anionic latex of an ethyl acrylate:vinylidene chloride:Nmethyol acrylamide (60:40:0.4) polymer having a T_3 of -13° C., and the temperature of the latex and precipitating solution was about 80° C.

The resultant nonwoven fabric was soft and flexible, and exhibited strength properties comparable to those of the non-woven fabric of this invention described in 5 Example 1.

EXAMPLE III

This example illustrates the process of this invention utilizing a polymer fibrous binding agent in the forma- 10 tion of a nonwoven comprising glass fibers.

The procedure of Example I was repeated except that the rayon fibers employed to form the nonwoven therein were replaced by an equal amount of glass fibers having a diameter of about 3.8 microns and a length of about 1 inch. Another nonwoven was prepared for comparison purposes employing the identical glass fibers with no binding agent. In each of the testing procedures identified in Example I, the nonwoven formed with the fibrous binding agent of this invention was found to exhibit substantially higher strength characteristics as compared to the nonwoven formed without such binder. Y. under The polcipitate This of fibrous 20 About a styrer about cipitate

EXAMPLE IV

This example illustrates a variation in the process of forming the nonwoven fabric of this invention. In this variation the fibrous binding agent is formed in situ directly in a suspension of fibers which are being utilized for the formation of the nonwoven fabric. This variation thereby eliminates the need for preparing the binding agent separately and can be useful in certain applications of the process.

To 1,000 milliliters of a 1 percent, by weight, of an 35 aqueous solution of the nitrate salt of poly(2aminoethyl acrylate: 2-hydroxypropyl acrylate) (62.5:37.5) was added 10 grams of rayon fibers as described in Example I. About 250 milliliters of an aqueous anionic latex of an ethyl acrylate:butyl acrylate:vi- 40 nyl actate:N-methylol acrylamide (60:30:10:3) polymer having a Tg of about -21°C. and 20 percent solids, by weight, was forced through a tubing device as described in Example I into the precipitating solution and thereby forming the fibrous precipitate. When the pre- 45 cipitation was completed, the solids of the resultant suspension were washed with water, and thereafter were formed into a nonwoven essentially as described in Example I. The finished nonwoven sheet after drying possessed a soft, flexible hand similar to the nonwoven 50 of this invention described in Example I.

EXAMPLE V

This example illustrates the preparation of additional fibrous binding agents of this invention utilizing other ⁵⁵ anionic latices and precipitation solutions.

About 400 milliliters of an aqueous, anionic latex of a vinylidene chloride:methyl acrylate:N-methylol acrylamide (90:10:3) terpolymer having a Tg of about -25° C. (20 percent solids, by weight) was forced 60 through a tubing device into a cationic precipitating solution prepared by dissolving 15 grams of polyethyleneimine in 1 liter of water. The precipitating solution was stirred at a moderate rate throughout the entire precipitating step. Close examination of the resultant precipitate after washing and drying revealed discrete, fibrous, thread-like particles.

In a repetition of the above procedure, the aqueous latex employed therein was replaced, in identical proportion, with an aqueous, anionic latex of a styrene:butyl acrylate:acrylic acid (45:55:2) terpolymer having a Tg of -9° C. In still another repetition of the above procedure, an aqueous, anionic latex of a copolymer (85:15) of vinyl acetate and a mixture of vinyl esters of isomers of an alpha-branched saturated aliphatic monocarboxylic acid having 10 carbon atoms in the carboxylic acid moiety was employed. The latter monomer is sold by Shell Chemical Company, New York, N. Y. under the product name "VV-10 Vinyl Monomer." The polymer exhibits a Tg of $+ 25^{\circ}$ C. The resultant precipitates exhibited a distinctly fibrous form in each instance.

EXAMPLE VI

This example illustrates the preparation of additional fibrous binding agents of this invention.

About 400 milliliters of an aqueous, anionic latex of a styrene:butadiene (30:70) copolymer having a Tg of about --52°C. (20 percent solids, by weight) was precipitated in the usual manner according to the procedure of this invention with a precipitating solution was
prepared by dispersing 10 grams of a high amylose corn starch which had previously been etherified by treatment with 12.5 percent, by weight, of beta diethyl aminoethyl chloride according to U.S. Pat. No. 2,813,093 in 1 liter of water. The precipitating solution was stirred at a moderate rate throughout the entire precipitating step. The resultant precipitate exhibited a distinct, fibrous form.

While the described process represents a preferred manner of preparing and obtaining the precipitated fibrous binding agent and of forming the nonwoven, it can be appreciated that inherent variations in the process can easily be utilized and are intended to be within the scope of the present invention. For example, instead of introducing the latex to a solution of the cationic polymer, it is also possible (with less desirable results, however) to introduce the cationic polymer into the latex. Likewise, another variation makes use of a Y-shaped mixing tube, wherein the tube is a means for simultaneously and intimately contacting the precipitating solution and the separately fed anionic latex which is emitted through tiny orifices. In still another variation of the described process, the drying of the wet nonwoven may be combined with sufficient pressure so as to soften the binder particles to a point where they will essentially envelope a large portion of the fibers of the nonwoven.

It is to be noted that while the preparation of the fibrous binding agent in accordance with the process of this invention has been described with respect to a batch process, it is also possible to utilize a continuous process for this purpose.

Summarizing, it is thus seen that this invention provides a novel process of preparing a polymeric binding agent in fibrous form as well as an improved nonwoven product displaying superior strength.

It will be understood that variations can be made in proportions, materials and procedures without departing from the scope of this invention which is defined by the following claims.

We claim:

1. A nonwoven fabric formed from a self-supporting web comprised of fibers bonded with a polymeric binding agent in fibrous form prepared by introducing an anionic latex of a polymer, having a glass transition temperature of from about -52°C to +25°C, selected from the group consisting of polymers having an anionic backbone and polymers having a neutral backbone in fine thread-like form into a stirred precipitating aqueous solution containing about 0.3 to about 5 percent, by weight, of a water soluble cationic polymer and thereby forming a fibrous precipitate of thread-like binder particles of the anionic latex in the cationic 10 polymer solution.

2. A process for preparing a polymeric binding agent in fibrous form which consists in introducing an anionic latex of a polymer, having a glass transition temperature of from about -52°C to +25°C, selected from the group consisting of polymers having an anionic backbone and polymers having a neutral backbone in fine thread-like form into an agitated precipitating aqueous solution containing about 0.3 to about 5 percent, by weight, of a water soluble cationic polymer and thereby 20 forming a fibrous precipitate of thread-like binder particles of the anionic latex in the cationic polymer solution.
2. A process for preparing a glass transition temperature of the anionic backbone in fine thread-like form into an agitated precipitating aqueous solution containing about 0.3 to about 5 percent, by weight, of a water soluble cationic polymer and thereby 20 forming a fibrous precipitate of thread-like binder particles of the anionic latex in the cationic polymer solution.

3. The process of claim 1, in which the anionic latex is introduced into the precipitating aqueous solution of 25 the cationic polymer through tubing having at least one orifice of a diameter of from 0.01 to 0.05 inches.

4. The process of claim 1, wherein the anionic latex is a homo- or copolymer of monomers selected from the group consisting of: vinyl acetate, vinyl chloride, 30 vinyl esters of alpha-branched saturated aliphatic monocarboxylic acids, vinylidene chloride, alkyl acrylates and methacrylates, butadiene, acrylonitrile and styrene.

5. The process of claim 1, wherein the polymer of the 35 anionic latex also contains a monomer selected from the group consisting of N-methylol acrylamide, ethylenically unsaturated monocarboxylic acids, and ethylenically unsaturated dicarboxylic acids.

6. The process of claim 1, wherein the water-soluble 40 cationic polymer is selected from the group consisting of: acid salts of aminoalkyl esters of carboxylic acid polymers, high molecular weight polysulfur amidoamines, copolymers of β -hydroxyalkyl ethylenically unsaturated ester with vinyl tertiary amine, polyamine 45 polymers, polyalkylenimine polymers, amine modified acrylamide polymers, quaternary amine-containing polymers, and starches which have beem modified to contain cationic groups.

7. A process for preparing a polymeric binding agent 50 in fibrous thread-like binder particles form which con-

sists in introducing in fine thread-like form an anionic latex of an ethyl acrylate:butyl acrylate:vinyl acetate: N-methylol acrylamide (60:30:10:3) polymer having a glass transition temperature (Tg) of about -21° C. into an agitated precipitating solution comprising an aqueous solution of a nitrate salt of poly(2-aminoethyl acrylate:2-hydroxypropyl acrylate) (62.5:37.5), said salt being present in a concentration of from about 0.3 to 4.5 percent, by weight.

8. The process of claim 7 in which the anionic latex is introduced into the precipitating solution through tubing having at least one orifice of a diameter of from 0.01 to 0.05 inches.

9. A process for preparing a nonwoven sheet which comprises:

- A. introducing an aqueous anionic latex of a polymer selected from the group consisting of polymers having an anionic backbone and polymers having a neutral backbone having a glass transition temperature of from about $+25^{\circ}$ to -52° C through at least one orifice having a diameter of from about 0.01 to 0.05 inches into an agitated, aqueous precipitating solution containing about 0.3 to 5%, by weight, of a water-soluble cationic polymer;
- B. admixing the resultant fibrous thread-like binder precipitated particles with natural or synthetic fibers in a concentration such that said binder constitutes from about 10 to 80 percent, by weight, of the dry nonwoven sheet;
- C. forming a nonwoven web from the resultant solids thereof, and
- D. drying the resultant nonwoven web.

10. A process for preparing a nonwoven sheet which comprises:

- A. introducing an aqueous anionic latex of a polymer selected from the group consisting of polymers having an anionic backbone and polymers having a neutral backbone and having a glass transition temperature of from about $+25^{\circ}$ to -52° C through at least one orifice having a diameter of from about 0.01 to 0.05 inches into an agitated, aqueous precipitating solution containing about 0.3% to about 5%, by weight, of a water-soluble cationic polymer thereby forming thread-like binder particles to which has been added from about 20 - 90 percent, by weight, based on the weight of the nonwoven, of natural or synthetic fibers;
- B. forming a nonwoven web from the resultant solids thereof, and
- C. drying the resultant nonwoven web.

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