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(71) Applicant: **KIMBERLY-CLARK WORLDWIDE, INC.** [US/US]; 401 N. Lake Street, Neenah, WI 54956 (US).

(72) Inventors: **BUNYARD, Clayton, W.**; 833 Manitowish Place, DePere, WI 54115 (US). **BRANHAM, Kelly, D.**; 6661 Cross Road, Winneconne, WI 54986 (US). **LOSTOCCO, Michael, R.**; 93 Bellevue Place, Appleton, WI 54913 (US). **CALHOUN, Glenn**; 2906 Buckingham Court, Waukesha, WI 53188 (US). **WESTON, Rod**; 11958 West Mill Road #14, Milwaukee, WI 53225 (US). **LANG, Frederick, J.**; 1541 Whitetail Drive, Neenah, WI 54956 (US). **POSSELL, Kevin**; 123 N. Green Bay Road, Appleton, WI 54911 (US).

(74) Agents: **RICHARDS, Robert, E.** et al.; KILPATRICK STOCKTON LLP, Suite 2800, 1100 Peachtree Street, Atlanta, GA 30309 (US).

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(54) Title: IMPROVED ION TRIGGERABLE, CATIONIC POLYMERS, A METHOD OF MAKING SAME AND ITEMS USING SAME

(57) **Abstract:** The present invention is directed to ion triggerable, water-dispersible cationic polymers. The present invention is also directed to a method of making ion triggerable, water-dispersible cationic polymers and their applicability as binder compositions. The present invention is further directed to fiber-containing fabrics and webs comprising ion triggerable, water-dispersible binder compositions and their applicability in water-dispersible personal care products, such as wet wipes.

IMPROVED ION TRIGGERABLE, CATIONIC POLYMERS, A METHOD OF MAKING SAME AND ITEMS USING SAME

FIELD OF THE INVENTION

The present invention is directed to ion-sensitive or triggerable, water-dispersible or water-soluble cationic polymers and polymer formulations. The present invention is also directed to a method of making ion-sensitive or triggerable, water-dispersible or water-soluble cationic polymers and polymer formulations and their applicability as binder compositions for disposable items. The present invention is further directed to disposable items, such as wet-wipes comprising ion-sensitive or triggerable, water-dispersible binder compositions including cationic polymer or polymer formulations.

BACKGROUND OF THE INVENTION

For many years, the problem of disposability has plagued industries that provide disposable items, such as, diapers, wet wipes, incontinent garments and feminine care products. While much headway has been made in addressing this problem, one of the weak links has been the inability to create an economical coherent fibrous web, which will readily dissolve or disintegrate in water, but still have sufficient in-use strength. See, for example, U.K. patent disclosure 2,241,373 and U.S. Pat. No. 4,186,233. Without such a product, the ability of the user to dispose of the product by flushing it down the toilet is greatly reduced, if not eliminated. Furthermore, the ability of the product to disintegrate in a landfill is quite limited because a large portion of the product components, which may well be biodegradable or photodegradable, are encapsulated in or bound together by plastic which degrades over a long period of time, if at all. Accordingly, if the plastic disintegrated in the presence of water, the internal components could degrade as a result of the rupture of the plastic encapsulation or binding.

Disposable products, such as diapers, feminine care products and adult incontinent care products may be made to be disposed by flushing down toilets. Usually such products comprise a body side liner which must rapidly pass fluids, such as urine or menses, so that the fluid may be absorbed by an absorbent core of the product. Typically, the body side liner may be a coherent fibrous web, which desirably possesses a number of characteristics, such as softness and flexibility. The fibrous web of the body side liner material may be typically formed by wet or dry (air) laying a generally random plurality of fibers and joining them together to form a coherent web with a binder compositions. Past binder compositions have preformed this function well. However, fibrous webs comprising these compositions tended to be non-dispersible and present problems in typical household sanitation systems.

Recent binder compositions have been developed which can be more dispersible and are more environmentally responsible than past binder compositions. One class of binder compositions includes polymeric materials having inverse solubility in water. These binder compositions are insoluble in warm water, but are soluble in cold water, such as found in a toilet. It is well known that a number of polymers exhibit cloud points or inverse solubility properties in aqueous media. These polymers have been cited in several publications for various applications, including (1) as evaporation retarders (JP 6207162); (2) as temperature sensitive compositions, which are useful as temperature indicators due to a sharp color change associated with a corresponding temperature change (JP 6192527); (3) as heat sensitive materials that are opaque at a specific temperature and become transparent when cooled to below the specific temperature (JP 51003248 and JP 81035703); (4) as wound dressings with good absorbing characteristics and easy removal (JP 6233809); and (5) as materials in flushable personal care products (U.S. Pat. No. 5,509,913, issued to Richard S. Yeo on April 23, 1996 and assigned to Kimberly-Clark Corporation).

Other recent binders of interest include a class of binders, which are ion-sensitive. Several U.S. and European patents assigned to Lion Corporation of Tokyo, Japan, disclose ion-sensitive polymers comprising acrylic acid and alkyl or aryl acrylates. See U.S. Pat. Nos. 5,312,883, 5,317,063 and 5,384,189, the disclosures of which are incorporated herein by reference, as well as, European Pat. No. 608460A1. In U.S. Pat. No. 5,312,883, terpolymers are disclosed as suitable binders for flushable nonwoven webs. The disclosed acrylic acid-based terpolymers, which comprise partially neutralized acrylic acid, butyl acrylate and 2-ethylhexyl acrylate, are suitable binders for use in flushable nonwoven webs in some parts of the world. However, because of the presence of a small amount of sodium acrylate in the partially neutralized terpolymer, these binders fail to disperse in water containing more than about 15 ppm Ca2+ and/or Mg2+. When placed in water containing more than about 15 ppm Ca2+ and/or Mg2+ ions, nonwoven webs using the above-described binders maintain a tensile strength greater than 30 g/in, which negatively affects the "dispersibility" of the web. The proposed mechanism for the failure is that each calcium ion binds with two carboxylate groups either intramolecularly or intermolecularly. Intramolecular association causes the polymer chain to coil up, which eventually leads to polymer precipitation. Intermolecular association yields crosslinking. Whether intramolecular or intermolecular associations are taking place, the terpolymer is not soluble in water containing more than about 15 ppm Ca^{2+} and/or Mg^{2+}. Due to the strong interaction between calcium ions and the carboxylate groups of the terpolymer, dissociation of the complex is highly unlikely because this association is irreversible. Therefore, the above-described polymer that has been exposed to a high Ca^{2+} and/or Mg^{2+} concentration solution will not disperse in water even if the calcium concentration decreases. This limits the application of the polymer as a flushable binder material because most areas across the U.S. have hard water, which contains more than 15 ppm Ca^{2+} and/or Mg^{2+}.

In US Patent 6,423,804 B1 assigned to Kimberly Clark, the disclosure of which is incorporated herein by reference, there is disclosed a modification of the acrylic acid terpolymers of the above-referenced patents to Lion Corporation. Specifically, 6,423,804 B1 discloses a sulfonate anion modified acrylic acid terpolymers which has improved dispersibility in relatively hard water; *e.g.*, up to 200 ppm Ca^{2+} and/or Mg^{2+}, compared to the unmodified Lion polymers. The wetted sheet is flexible and soft. However, the Lion Corporation ion-sensitive polymers and the sulfonate anion modified acrylic acid terpolymers of the above-referenced patents, when used as binders for personal care products, such as wet wipes, typically have reduced initial sheet wettability, increased dry sheet stiffness, increased sheet stickiness, reduced binder sprayability and relatively high product cost.

Another approach to dispersible personal care products is disclosed in U.S. Pat. No. 5,281,306 to Kao Corporation of Tokyo, Japan. This patent discloses a water-disintegratable cleansing sheet; *i.e.*, wet wipe, comprising water-dispersible fibers treated with a water-soluble binder having a carboxyl group. The cleansing sheet is treated with a cleansing agent containing 5%-95% of a water-compatible organic solvent and 95%-5% water. A preferred organic solvent is propylene glycol. The cleansing sheet retains wet strength and does not disperse in the organic solvent-based cleansing agent, but disperses in water. The sheets must have these levels of organic solvents as these solvents ensure the in-use wet strength for the sheets. Without the solvents, the sheets would have little in-use wet strength and would not be effective as a wet wipe. However, the use of such high amounts of organic solvent results in a greasy after-feel when the product is used, and these organic solvents may cause discomfort to skin in higher amounts.

Although many patents disclose various ion and temperature sensitive compositions for water-dispersible or flushable materials, there exists a need for dispersible products possessing softness, flexibility, three dimensionality, and resiliency; wicking and structural integrity in the presence of body fluids (including feces) at body temperature; and true fiber dispersion after toilet flushing so that product does not become entangled with tree roots or at bends in sewer pipes. Moreover, there is a need in the art for flushable products having water-dispersibility in all areas of the world, including soft and hard water areas. Furthermore, there is a need for water-dispersible binders that do not reduce wettability of product with which they are used and are sprayable for relatively easy and uniform application to and penetration into products. Finally, there is a need for water-dispersible, flushable wet wipes that are stable during storage and retain a desired level of wet strength during use and are wetted with a wetting composition that is relatively free, or is substantially free, of organic solvents. Such a product is needed at a reasonable cost without compromising product safety and environmental concerns, something that past products have failed to do.

SUMMARY OF THE INVENTION

The present invention is directed to triggerable cationic polymers and polymer formulations, which have been developed to address the above-described problems associated with currently available, ion-sensitive polymers and other polymers described in literature. The binder of the present invention provides strength in the dry state, but more importantly, helps maintain a desired level of strength in the wet state by ion triggerability. A controlled concentration of salt in the wetting solution insolubilizes the binder and allows it to function as an adhesive for the web. When the wet wipe is discarded into the wastewater stream, the salt concentration is diluted, the binder becomes soluble, and the strength drops below a critical level. The ion triggerable polymer formulations of the present invention have a "trigger property," such that the polymers are insoluble in a wetting composition comprising an insolublizing agent of a particular type and concentration, such as monovalent and/or divalent salt solutions at concentrations above about 0.3% by weight, but are soluble when diluted with water, including hard water with up to 200 ppm (parts per million) calcium and magnesium ions. This allows the web to break apart into small pieces and, ultimately, disperse.

Unlike some ion-sensitive polymer formulations, which lose dispersibility in hard water because of ion cross-linking by calcium ions, the triggerable cationic polymer formulations of the present invention are insensitive to calcium and/or magnesium ions at concentrations of a few hundred ppm and are insensitive to pH variations. Consequently, flushable products containing the polymer formulations of the present invention maintain dispersibility in hard water or soft water.

The binder compositions provide an optimum level of wet strength utilizing sodium chloride as the sole or primary triggering agent, not requiring the use of a high concentration of divalent metal ions. Also, the level of sodium chloride necessary to provide trigger properties is very low ($\leq$1%) under certain conditions. Because of this low level of monovalent salt needed to produce trigger activity, these binders may now maintain sufficient strength in the presence of urine, menses, and other biological fluids without the use of an external triggering agent. Therefore, they may be much more suitable for personal care applications beyond pre-wetted products. Also, the binders of the present invention may also be suitable for providing wet strength and/or temporary wet strength in the absence of added salt for dry tissue products due to their solubility characteristics. In addition, the properties of the improved binders are affected without the use of a nonionic, hydrophilic co-monomer, which may be undesirable because of toxicity, mis-match in reactivity, or adverse effect on the binder performance.

The polymer formulations of the present invention are useful as binders and structural components for air-laid and wet-laid nonwoven fabrics for applications, such as body-side liners, fluid distribution materials, fluid in-take materials (surge) or cover stock in various personal care products. The polymer formulations of the present invention are particularly useful as a binder material for flushable personal care products, particularly wet wipes for personal use, such as cleaning or treating skin, make-up removal, nail polish removal, medical care, and also wipes for use in hard surface cleaning, automotive care, including wipes comprising cleaning agents, disinfectants, and the like. The flushable products maintain integrity or wet strength during storage and use, and break apart or disperse after disposal in the toilet when the salt or ion concentration falls below a critical level. Suitable substrates for treatment include tissue, such as creped or uncreped tissue, coform products, hydroentangled webs, airlaid mats, fluff pulp, nonwoven webs, and composites thereof. Methods for producing uncreped tissues and molded three-dimensional tissue webs of use in the present invention can be found in commonly owned U.S. patent application, Serial Number 08/912,906, "Wet Resilient Webs and Disposable Articles Made Therewith," by F.-J. Chen et al., filed Aug. 15, 1997; U.S. Pat. No. 5,429,686, issued to Chiu et al. on July 4, 1995; U.S. Pat. No. 5,399,412, issued to S.J. Sudall and S.A. Engel on March 21, 1995; U.S. Pat. No. 5,672,248, issued to Wendt et al. on Sept. 30, 1997; and U.S. Pat. No. 5,607,551, issued to Farrington et al. on March 4, 1997; all of which are incorporated herein by reference in their entirety. The molded tissue structures of the above patents can be especially helpful in providing good cleaning in a wet wipe. Good cleaning can also be promoted by providing a degree of texture in other substrates as well by embossing, molding, wetting and through-air drying on a textured fabric, and the like. The cationic polymers and polymer formulations of the present invention are particularly useful as a binder for fibrous materials because the polymers and polymer formulations are substantive to the fibers.

Airlaid material can be formed by metering an airflow containing the fibers and other optional materials, in substantially dry condition, onto a typically horizontally moving wire forming screen. Suitable systems and apparatus for air-laying mixtures of fibers and thermoplastic material are disclosed in, for example, U.S. Pat. No. 4,157,724 (Persson), issued Jun. 12, 1979, and reissued Dec. 25, 1984 as Re. U.S. Pat. No. 31,775; U.S. Pat. No. 4,278,113 (Persson), issued Jul. 14, 1981; U.S. Pat. No. 4,264,289 (Day), issued Apr. 28, 1981; U.S. Pat. No. 4,352,649 (Jacobsen et al.), issued Oct. 5, 1982; U.S. Pat. No. 4,353,687 (Hosler, et al.), issued Oct. 12, 1982; U.S. Pat. No. 4,494,278 (Kroyer, et al.), issued Jan. 22, 1985; U.S. Pat. No. 4,627,806 (Johnson), issued Dec. 9, 1986; U.S. Pat. No. 4,650,409 (Nistri, et al.), issued Mar. 17, 1987; and U.S. Pat. No. 4,724,980

(Farley), issued Feb. 16, 1988; and U.S. Pat. No. 4,640,810 (Laursen et al.), issued Feb. 3, 1987, the disclosures of which are all incorporated herein by reference.

The present invention also discloses how to make water-dispersible nonwovens, including cover stock (liner), intake (surge) materials and wet wipes, which are stable in fluids having a first ionic composition, such as monovalent and/or divalent ions at a particular concentration substantially greater than is found in typical hard water or soft water, using the above-described unique polymer formulations as binder compositions. The resultant nonwovens are flushable and water-dispersible due to the tailored ion sensitivity, which can be triggered regardless of the hardness of water found in toilets throughout the United States and the world.

The present invention further discloses a suitable wetting composition for wet wipes. Wet wipes employing the polymer formulations of the present invention are stable during storage and retain a desired level of wet strength during use and are wetted with a wetting composition or cleaning agent that can be relatively free, or is substantially free, of organic solvents. As used herein the term “substantially free” shall mean containing only trivial or inconsequential amounts.

These and other objects, features and advantages of the present invention will become apparent after a review of the following detailed description of the disclosed embodiments and the appended claims.

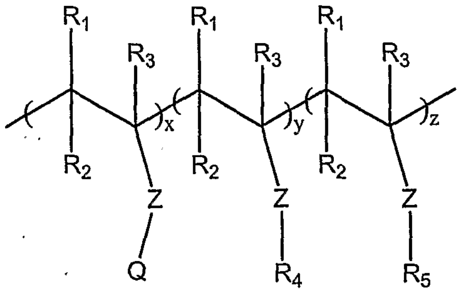
DETAILED DESCRIPTION OF THE DISCLOSED EMBODIMENTS

The present invention is practiced using triggerable cationic polymers or polymer compositions. The triggerable, cationic polymer composition is an ion-sensitive cationic polymer composition. In order to be an effective ion-sensitive or triggerable cationic polymer or cationic polymer formulation suitable for use in flushable or water-dispersible personal care products, the formulations should desirably be (1) functional; *i.e.*, maintain wet strength under controlled conditions and dissolve or disperse in a reasonable period of time in soft or hard water, such as found in toilets and sinks around the world; (2) safe (not toxic); and (3) relatively economical. In addition to the foregoing factors, the ion-sensitive or triggerable formulations when used as a binder composition for a non-woven substrate, such as a wet wipe, desirably should be (4) processable on a commercial basis; *i.e.*, may be applied relatively quickly on a large scale basis, such as by spraying (which thereby requires that the binder composition have a relatively low viscosity at high shear); (5) provide acceptable levels of sheet or substrate wettability; (6) provide reduced levels of sheet stiffness; and (7) reduced tackiness. The wetting composition with which the wet wipes of the present invention are treated can provide some of the foregoing advantages, and, in addition, can provide one or more of (8) improved skin care, such as reduced skin irritation or other benefits, (9) improved tactile properties, and (10) promote good cleaning by providing a balance in use between friction and lubricity on the skin (skin glide). The ion-sensitive or triggerable cationic polymers and polymer formulations of the present invention and articles made therewith, especially wet wipes comprising particular wetting compositions set forth below, can meet many or all of the above criteria. Of course, it is not necessary for all of the advantages of the preferred embodiments of the present invention to be met to fall within the scope of the present invention.

Ion Triggerable Cationic Polymer Compositions

The ion triggerable cationic polymers of the present invention are the polymerization product of a vinyl-functional cationic monomer, and one or more hydrophobic vinyl monomers with alkyl side chain sizes of up to 4 carbons long. In a preferred embodiment the ion triggerable cationic polymers of the present invention are the polymerization product of a vinyl-functional cationic monomer, and one or more hydrophobic vinyl monomers with alkyl side chain sizes of up to 4 carbons long incorporated in a random manner. Additionally, a minor amount of another vinyl monomer with linear or branched alkyl groups 4 carbons or longer, alkyl hydroxy, polyoxyalkylene, or other functional groups may be employed. The ion triggerable cationic polymers function as adhesives for tissue, airlaid pulp, and other nonwoven webs and provide sufficient in-use strength (typically >300 g/in.) in salt solutions, especially sodium chloride. The nonwoven webs are also dispersible in tap water (including hard water up to 200 ppm as metal ion), typically losing most of their wet strength (<30-75 g/in.) in 24 hours, or less.

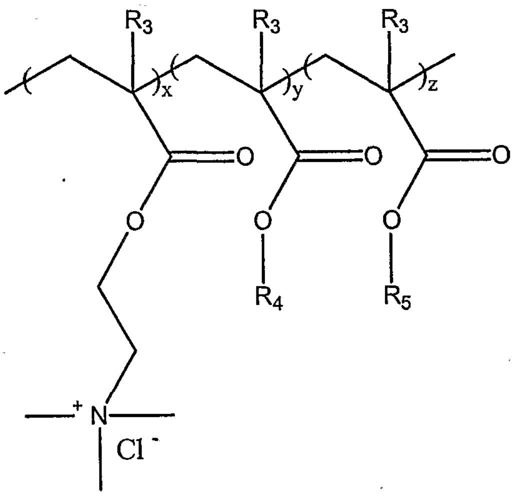
The generic structure for the ion triggerable cationic polymers of the present invention is shown below:



wherein x = 1 to about 15 mole percent; y = about 60 to about 99 mole percent; and z = 0 to about 30 mole percent; Q is selected from C_1-C_4 alkyl ammonium, quaternary C_1-C_4 alkyl ammonium and benzyl ammonium; Z is selected from –O-, -COO-, -OOC-, -CONH-, and –NHCO-; R_1, R_2, R_3 are independently selected from hydrogen and methyl; R_4 is selected from methyl and ethyl; and R_5 is selected from hydrogen, methyl, ethyl, butyl, ethylhexyl, decyl, dodecyl, hydroxyethyl, hydroxypropyl, polyoxyethylene, and polyoxypropylene. Vinyl-functional cationic monomers of the present invention desirably include, but are not limited to, [2-(acryloxy)ethyl] trimethyl ammonium chloride (ADAMQUAT); [2-(methacryloxy)ethyl) trimethyl ammonium chloride (MADQUAT); (3-acrylamidopropyl) trimethyl ammonium chloride; N,N-diallyldimethyl ammonium chloride; [2-(acryloxy) ethyl] dimethylbenzyl ammonium chloride; (2-(methacryloxy) ethyl] dimethylbenzyl ammonium chloride; [2-(acryloxy)ethyl] dimethyl ammonium chloride; [2-(methacryloxy)ethyl] dimethyl ammonium chloride. Precursor monomers, such as vinylpyridine, dimethylaminoethyl acrylate, and dimethylaminoethyl methacrylate, which can be polymerized and quaternized through post-polymerization reactions are also possible. Monomers or quaternization reagents which provide different counter-ions, such as bromide, iodide, or methyl sulfate are also useful. Other vinyl-functional cationic monomers which may be copolymerized with a hydrophobic vinyl monomer are also useful in the present invention.

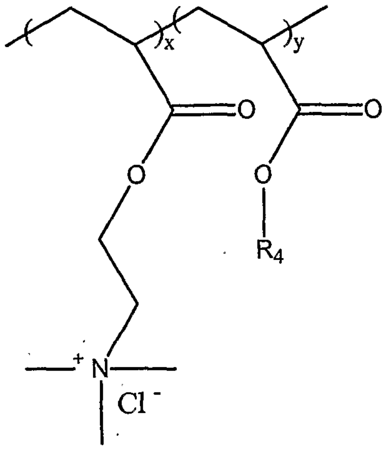
Desirable hydrophobic monomers for use in the ion-sensitive cationic polymers of the present invention include, but are not limited to, branched or linear C_1-C_{18} alkyl vinyl ethers, vinyl esters, acrylamides, acrylates, and other monomers that can be copolymerized with the cationic monomer. As used herein the monomer methyl acrylate is considered to be a hydrophobic monomer. Methyl acrylate has a solubility of 6 g/100 ml in water at 20° C.

In a preferred embodiment, the binder is the polymerization product of a cationic acrylate or methacrylate and one or more alkyl acrylates or methacrylates having the generic structure:



wherein x = 1 to about 15 mole percent; y = about 60 to about 99 mole percent; and z = 0 to about 30 mole percent; R_4 is selected from methyl and ethyl; R_5 is selected from hydrogen, methyl, ethyl, butyl, ethylhexyl, decyl, dodecyl, hydroxyethyl, hydroxypropyl, polyoxyethylene, and polyoxypropylene.

In an especially preferred embodiment of the present invention, the ion triggerable polymer has the structure:



wherein x = 1 to about 15 mole percent; y = about 85 to about 99 mole percent and R_4 is C_1-C_4 alkyl. In a most desirable embodiment, when R_4 is methyl, x = 3 to about 6 mole percent; y = about 94 to about 97 mole percent.

The ion triggerable cationic polymers of the present invention may have an average molecular weight that varies depending on the ultimate use of the polymer. The ion triggerable cationic polymers of the present invention have a weight average molecular weight ranging from about 10,000 to about 5,000,000 grams per mol. More specifically, the ion triggerable cationic polymers of the present invention have a weight average molecular weight ranging from about 25,000 to about 2,000,000 grams per mol., or, more specifically still, from about 200,000 to about 1,000,000 grams per mol.

The ion triggerable cationic polymers of the present invention may be prepared according to a variety of polymerization methods, desirably a solution polymerization method. Suitable solvents for the polymerization method include, but are not limited to, lower alcohols, such as methanol, ethanol and propanol; a mixed solvent of water and one or more lower alcohols mentioned above; and a mixed solvent of water and one or more lower ketones, such as acetone or methyl ethyl ketone.

In the polymerization methods of the present invention, any free radical polymerization initiator may be used. Selection of a particular initiator may depend on a number of factors including, but not limited to, the polymerization temperature, the solvent, and the monomers used. Suitable polymerization initiators for use in the present invention include, but are not limited to, 2,2′-azobisisobutyronitrile, 2,2′-azobis(2-methylbutyronitrile), 2,2′-azobis(2,4-dimethylvaleronitrile), 2,2′-azobis(2-amidinopropane)dihydrochloride, 2,2′-azobis(N,N′-dimethyleneisobutylamidine), potassium persulfate, ammonium persulfate, and aqueous hydrogen peroxide. The amount of polymerization initiator may desirably range from about 0.01 to 5 weight percent based on the total weight of monomer present.

The polymerization temperature may vary depending on the polymerization solvent, monomers, and initiator used, but in general, ranges from about 20° C. to about 90° C. Polymerization time generally ranges from about 2 to about 8 hours.

In a further embodiment of the present invention, the above-described ion triggerable cationic polymer formulations are used as binder materials for flushable and/or non-flushable products. In order to be effective as a binder material in flushable products throughout the United States, the ion triggerable cationic polymer formulations of the present invention remain stable and maintain their integrity while dry or in relatively high concentrations of monovalent and/or divalent ions, but become soluble in water containing up to about 200 ppm or more divalent ions, especially calcium and magnesium. Desirably, the ion triggerable cationic polymer formulations of the present invention are insoluble in a salt solution containing at least about 0.3 weight percent of one or more inorganic and/or organic salts containing monovalent and/or divalent ions. More desirably, the ion triggerable cationic polymer formulations of the present invention are insoluble in a salt solution containing from about 0.3% to about 10% by weight of one or more inorganic and/or organic salts containing monovalent and/or divalent ions. Even more desirably, the ion triggerable cationic polymer formulations of the present invention are insoluble in salt solutions containing from about 0.5% to about 5% by weight of one or more inorganic and/or organic salts containing monovalent and/or divalent ions. Especially desirably, the ion triggerable cationic polymer formulations of the present invention are insoluble in salt solutions containing from about 1.0% to about 4.0% by weight of one or more inorganic and/or organic salts containing monovalent and/or divalent ions. Suitable monovalent ions include, but are not limited to, Na^+ ions, K^+ ions, Li^+ ions, NH_4^+ ions, low molecular weight quaternary ammonium compounds (e.g., those having fewer than 5 carbons on any side group), and a combination thereof. Suitable multivalent ions include, but are not limited to, Zn^{2+}, Ca^{2+} and Mg^{2+}. The monovalent and divalent ions can be derived from organic and inorganic salts including, but not limited to, NaCl, NaBr, KCl, NH_4Cl, Na_2SO_4, $ZnCl_2$, $CaCl_2$, $MgCl_2$, $MgSO_4$, $NaNO_3$, $NaSO_4CH_3$, and combinations thereof. Typically, alkali metal halides are most desirable because of cost, purity, low toxicity, and availability. A particularly desirable salt is NaCl.

Based on a recent study conducted by the American Chemical Society, water hardness across the United States varies greatly, with $CaCO_3$ concentration ranging from near zero for soft water to about 500 ppm $CaCO_3$ (about 200 ppm Ca^{2+} ion) for very hard water. To ensure polymer formulation dispersibility across the country (and throughout the whole world), the ion triggerable cationic polymer formulations of the present invention are desirably soluble in water containing up to about 50 ppm Ca^{2+} and/or

Mg^{2+} ions. More desirably, the ion triggerable cationic polymer formulations of the present invention are soluble in water containing up to about 100 ppm Ca^{2+} and/or Mg^{2+} ions. Even more desirably, the ion triggerable cationic polymer formulations of the present invention are soluble in water containing up to about 150 ppm Ca^{2+} and/or Mg^{2+} ions. Even more desirably, the ion triggerable cationic polymer formulations of the present invention are soluble in water containing up to about 200 ppm Ca^{2+} and/or Mg^{2+} ions.

Co-binder Polymers

As stated above, the cationic polymer formulations of the present invention are formed from a single triggerable cationic polymer or a combination of two or more different polymers, wherein at least one polymer is a triggerable polymer. The second polymer may be a co-binder polymer. A co-binder polymer is of a type and in an amount such that when combined with the triggerable cationic polymer, the co-binder polymer desirably is largely dispersed in the triggerable cationic polymer; *i.e.*, the triggerable cationic polymer is desirably the continuous phase and the co-binder polymer is desirably the discontinuous phase. Desirably, the co-binder polymer can also meet several additional criteria. For example, the co-binder polymer can have a glass transition temperature; *i.e.*, T_g, that is lower than the glass transition temperature of the ion triggerable cationic polymer. Furthermore or alternatively, the co-binder polymer can be insoluble in water, or can reduce the shear viscosity of the ion triggerable cationic polymer. The co-binder can be present at a level relative to the solids mass of the triggerable polymer of about 45% or less, specifically about 30% or less, more specifically about 20% or less, more specifically still about 15% or less, and most specifically about 10% or less, with exemplary ranges of from about 1% to about 45% or from about 25% to about 35%, as well as from about 1% to about 20% or from about 5% to about 25%. The amount of co-binder present should be low enough, for co-binders with the potential to form water insoluble bonds or films, that the co-binder remains a discontinuous phase unable to create enough crosslinked, or insoluble bonds, to jeopardize the dispersibility of the treated substrate.

Desirably, but not necessarily, the co-binder polymer when combined with the ion triggerable cationic polymer will reduce the shear viscosity of the ion triggerable cationic polymer to such an extent that the combination of the ion triggerable cationic polymer and the co-binder polymer is sprayable. By sprayable is meant that the polymer can be applied to a nonwoven fibrous substrate by spraying and the distribution of the polymer across the substrate and the penetration of the polymer into the substrate are such that the polymer formulation is uniformly applied to the substrate.

In some embodiments, the combination of the ion triggerable cationic polymer and the co-binder polymer can reduce the stiffness of the article to which it is applied compared to the article with just the ion triggerable cationic polymer.

The co-binder polymer of the present invention can have an average molecular weight, which varies depending on the ultimate use of the polymer. Desirably, the co-binder polymer has a weight average molecular weight ranging from about 500,000 to about 200,000,000 grams per mol. More desirably, the co-binder polymer has a weight average molecular weight ranging from about 500,000 to about 100,000,000 grams per mol.

The co-binder polymer can be in the form of an emulsion latex. The surfactant system used in such a latex emulsion should be such that it does not substantially interfere with the dispersibility of the ion triggerable cationic polymer. Therefore, weakly anionic, nonionic, or cationic latexes may be useful for the present invention. In one embodiment, the ion triggerable cationic polymer formulations of the present invention comprises about 55 to about 95 weight percent ion triggerable cationic polymer and about 5 to about 45 weight percent poly(ethylene-vinyl acetate). More desirably, the ion triggerable cationic polymer formulations of the present invention comprises about 75 weight percent ion triggerable cationic polymer and about 25 weight percent poly(ethylene-vinyl acetate). A particularly preferred non-crosslinking poly(ethylene-vinyl acetate) is Dur-O-Set® RB available from National Starch and Chemical Co., Bridgewater, NJ.

When a latex co-binder, or any potentially crosslinkable co-binder, is used the latex should be prevented from forming substantial water-insoluble bonds that bind the fibrous substrate together and interfere with the dispersibility of the article. Thus, the latex can be free of crosslinking agents, such as N-methylol-acrylamide (NMA), or free of catalyst for the crosslinker, or both. Alternatively, an inhibitor can be added that interferes with the crosslinker or with the catalyst such that crosslinking is impaired even when the article is heated to normal crosslinking temperatures. Such inhibitors can include free radical scavengers, methyl hydroquinone, t-butylcatechol, pH control agents such as potassium hydroxide, and the like. For some latex crosslinkers, such as N-methylol-acrylamide (NMA), for example, elevated pH such as a pH of 8 or higher can interfere with crosslinking at normal crosslinking temperatures (*e.g.*, about 130° C or higher). Also alternatively, an article comprising a latex co-binder can be maintained at temperatures below the temperature range at which crosslinking takes place, such that the presence of a crosslinker does not lead to crosslinking, or such that the degree of crosslinking remains sufficiently low that the dispersibility of the article is not jeopardized. Also alternatively, the amount of crosslinkable latex can be kept below a threshold level such that even with crosslinking, the article remains dispersible. For example, a small quantity of crosslinkable latex dispersed as discrete particles in an ion-sensitive binder can permit dispersibility even when fully crosslinked. For the later embodiment, the amount of latex can be below about 20 weight percent, and, more specifically, below about 15 weight percent relative to the ion-sensitive binder.

Latex compounds, whether crosslinkable or not, need not be the co-binder. SEM micrography of successful ion-sensitive binder films with useful non-crosslinking latex emulsions dispersed therein has shown that the latex co-binder particles can remain as discrete entities in the ion-sensitive binder, possibly serving in part as filler material. It is believed that other materials could serve a similar role, including a dispersed mineral or particulate filler in the triggerable binder, optionally comprising added surfactants/dispersants. For example, in one envisioned embodiment, freeflowing Ganzpearl PS-8F particles from Presperse, Inc. (Piscataway, NJ), a styrene/divinylbenzene copolymer with about 0.4 micron particles, can be dispersed in a triggerable binder at a level of about 2 to 10 weight percent to modify the mechanical, tactile, and optical properties of the triggerable binder. Other filler-like approaches may include microparticles, microspheres, or microbeads of metal, glass, carbon, mineral, quartz, and/or plastic, such as acrylic or phenolic, and hollow particles having inert gaseous atmospheres sealed within their interiors. Examples include EXPANCEL phenolic microspheres from Expancel of Sweden, which expand substantially when heated, or the acrylic microspheres known as PM 6545 available from PQ Corporation of Pennsylvania. Foaming agents, including CO_2 dissolved in the triggerable binder, could also provide helpful discontinuities as gas bubbles in the matrix of an triggerable binder, allowing the dispersed gas phase in the triggerable binder to serve as the co-binder. In general, any compatible material that is not miscible with the binder, especially one with adhesive or binding properties of its own, can be used as the co-binder, if it is not provided in a state that imparts substantial covalent bonds joining fibers in a way that interferes with the water-dispersibility of the product. However, those materials that also provide additional benefits, such as reduced spray viscosity, can be especially preferred. Adhesive co-binders, such as latex that do not contain crosslinkers or contain reduced amounts of crosslinkers, have been found to be especially helpful in providing good results over a wide range of processing conditions, including drying at elevated temperatures.

The co-binder polymer can comprise surface active compounds that improve the wettability of the substrate after application of the binder mixture. Wettability of a dry substrate that has been treated with a triggerable polymer formulation can be a problem in some embodiments, because the hydrophobic portions of the triggerable polymer formulation can become selectively oriented toward the air phase during drying, creating a hydrophobic surface that can be difficult to wet when the wetting composition is later applied unless surfactants are added to the wetting composition. Surfactants, or other surface active ingredients, in co-binder polymers can improve the wettability of the dried substrate that has been treated with a triggerable polymer formulation. Surfactants in the co-binder polymer should not significantly interfere with the triggerable polymer formulation. Thus, the binder should maintain good integrity and tactile properties in the pre-moistened wipes with the surfactant present.

In one embodiment, an effective co-binder polymer replaces a portion of the ion triggerable cationic polymer formulation and permits a given strength level to be achieved in a pre-moistened wipe with at least one of lower stiffness, better tactile properties (*e.g.*, lubricity or smoothness), or reduced cost, relative to an otherwise identical pre-moistened wipe lacking the co-binder polymer and comprising the ion triggerable cationic polymer formulation at a level sufficient to achieve the given tensile strength.

Other Co-binder polymers

The Dry Emulsion Powder (DEP) binders of Wacker Polymer Systems (Burghausen, Germany) such as the VINNEK® system of binders, can be applied in some embodiments of the present invention. These are redispersible, free flowing binder powders formed from liquid emulsions. Small polymer particles from a dispersion are provided in a protective matrix of water soluble protective colloids in the form of a powder particle. The surface of the powder particle is protected against caking by platelets of mineral crystals. As a result, polymer particles that once were in a liquid dispersion are now available in a free flowing, dry powder form that can be redispersed in water or turned into swollen, tacky particles by the addition of moisture. These particles can be applied in highloft nonwovens by depositing them with the fibers during the airlaid process, and then later adding 10% to 30% moisture to cause the particles to swell and adhere to the fibers. This can be called the "chewing gum effect," meaning that the dry, non-tacky fibers in the web become sticky like chewing gum once moistened. Good adhesion to polar surfaces and other surfaces is obtained. These binders are available as free flowing particles formed from latex emulsions that have been dried and treated with agents to prevent cohesion in the dry state. They can be entrained in air and deposited with fibers during the airlaid process, or can be applied to a substrate by electrostatic means, by direct contact, by gravity feed devices, and other means. They can be applied apart from the binder, either before or after the binder has been dried. Contact with moisture, either as liquid or steam, rehydrates the latex particles and causes them to swell and to adhere to the fibers. Drying and heating to elevated temperatures (*e.g.*, above 160° C.) causes the binder particles to become crosslinked and water resistant, but drying at lower temperatures (*e.g.*, at 110° C. or less) can result in film formation and a degree of fiber binding without seriously impairing the water dispersibility of the pre-moistened wipes. Thus, it is believed that the commercial product can be used without reducing the amount of crosslinker by controlling the curing of the co-binder polymer, such as limiting the time and temperature of drying to provide a degree of bonding without significant crosslinking.

As pointed out by Dr. Klaus Kohlhammer in "New Airlaid Binders," Nonwovens Report International, Sept. 1999, issue 342, pp. 20-22, 28-31, dry emulsion binder powders have the advantage that they can easily be incorporated into a nonwoven or airlaid web during formation of the web, as opposed to applying the material to an existing substrate, permitting increased control over placement of the co-binder polymer. Thus, a nonwoven or airlaid web can be prepared already having dry emulsion binders therein, followed by moistening when the ion triggerable cationic polymer formulation solution is applied, whereupon the dry emulsion powder becomes tacky and contributes to binding of the substrate. Alternatively, the dry emulsion powder can be entrapped in the substrate by a filtration mechanism after the substrate has been treated with triggerable binder and dried, whereupon the dry emulsion powder is rendered tacky upon application of the wetting composition.

In another embodiment, the dry emulsion powder is dispersed into the triggerable polymer formulation solution either by application of the powder as the ion triggerable cationic polymer formulation solution is being sprayed onto the web or by adding and dispersing the dry emulsion powder particles into the ion triggerable cationic polymer formulation solution, after which the mixture is applied to a web by spraying, by foam application methods, or by other techniques known in the art.

Binder Formulations and Fabrics Containing the Same

The ion triggerable cationic polymer formulations of the present invention may be used as binders. The triggerable binder formulations of the present invention may be applied to any fibrous substrate. The binders are particularly suitable for use in water-dispersible products. Suitable fibrous substrates include, but are not limited to, nonwoven and woven fabrics. In many embodiments, particularly personal care products, preferred substrates are nonwoven fabrics. As used herein, the term “nonwoven fabric” refers to a fabric that has a structure of individual fibers or filaments randomly arranged in a mat-like fashion (including papers). Nonwoven fabrics can be made from a variety of processes including, but not limited to, air-laid processes, wet-laid processes, hydroentangling processes, staple fiber carding and bonding, and solution spinning.

The triggerable binder composition may be applied to the fibrous substrate by any known process of application. Suitable processes for applying the binder material include, but are not limited to, printing, spraying, electrostatic spraying, coating, flooded nips, metered press rolls, impregnating or by any other technique. The amount of binder composition may be metered and distributed uniformly within the fibrous substrate or may be non-uniformly distributed within the fibrous substrate. The binder composition may be distributed throughout the entire fibrous substrate or it may be distributed within a multiplicity of small closely spaced areas. In most embodiments, uniform distribution of binder composition is desired.

For ease of application to the fibrous substrate, the triggerable binder may be dissolved in water, or in a non-aqueous solvent, such as methanol, ethanol, acetone, or the like, with water being the preferred solvent. The amount of binder dissolved in the solvent may vary depending on the polymer used and the fabric application. Desirably, the binder solution contains up to about 50 percent by weight of binder composition solids. More desirably, the binder solution contains from about 10 to 30 percent by weight of binder composition solids, especially about 15-25 percent by weight binder composition solids. Plasticizers, perfumes, coloring agents, antifoams, bactericides, preservative, surface active agents, thickening agents, fillers, opacifiers, tackifiers, detackifiers, and similar additives can be incorporated into the solution of binder components, if so desired.

Once the triggerable binder composition is applied to the substrate, the substrate is dried by any conventional means. Once dry, the coherent fibrous substrate exhibits improved tensile strength when compared to the tensile strength of the untreated wet-laid or dry-laid substrates, and yet has the ability to rapidly "fall apart", or disintegrate when placed in soft or hard water having a divalent ion concentration up to about 200 ppm and agitated. For example, the dry tensile strength of the fibrous substrate may be increased by at least 25 percent as compared to the dry tensile strength of the untreated substrate not containing the binder. More particularly, the dry tensile strength of the fibrous substrate may be increase by at least 100 percent as compared to the dry tensile strength of the untreated substrate not containing the binder. Even more particularly, the dry tensile strength of the fibrous substrate may be increased by at least 500 percent as compared to the dry tensile strength of the untreated substrate not containing the binder.

A desirable feature of the present invention is that the improvement in tensile strength is effected where the amount of binder composition present, "add-on", in the resultant fibrous substrate represents only a small portion by weight of the entire substrate. The amount of "add-on" can vary for a particular application; however, the optimum amount of "add-on" results in a fibrous substrate which has integrity while in use and also quickly disperses when soaked in water. For example, the binder components typically are from about 5 to about 65 percent, by weight, of the total weight of the substrate. More particularly, the binder components may be from about 7 to about 35 percent, by weight, of the total weight of the substrate. Even more particularly, the binder components may be from about 10 to about 20 percent by weight of the total weight of the substrate.

The nonwoven fabrics of the present invention have good in-use tensile strength, as well as, ion triggerability. Desirably, the nonwoven fabrics of the present invention are abrasion resistant and retain significant tensile strength in aqueous solutions containing the specific amount and type of ions disclosed above. Because of this latter property, nonwoven fabrics of the present invention are well suited for disposable products, such as sanitary napkins, diapers, adult incontinence products, and dry and premoistened wipes (wet wipes), which can be thrown in a flush toilet after use in any part of the world.

The fibers forming the fabrics above can be made from a variety of materials including natural fibers, synthetic fibers, and combinations thereof. The choice of fibers depends upon, for example, the intended end use of the finished fabric and fiber cost. For instance, suitable fibrous substrates may include, but are not limited to, natural fibers such as cotton, linen, jute, hemp, wool, wood pulp, etc. Similarly, regenerated cellulosic fibers, such as viscose rayon and cuprammonium rayon, modified cellulosic fibers, such as cellulose acetate, or synthetic fibers, such as those derived from polypropylenes, polyethylenes, polyolefins, polyesters, polyamides, polyacrylics, etc., alone or in combination with one another, may likewise be used. Blends of one or more of the above fibers may also be used, if so desired. Among wood pulp fibers, any known papermaking fibers may be used, including softwood and hardwood fibers. Fibers, for example, may be chemically pulped or mechanically pulped, bleached or unbleached, virgin or recycled, high yield or low yield, and the like. Mercerized, chemically stiffened or crosslinked fibers may also be used.

Synthetic cellulose fiber types include rayon in all its varieties and other fibers derived from viscose or chemically modified cellulose, including regenerated cellulose and solvent-spun cellulose, such as Lyocell. Chemically treated natural cellulosic fibers can be used, such as mercerized pulps, chemically stiffened or crosslinked fibers, or sulfonated fibers. Recycled fibers, as well as virgin fibers, can be used. Cellulose produced by microbes and other cellulosic derivatives can be used. As used herein, the term "cellulosic" is meant to include any material having cellulose as a major constituent, and, specifically, comprising at least 50 percent by weight cellulose or a cellulose derivative. Thus, the term includes cotton, typical wood pulps, non-woody cellulosic fibers, cellulose acetate, cellulose triacetate, rayon, thermomechanical wood pulp, chemical wood pulp, debonded chemical wood pulp, milkweed, or bacterial cellulose.

The triggerable binder of the present invention may also be applied to other fibers or particles. Other fibers that may be treated with the triggerable binder of the present invention include fiber such as those made fibers made from carboxymethyl cellulose, chitin, and chitosan. The triggerable binder of the present invention may also be applied to particles, such as sodium polyacrylate super absorbent particles. Super absorbent particles are frequently incorporated on or into fibrous substrates used for personal care items, especially nonwoven fabrics.

The fiber length is important in producing the fabrics of the present invention. In some embodiments, such as flushable products, fiber length is of more importance. The minimum length of the fibers depends on the method selected for forming the fibrous substrate. For example, where the fibrous substrate is formed by carding, the length of the fiber should usually be at least about 42 mm in order to insure uniformity.

Where the fibrous substrate is formed by air-laid or wet-laid processes, the fiber length may desirably be about 0.2 to 6 mm. Although fibers having a length of greater than 50 mm are within the scope of the present invention, it has been determined that when a substantial quantity of fibers having a length greater than about 15 mm is placed in a flushable fabric, though the fibers will disperse and separate in water, their length tends to form "ropes" of fibers, which are undesirable when flushing in home toilets. Therefore, for these products, it is desired that the fiber length be about 15 mm or less so that the fibers will not have a tendency to "rope" when they are flushed through a toilet. Although fibers of various lengths are applicable in the present invention, desirably fibers are of a length less than about 15 mm so that the fibers disperse easily from one another when in contact with water. The fibers, particularly synthetic fibers, can also be crimped.

The fabrics of the present invention may be formed from a single layer or multiple layers. In the case of multiple layers, the layers are generally positioned in a juxtaposed or surface-to-surface relationship and all or a portion of the layers may be bound to adjacent layers. Nonwoven webs of the present invention may also be formed from a plurality of separate nonwoven webs wherein the separate nonwoven webs may be formed from single or multiple layers. In those instances where the nonwoven web includes multiple layers, the entire thickness of the nonwoven web may be subjected to a binder application or each individual layer may be separately subjected to a binder application and then combined with other layers in a juxtaposed relationship to form the finished nonwoven web.

In one embodiment, the fabric substrates of the present invention may be incorporated into cleansing and body fluid absorbent products, such as sanitary napkins, diapers, adult incontinence products, surgical dressings, tissues, wet wipes, and the like. These products may include an absorbent core, comprising one or more layers of an absorbent fibrous material. The core may also comprise one or more layers of a fluid-pervious element, such as fibrous tissue, gauze, plastic netting, etc. These are generally useful as wrapping materials to hold the components of the core together. Additionally, the core may comprise a fluid-impervious element or barrier means to preclude the passage of fluid through the core and on the outer surfaces of the product. Desirably, the barrier means also is water-dispersible. A film of a polymer having substantially the same composition as the aforesaid water-dispersible binder is particularly well-suited for this purpose. In accordance with the present invention, the polymer compositions are useful for forming each of the above-mentioned product components including the layers of absorbent core, the fluid-pervious element, the wrapping materials, and the fluid-impervious element or barrier means.

The triggerable binder formulations of the present invention are particularly useful for binding fibers of air-laid nonwoven fabrics. These air-laid materials are useful for body-side liners, fluid distribution materials, fluid in-take materials, such as a surge material, absorbent wrap sheet and cover stock for various water-dispersible personal care products. Air-laid materials are particularly useful for use as a pre-moistened wipe (wet wipe). The basis weights for air-laid non-woven fabrics may range from about 20 to about 200 grams per square meter ("gsm") with staple fibers having a denier of about 0.5-10 and a length of about 6-15 millimeters. Surge, or in-take, materials need better resiliency and higher loft so staple fibers having about 6 denier or greater are used to make these products. A desirable final density for the surge, or in-take, materials is between about 0.025 grams per cubic centimeter ("g/cc") to about 0.10 g/cc. Fluid distribution materials may have a higher density, in the desired range of about 0.10 to about 0.20 g/cc using fibers of lower denier, most desirable fibers have a denier of less than about 1.5. Wipes generally can have a fiber density of about 0.025 g/cc to about 0.2 g/cc and a basis weight of about 20 gsm to about 150 gsm; specifically from about 30 to about 90 gsm, and most specifically from about 60 gsm to about 65 gsm.

The nonwoven fabrics of the present invention may also be incorporated into such body fluid absorbing products as sanitary napkins, diapers, surgical dressings, tissues and the like. In one embodiment, the triggerable binder is such that it will not dissolve when contacted by body fluids since the concentration of monovalent ions in the body fluids is above the level needed for dissolution; *i.e.*, greater than 1% by weight. The nonwoven fabric retains its structure, softness and exhibits a toughness satisfactory for practical use. However, when brought into contact with water having a concentration of divalent ions, such as Ca^{2+} and Mg^{2+} ions, of up to about 200 ppm or more, the binder disperses. The nonwoven fabric structure is then easily broken and dispersed in the water.

In one embodiment of the present invention, the in-use tensile strength of a nonwoven fabric is enhanced by forming the nonwoven fabric with a binder material comprising the ion triggerable cationic polymer formulation of the present invention and subsequently applying either one or more monovalent and/or divalent salts to the nonwoven fabric. The salt may be applied to the nonwoven fabric by any method known to those of ordinary skill in the art including, but not limited to, applying a solid powder onto the fabric and spraying a salt solution onto the fabric. The amount of salt may vary depending on a particular application. However, the amount of salt applied to the fabric is typically from about 0.3 weight percent to about 10 weight percent salt solids based on the total weight of the fabric. The salt-containing fabrics of the present invention may be used in a variety of fabric applications including, but not limited to, feminine pads, surgical dressings, and diapers.

Those skilled in the art will readily understand that the binder formulations and fibrous substrates of the present invention may be advantageously employed in the preparation of a wide variety of products, including but not limited to, absorbent personal care products designed to be contacted with body fluids. Such products may only comprise a single layer of the fibrous substrate, or may comprise a combination of elements, as described above. Although the binder formulations and fibrous substrates of the present invention are particularly suited for personal care products, the binder formulations and fibrous substrates may be advantageously employed in a wide variety of consumer products.

Unlike other binder systems known in the art, the ion triggerable cationic polymer formulations of the present invention can be activated as binders without the need for elevated temperature. While drying or water removal is useful in achieving a good distribution of the binder in a fibrous web, elevated temperature, per se, is not essential because the binder does not require crosslinking or other chemical reactions with high activation energy to serve as a binder. Rather, the interaction with a soluble insolubilizing compound, typically a salt, is sufficient to cause the binder to become insoluble; i.e., "salted out" or activated by interaction between the cation of the polymer the salt. Thus, a drying step can be avoided, if desired, or replaced with low-temperature water removal operations such as room-temperature drying or freeze drying. Elevated temperature is generally helpful for drying, but the drying can be done at temperatures below what is normally needed to drive crosslinking reactions. Thus, the peak temperature to which the substrate is exposed or to which the substrate is brought can be below any of the following: 200° C., 180° C., 160° C., 140° C., 120° C., 110° C., 105° C., 100° C., 90° C., 75° C., and 60° C. While polymer systems, such as commercial latex emulsions, may also comprise crosslinkers suited for reaction at temperatures of 160° C. or higher, maintaining a lower peak temperature can be beneficial in preventing development of excessive strength in the polymer that might otherwise hinder the water dispersibility of the pre-moistened wipe.

Wet Wipe Wetting Composition and Wet Wipes Containing the Same

One particularly interesting embodiment of the present invention is the production of pre-moistened wipes, or wet wipes, from the above-described triggerable binder compositions and fibrous materials. For wipes, the fibrous material may be in the form of a woven or nonwoven fabric; however, nonwoven fabrics are more desirable. The nonwoven fabric is desirably formed from relatively short fibers, such as wood pulp fibers. The minimum length of the fibers depends on the method selected for forming the nonwoven fabric. Where the nonwoven fabric is formed by a wet or dry method, the fiber length is desirably from about 0.1 millimeters to 15 millimeters. Desirably, the nonwoven fabric of the present invention has a relatively low wet cohesive strength when it is not bonded together by an adhesive or binder material. When such nonwoven fabrics are bonded together by a binder composition, which loses its bonding strength in tap water and in sewer water, the fabric will break up readily by the agitation provided by flushing and moving through the sewer pipes.

The finished wipes may be individually packaged, desirably in a folded condition, in a moisture proof envelope or packaged in containers holding any desired number of sheets in a water-tight package with a wetting composition applied to the wipe. The finished wipes may also be packaged as a roll of separable sheets in a moisture-proof container holding any desired number of sheets on the roll with a wetting composition applied to the wipes. The roll can be coreless and either hollow or solid. Coreless rolls, including rolls with a hollow center or without a solid center, can be produced with known coreless roll winders, including those of SRP Industry, Inc. (San Jose, CA); Shimizu Manufacturing (Japan), and the devices disclosed in U.S. Pat. No. 4,667,890, issued May 26, 1987 to Gietman. Solid-wound coreless rolls can offer more product for a given volume and can be adapted for a wide variety of dispensers.

Relative to the weight of the dry fabric, the wipe may desirably contain from about 10 percent to about 400 percent of the wetting composition, more desirably from about 100 percent to about 300 percent of the wetting composition, and even more desirably from about 180 percent to about 240 percent of the wetting composition. The wipe maintains its desired characteristics over the time periods involved in warehousing, transportation, retail display and storage by the consumer. Accordingly, shelf life may range from two months to two years.

Various forms of impermeable envelopes and storage means for containing wet-packaged materials, such as wipes and towelettes and the like, are well known in the art. Any of these may be employed in packaging the pre-moistened wipes of the present invention.

Desirably, the pre-moistened wipes of the present invention are wetted with an aqueous wetting composition, which has one or more of the following properties:

(1) is compatible with the above-described triggerable binder compositions of the present invention;

(2) enables the pre-moistened wipe to maintain its wet strength during converting, storage and usage (including dispensing), as well as, dispersibility in a toilet bowl;

(3) does not cause skin irritation;

(4) reduces tackiness of the wipe, and provides tactile properties, such as skin glide and a "lotion-like feel"; and

(5) acts as a vehicle to deliver "moist cleansing" and other skin health benefits.

One aspect of the present invention is a wetting composition, which contains an insolubilizing agent that maintains the strength of a water-dispersible binder until the insolubilizing agent is diluted with water, whereupon the strength of the water-dispersible binder begins to decay. The water-dispersible binder may be any of the triggerable binder compositions of the present invention or any other triggerable binder composition. The insolubilizing agent in the wetting composition can be a salt, such as those disclosed for the various triggerable polymers, a blend of salts having both monovalent and multivalent ions, or any other compound, which provides in-use and storage strength to the water-dispersible binder composition, and can be diluted in water to permit dispersion of the substrate as the binder polymer triggers to a weaker state. Desirably, the wetting composition contains more than about 0.3 weight percent of an insolubilizing agent based on the total weight of the wetting composition for ion-sensitive polymers. Specifically, the wetting composition may contain from about 0.3 weight percent to about 10 weight percent of an insolubilizing agent. Even more specifically, the wetting composition may contain from about 0.5 weight percent to about 5 weight percent of an insolubilizing agent. More precisely, the wetting composition may contain from about 1 weight percent to about 4 weight percent of an insolubilizing agent.

The wetting composition of the present invention may further comprise a variety of additives compatible with the insolubilizing agent and the water-dispersible binder, such that the strength and dispersibility functions of the wipe are not jeopardized. Suitable additives in the wetting composition include, but are not limited to, the following additives: skin-care additives; odor control agents; detackifying agents to reduce the tackiness of the binder; particulates; antimicrobial agents; preservatives; wetting agents and cleaning agents, such as detergents, surfactants, some silicones; emollients; surface feel modifiers for improved tactile sensation (e.g., lubricity) on the skin; fragrance; fragrance solubilizers; opacifiers; fluorescent whitening agents; UV absorbers; pharmaceuticals; and pH control agents, such as malic acid or potassium hydroxide.

Skin-Care Additives

As used herein, the term "skin-care additives" represents additives, which provide one or more benefits to the user, such as a reduction in the probability of having diaper rash and/or other skin damage caused by fecal enzymes. These enzymes, particularly trypsin, chymotrypsin and elastase, are proteolytic enzymes produced in the gastrointestinal tract to digest food. In infants, for example, the feces tend to be watery and contain, among other materials, bacteria, and some amounts of undegraded digestive enzymes. These enzymes, if they remain in contact with the skin for any appreciable period of time, have been found to cause an irritation that is uncomfortable in itself and can predispose the skin to infection by microorganisms. As a countermeasure, skin-care additives include, but are not limited to, the enzyme inhibitors and sequestrants set forth hereafter. The wetting composition may contain less than about 5 weight percent of skin-care additives based on the total weight of the wetting composition. More specifically, the wetting composition may contain from about 0.01 weight percent to about 2 weight percent of skin-care additives. Even more specifically, the wetting composition may contain from about 0.01 weight percent to about 0.05 weight percent of skin-care additives.

A variety of skin-care additives may be added to the wetting composition and the pre-moistened wipes of the present invention or included therein. In one embodiment of the present invention, skin-care additives in the form of particles are added to serve as fecal enzyme inhibitors, offering potential benefits in the reduction of diaper rash and skin damage caused by fecal enzymes. U.S. Pat. No. 6,051,749, issued April 18, 2000 to Schulz et al., the entirety of which is herein incorporated by reference, discloses organophilic clays in a woven or nonwoven web, said to be useful for inhibiting fecal enzymes. Such materials may be used in the present invention, including reaction products of a long chain organic quaternary ammonium compound with one or more of the following clays: montmorillonite, bentonite, beidellite, hectorite, saponite, and stevensite.

Other known enzyme inhibitors and sequestrants may be used as skin-care additives in the wetting composition of the present invention, including those that inhibit trypsin and other digestive or fecal enzymes, and inhibitors for urease. For example, enzyme inhibitors and anti-microbial agents may be used to prevent the formation of odors in body fluids. For example, urease inhibitors, which are also said to play a role in odor absorption, are disclosed by T. Trinh in World Patent Application No. 98/26808, "Absorbent Articles with Odor Control System," published June 25, 1998, the entirety of which is herein incorporated by reference. Such inhibitors may be incorporated into the wetting composition and the pre-moistened wipes of the present invention and include transition metal ions and their soluble salts, such as silver, copper, zinc, ferric, and aluminum salts. The anion may also provide urease inhibition, such as borate, phytate, etc. Compounds of potential value include, but are not limited to, silver chlorate, silver nitrate, mercury acetate, mercury chloride, mercury nitrate, copper metaborate, copper bromate, copper bromide, copper chloride, copper dichromate, copper nitrate, copper salicylate, copper sulfate, zinc acetate, zinc borate, zinc phytate, zinc bromate, zinc bromide, zinc chlorate, zinc chloride, zinc sulfate, cadmium acetate, cadmium borate, cadmium bromide, cadmium chlorate, cadmium chloride, cadmium formate, cadmium iodate, cadmium iodide, cadmium permanganate, cadmium nitrate, cadmium sulfate, and gold chloride.

Other salts that have been disclosed as having urease inhibition properties include ferric and aluminum salts, especially the nitrates, and bismuth salts. Other urease inhibitors are disclosed by Trinh, including hydroxamic acid and its derivatives; thiourea; hydroxylamine; salts of phytic acid; extracts of plants of various species, including various tannins, e.g. carob tannin, and their derivatives such as chlorogenic acid derivatives; naturally occurring acids such as ascorbic acid, citric acid, and their salts; phenyl phosphoro diamidate/diamino phosphoric acid phenyl ester; metal aryl phosphoramidate complexes, including substituted phosphorodiamidate compounds; phosphoramidates without substitution on the nitrogen; boric acid and/or its salts, including especially, borax, and/or organic boron acid compounds; the compounds disclosed in European Patent Application 408,199; sodium, copper, manganese, and/or zinc dithiocarbamate; quinones; phenols; thiurams; substituted rhodanine acetic acids; alkylated benzoquinones; formarnidine disulphide; 1:3-diketones maleic anhydride; succinamide; phthalic anhydride; phenic acid; /N,N-dihalo-2-imidazolidinones; N-halo2-oxazolidinones; thio- and/or acyl-phosphoryltnamide and/or substituted derivatives thereof-, thiopyridine-N-oxides, thiopyridines, and thiopyrimidines; oxidized sulfur derivatives of diarninophosphinyl compounds; cyclotriphosphazatriene derivatives; ortho-diaminophosphinyl derivatives of oximes; bromo-nitro compounds; S-aryl and/or alkyl diamidophosphorothiolates; diaminophosphinyl derivatives; mono- and/or polyphosphorodiamide; 5-substituted-benzoxathiol-2-ones; N(diaminophosphinyl)arylcarboxamides; alkoxy-1,2-benzothaizin compounds; etc.

Many other skin-care additives may be incorporated into the wetting composition and pre-moistened wipes of the present invention, including, but not limited to, sun blocking agents and UV absorbers, acne treatments, pharmaceuticals, baking soda (including encapsulated forms thereof), vitamins and their derivatives such as Vitamins A or E, botanicals such as witch hazel extract and aloe vera, allantoin, emollients, disinfectants, hydroxy acids for wrinkle control or anti-aging effects, sunscreens, tanning promoters, skin lighteners, deodorants and antiperspirants, ceramides for skin benefits and other uses, astringents, moisturizers, nail polish removers, insect repellants, antioxidants, antiseptics, anti-inflammatory agents and the like, provided that the additives are compatible with an ion-sensitive binder composition associated therewith, and especially the ion-sensitive binder compositions of the present invention (i.e., they do not cause a substantial loss of strength in the wet state of the pre-moistened wipes, prior to dilution in water, while permitting dispersibility in water).

Useful materials for skin care and other benefits are listed in McCutcheon's 1999, Vol. 2: Functional Materials, MC Publishing Company, Glen Rock, NJ. Many useful botanicals for skin care are provided by Active Organics, Lewisville, Texas.

Odor Control Additives

Suitable odor control additives for use in the wetting composition and pre-moistened wipes of the present invention include, but are not limited to, zinc salts; talc powder; encapsulated perfumes (including microcapsules, macrocapsules, and perfume encapsulated in liposomes, vessicles, or microemulsions); chelants, such as ethylenediamine tetra-acetic acid; zeolites; activated silica, activated carbon granules or fibers; activated silica particulates; polycarboxylic acids, such as citric acid; cyclodextrins and cyclodextrin derivatives; chitosan or chitin and derivatives thereof; oxidizing agents; antimicrobial agents, including silver-loaded zeolites (e.g., those of BF Technologies, located in Beverly, Massachusetts, sold under the trademark HEALTHSHIELDTM); triclosan; kieselguhr; and mixtures thereof. In addition to controlling odor from the body or body wastes, odor control strategies can also be employed to mask or control any odor of the treated substrate. Desirably, the wetting composition contains less than about 5 weight percent of odor control additives based on the total weight of the wetting composition. More desirably, the wetting composition contains from about 0.01 weight percent to about 2 weight percent of odor control additives. Even more desirably, the wetting composition contains from about 0.03 weight percent to about 1 weight percent of odor control additives.

In one embodiment of the present invention, the wetting composition and/or pre-moistened wipes comprise derivatized cyclodextrins, such as hydroxypropyl beta-cyclodextrin in solution, which remain on the skin after wiping and provide an odor-absorbing layer. In other embodiments, the odor source is removed or neutralized by application of an odor-control additive, exemplified by the action of a chelant that binds metal groups necessary for the function of many proteases and other enzymes that commonly produce an odor. Chelating the metal group interferes with the enzyme's action and decreases the risk of malodor in the product.

Principles for the application of chitosan or chitin derivatives to nonwoven webs and cellulosic fibers are described by S. Lee et al. in "Antimicrobial and Blood Repellent Finishes for Cotton and Nonwoven Fabrics Based on Chitosan and Fluoropolymers," Textile Research Journal, 69(2); 104-112, Feb. 1999.

Detackifying Agents

While elevated salt concentrations may reduce the tack of the triggerable binder, other means of tack reduction are often desirable. Thus, detackifying agents may be used in the wetting composition to reduce the tackiness, if any, of the triggerable binder. Suitable detackifiers include any substance known in the art to reduce tack between two adjacent fibrous sheets treated with an adhesive-like polymer or any substance capable of reducing the tacky feel of an adhesive-like polymer on the skin, reducing product peel force, or reduce dispensing force. Detackifiers may be applied as solid particles in dry form, as a suspension or as a slurry of particles. Deposition may be by spray, coating, electrostatic deposition, impingement, filtration (i.e., a pressure differential drives a particle-laden gas phase through the substrate, depositing particles by a filtration mechanism), and the like, and may be applied uniformly on one or more surfaces of the substrate or may be applied in a pattern (e.g., repeating or random patterns) over a portion of the surface or surfaces of the substrate. The detackifier may be present throughout the thickness of the substrate, but may be concentrated at one or both surfaces, and may be substantially only present on one or both surfaces of the substrate.

Specific detackifiers include, but are not limited to, powders, such as talc powder, calcium carbonate, mica; starches, such as corn starch; lycopodium powder; mineral fillers, such as titanium dioxide; silica powder; alumina; metal oxides in general; baking powder; kieselguhr; and the like. Polymers and other additives having low surface energy may also be used, including a wide variety of fluorinated polymers, silicone additives, polyolefins and thermoplastics, waxes, debonding agents known in the paper industry including compounds having alkyl side chains such as those having 16 or more carbons, and the like. Compounds used as release agents for molds and candle making may also be considered, as well as, dry lubricants and fluorinated release agents.

In one embodiment, the detackifier comprises polytetrafluorethylene (PTFE), such as PTFE telomer (KRYTOX® DF) compound, used in the PTFE release agent dry lubricant MS-122DF, marketed by Miller-Stephenson (Danbury, CT) as a spray product. For example, PTFE particles may be applied by spray to one side of the substrate prior to winding of the pre-moistened wipes. In one embodiment, a detackifying agent is applied to only one surface of the substrate prior to winding into a roll.

The wetting composition desirably contains less than about 25 weight percent of detackifying agents based on the total weight of the wetting composition. More desirably, the wetting composition contains from about 0.01 weight percent to about 10 weight percent of detackifying agents, more specifically about 5% or less. Even more specifically, the wetting composition contains from about 0.05 weight percent to about 2 weight percent of detackifying agents.

In addition to acting as a detackifying agent, starch compounds may also improve the strength properties of the pre-moistened wipes. For example, it has been found that ungelled starch particles, such as hydrophilic tapioca starch, when present at a level of about 1% or higher by weight relative to the weight of the wetting composition, can permit the pre-moistened wipe to maintain the same strength at a lower salt concentration than is possible without the presence of starch. Thus, for example, a given strength can be achieved with 2% salt in the wetting composition in the presence of salt compared to a level of 4% salt being needed without starch. Starch may be applied by adding the starch to a suspension of laponite to improve the dispersion of the starch within the wetting composition.

Microparticulates

The wetting composition of the present invention may be further modified by the addition of solid particulates or microparticulates. Suitable particulates include, but are not limited to, mica, silica, alumina, calcium carbonate, kaolin, talc, and zeolites. The particulates may be treated with stearic acid or other additives to enhance the attraction or bridging of the particulates to the binder system, if desired. Also, two-component microparticulate systems, commonly used as retention aids in the papermaking industry, may also be used. Such two-component microparticulate systems generally comprise a colloidal particle phase, such as silica particles, and a water-soluble cationic polymer for bridging the particles to the fibers of the web to be formed. The presence of particulates in the wetting composition can serve one or more useful functions, such as (1) increasing the opacity of the pre-moistened wipes; (2) modifying the rheology or reducing the tackiness of the pre-moistened wipe; (3) improving the tactile properties of the wipe; or (4) delivering desired agents to the skin via a particulate carrier, such as a porous carrier or a microcapsule. Desirably, the wetting composition contains less than about 25 weight percent of particulate based on the total weight of the wetting composition. More specifically, the wetting composition may contain from about 0.05 weight percent to about 10 weight percent of microparticulate. Even more specifically, the wetting composition may contain from about 0.1 weight percent to about 5 weight percent of microparticulate.

Microcapsules and Other Delivery Vehicles

Microcapsules and other delivery vehicles may also be used in the wetting composition of the present invention to provide skin-care agents; medications; comfort promoting agents, such as eucalyptus; perfumes; skin care agents; odor control additives; vitamins; powders; and other additives to the skin of the user. Specifically, the wetting composition may contain up to about 25 weight percent of microcapsules or other delivery vehicles based on the total weight of the wetting composition. More specifically, the wetting composition may contain from about 0.05 weight percent to about 10 weight percent of microcapsules or other delivery vehicles. Even more specifically, the wetting composition may contain from about 0.2 weight percent to about 5.0 weight percent of microcapsules or other delivery vehicles.

Microcapsules and other delivery vehicles are well known in the art. For example, POLY-PORE® E200 (Chemdal Corp., Arlington Heights, IL), is a delivery agent comprising soft, hollow spheres that can contain an additive at over 10 times the weight of the delivery vehicle. Known additives reported to have been used with POLY-PORE®

E200 include, but are not limited to, benzoyl peroxide, salicylic acid, retinol, retinyl palmitate, octyl methoxycinnamate, tocopherol, silicone compounds (DC 435), and mineral oil. Another useful delivery vehicle is a sponge-like material marketed as POLY-PORE® L200, which is reported to have been used with silicone (DC 435) and mineral oil. Other known delivery systems include cyclodextrins and their derivatives, liposomes, polymeric sponges, and spray-dried starch.

Additives present in microcapsules are isolated from the environment and the other agents in the wetting composition until the wipe is applied to the skin, whereupon the microcapsules break and deliver their load to the skin or other surfaces.

Preservatives and Anti-Microbial Agents

The wetting composition of the present invention may also contain preservatives and/or anti-microbial agents. Several preservatives and/or anti-microbial agents, such as Mackstat H 66 (available from McIntyre Group, Chicago, IL), have been found to give excellent results in preventing bacteria and mold growth. Other suitable preservatives and anti-microbial agents include, but are not limited to DMDM hydantoin (e.g., Glydant Plus™, Lonza, Inc., Fair Lawn, NJ), iodopropynyl butylcarbamate, Kathon (Rohm and Hass, Philadelphia, PA), methylparaben, propylparaben, 2-bromo-2-nitropropane-1,3-diol, benzoic acid, benzalkonium chloride, benzethonium chloride, and the like. Desirably, the wetting composition contains less than about 2 weight percent on an active basis of preservatives and/or anti-microbial agents based on the total weight of the wetting composition. More desirably, the wetting composition contains from about 0.01 weight percent to about 1 weight percent of preservatives and/or anti-microbial agents. Even more desirably, the wetting composition contains from about 0.01 weight percent to about 0.5 weight percent of preservatives and/or anti-microbial agents.

Wetting Agents and Cleaning Agents

A variety of wetting agents and/or cleaning agents may be used in the wetting composition of the present invention. Suitable wetting agents and/or cleaning agents include, but are not limited to, detergents and nonionic, amphoteric, cationic, and anionic surfactants. Desirably, the wetting composition contains less than about 3 weight percent of wetting agents and/or cleaning agents based on the total weight of the wetting composition. More desirably, the wetting composition contains from about 0.01 weight percent to about 2 weight percent of wetting agents and/or cleaning agents. Even more desirably, the wetting composition contains from about 0.1 weight percent to about 0.5 weight percent of wetting agents and/or cleaning agents. Suitable cationic surfactants may include, but are not limited to, quaternary ammonium alkyl halides like cetyl trimethyl ammonium chloride and cetyl trimethyl ammonium bromide.

Amino acid-based surfactant systems, such as those derived from amino acids L-glutamic acid and other natural fatty acids, offer pH compatibility to human skin and good cleansing power, while being relatively safe and providing improved tactile and moisturization properties compared to other anionic surfactants. One function of the surfactant is to improve wetting of the dry substrate with the wetting composition. Another function of the surfactant can be to disperse bathroom soils when the pre-moistened wipe contacts a soiled area and to enhance their absorption into the substrate. The surfactant can further assist in make-up removal, general personal cleansing, hard surface cleansing, odor control, and the like. One commercial example of an amino-acid based surfactant is acylglutamate, marketed under the Amisoft name by Ajinomoto Corp., Tokyo, Japan.

Suitable non-ionic surfactants include, but are not limited to, the condensation products of ethylene oxide with a hydrophobic (oleophilic) polyoxyalkylene base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of these compounds desirably has a molecular weight sufficiently high so as to render it water-insoluble. The addition of polyoxyethylene moieties to this hydrophobic portion increases the water-solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product. Examples of compounds of this type include commercially-available Pluronic surfactants (BASF Wyandotte Corp.), especially those in which the polyoxypropylene ether has a molecular weight of about 1500-3000 and the polyoxyethylene content is about 35-55% of the molecule by weight, i.e. Pluronic L-62.

Other useful nonionic surfactants include, but are not limited to, the condensation products of C8-C22 alkyl alcohols with 2-50 moles of ethylene oxide per mole of alcohol. Examples of compounds of this type include the condensation products of C11-C15 secondary alkyl alcohols with 3-50 moles of ethylene oxide per mole of alcohol, which are commercially-available as the Poly-Tergent SLF series from Olin Chemicals or the TERGITOL® series from Union Carbide; i.e., TERGITOL® 25-L-7, which is formed by condensing about 7 moles of ethylene oxide with a C12-C15 alkanol.

Other nonionic surfactants, which may be employed in the wetting composition of the present invention, include the ethylene oxide esters of C6-C12 alkyl phenols such as (nonylphenoxy)polyoxyethylene ether. Particularly useful are the esters prepared by condensing about 8-12 moles of ethylene oxide with nonylphenol, i.e. the IGEPAL® CO series (GAF Corp.). Further non-ionic surface active agents include, but are not limited to, alkyl polyglycosides (APG), derived as a condensation product of dextrose (D-glucose) and a straight or branched chain alcohol. The glycoside portion of the surfactant provides a hydrophile having high hydroxyl density, which enhances water solubility. Additionally, the inherent stability of the acetal linkage of the glycoside provides chemical stability in alkaline systems. Furthermore, unlike some non-ionic surface active agents, alkyl polyglycosides have no cloud point, allowing one to formulate without a hydrotrope, and these are very mild, as well as readily biodegradable non-ionic surfactants. This class of surfactants is available from Horizon Chemical under the trade names of APG-300, APG-350, APG-500, and APG-500.

Silicones are another class of wetting agents available in pure form, or as microemulsions, macroemulsions, and the like. One exemplary non-ionic surfactant group is the silicone-glycol copolymers. These surfactants are prepared by adding poly(lower)alkylenoxy chains to the free hydroxyl groups of dimethylpolysiloxanols and are available from the Dow Corning Corp as Dow Corning 190 and 193 surfactants (CTFA name: dimethicone copolyol). These surfactants function, with or without any volatile silicones used as solvents, to control foaming produced by the other surfactants, and also impart a shine to metallic, ceramic, and glass surfaces.

Anionic surfactants may also be used in the wetting compositions of the present invention. Anionic surfactants are useful due to their high detergency include anionic detergent salts having alkyl substituents of 8 to 22 carbon atoms such as the water-soluble higher fatty acid alkali metal soaps, e.g., sodium myristate and sodium palmitate. A preferred class of anionic surfactants encompasses the water-soluble sulfated and sulfonated anionic alkali metal and alkaline earth metal detergent salts containing a hydrophobic higher alkyl moiety (typically containing from about 8 to 22 carbon atoms) such as salts of higher alkyl mono or polynuclear aryl sulfonates having from about 1 to 16 carbon atoms in the alkyl group, with examples available as the Bio-Soft series, *i.e.* Bio-Soft D-40 (Stepan Chemical Co.).

Other useful classes of anionic surfactants include, but are not limited to, the alkali metal salts of alkyl naphthalene sulfonic acids (methyl naphthalene sodium sulfonate, Petro AA, Petrochemical Corporation); sulfated higher fatty acid monoglycerides such as the sodium salt of the sulfated monoglyceride of cocoa oil fatty acids and the potassium salt of the sulfated monoglyceride of tallow fatty acids; alkali metal salts of sulfated fatty alcohols containing from about 10 to 18 carbon atoms (e.g., sodium lauryl sulfate and sodium stearyl sulfate); sodium C_{14}-C_{16} -alphaolefin sulfonates such as the Bio-Terge series (Stepan Chemical Co.); alkali metal salts of sulfated ethyleneoxy fatty alcohols (the sodium or ammonium sulfates of the condensation products of about 3 moles of ethylene oxide with a C_{12}-C_{15} n-alkanol; *i.e.*, the Neodol ethoxysulfates, Shell Chemical Co.); alkali metal salts of higher fatty esters of low molecular weight alkylol sulfonic acids, e.g. fatty acid esters of the sodium salt of isothionic acid, the fatty ethanolamide sulfates; the fatty acid amides of amino alkyl sulfonic acids; e.g., lauric acid amide of taurine; as well as numerous other anionic organic surface active agents such as sodium xylene sulfonate, sodium naphthalene sulfonate, sodium toulene sulfonate and mixtures thereof.

A further useful class of anionic surfactants includes the 8-(4-n-alkyl-2-cyclohexenyl)-octanoic acids, wherein the cyclohexenyl ring is substituted with an additional carboxylic acid group. These compounds or their potassium salts, are commercially-available from Westvaco Corporation as Diacid 1550 or H-240. In general, these anionic surface active agents can be employed in the form of their alkali metal salts, ammonium or alkaline earth metal salts.

Macroemulsions and Microemulsion of Silicone Particles

The wetting composition may further comprise an aqueous microemulsion of silicone particles. For example, U.S. Pat. No. 6,037,407, "Process for the Preparation of Aqueous Emulsions of Silicone Oils and/or Gums and/or Resins" issued March 14, 2000, discloses organopolysiloxanes in an aqueous microemulsion. Desirably, the wetting composition contains less than about 5 weight percent of a microemulsion of silicone particles based on the total weight of the wetting composition. More desirably, the wetting composition contains from about 0.02 weight percent to about 3 weight percent of a microemulsion of silicone particles. Even more desirably, the wetting composition contains from about 0.02 weight percent to about 0.5 weight percent of a microemulsion of silicone particles.

Silicone emulsions in general may be applied to the pre-moistened wipe by any known coating method. For example, the pre-moistened wipe may be moistened with an aqueous composition comprising a water-dispersible or water-miscible, silicone-based component that is compatible with the insolubilizing compound in the wetting composition. Further, the wipe can comprise a nonwoven web of fibers having a water-dispersible binder, wherein the web is moistened with a lotion comprising a silicone-based sulfosuccinate. The silicone-based sulfosuccinate provides gentle and effective cleansing without a high level of surfactant. Additionally, the silicone-based sulfosuccinate provides a solubilization function, which prevents precipitation of oil-soluble components, such as fragrance components, vitamin extracts, plant extracts, and essential oils.

In one embodiment of the present invention, the wetting composition comprises a silicone copolyol sulfosuccinate, such as disodium dimethicone copolyol sulfosuccinate and diammonium dimethicone copolyolsulfosuccinate. Desirably, the wetting composition comprises less than about 2 percent by weight of the silicone-based sulfosuccinate, and more desirably from about 0.05 percent to about 0.30 percent by weight of the silicone-based sulfosuccinate.

In another example of a product comprising a silicone emulsions, Dow Corning 9506 powder may also be present in the wetting composition. Dow Corning 9506 powder is believed to comprise a dimethicone/vinyldimethicone cross-polymer and is a spherical powder, which is said to be useful in controlling skin oils (see "New Chemical

Perspectives," Soap and Cosmetics, Vol. 76, No. 3, March 2000, p. 12). Thus, a water-dispersible wipe, which delivers a powder effective in controlling skin oil, is also within the scope of the present invention. Principles for preparing silicone emulsions are disclosed in WO 97/10100, published March 20, 1997.

Emollients

The wetting composition of the present invention may also contain one or more emollients. Suitable emollients include, but are not limited to, PEG 75 lanolin, methyl gluceth 20 benzoate, C12-C15 alkyl benzoate, ethoxylated cetyl stearyl alcohol, products marketed as Lambent wax WS - L, Lambent WD - F, Cetiol HE (Henkel Corp.), Glucam P20 (Amerchol), Polyox WSR N-10 (Union Carbide), Polyox WSR N-3000 (Union Carbide), Luviquat (BASF), Finsolv SLB 101 (Finetex Corp.), mink oil, allantoin, stearyl alcohol, Estol 1517 (Unichema), and Finsolv SLB 201 (Finetex Corp.).

An emollient can also be applied to a surface of the article prior to or after wetting with the wetting composition. Such an emollient may be insoluble in the wetting composition and can be immobile except when exposed to a force. For example, a petrolatum-based emollient can be applied to one surface in a pattern, after which the other surface is wetted to saturate the wipe. Such a product could provide a cleaning surface and an opposing skin treatment surface.

The emollient composition in such products and other products of the present invention can comprise a plastic or fluid emollient such as one or more liquid hydrocarbons (*e.g.*, petrolatum), mineral oil and the like, vegetable and animal fats (*e.g.*, lanolin, phospholipids and their derivatives) and/or a silicone materials such as one or more alkyl substituted polysiloxane polymers, including the polysiloxane emollients disclosed in U.S. Pat. No. 5,891,126, issued Apr. 6, 1999 to Osborn, III et al. (the disclosure of which is incorporated herein by reference). Optionally, a hydrophilic surfactant may be combined with a plastic emollient to improve wettability of the coated surface. In some embodiments of the present invention, it is contemplated that liquid hydrocarbon emollients and/or alkyl substituted polysiloxane polymers may be blended or combined with one or more fatty acid ester emollients derived from fatty acids or fatty alcohols.

In an embodiment of the present invention, the emollient material is in the form of an emollient blend. Desirably, the emollient blend comprises a combination of one or more liquid hydrocarbons (e.g., petrolatum), mineral oil and the like, vegetable and animal fats (e.g., lanolin, phospholipids and their derivatives), with a silicone material such as one or more alkyl substituted polysiloxane polymers. More desirably, the emollient blend comprises a combination of liquid hydrocarbons (e.g., petrolatum) with dimethicone or with dimethicone and other alkyl substituted polysiloxane polymers. In some embodiments of the present invention, it is contemplated that blends of liquid hydrocarbon emollients and/or alkyl substituted polysiloxane polymers may be blended with one or more fatty acid ester emollients derived from fatty acids or fatty alcohols. PEG-7 glyceryl cocoate, available as Standamul HE (Henkel Corp., Hoboken, N.J), can also be considered.

Water-soluble, self-emulsifying emollient oils, which are useful in the present wetting compositions, include the polyoxyalkoxylated lanolins and the polyoxyalkoxylated fatty alcohols, as disclosed in U.S. Pat. No. 4,690,821, issued Sep. 1, 1987 to Smith et al. (the disclosure of which is incorporated herein by reference). The polyoxyalkoxy chains desirably will comprise mixed propylenoxy and ethyleneoxy units. The lanolin derivatives will typically comprise about 20-70 such lower-alkoxy units while the C12-C20 - fatty alcohols will be derivatized with about 8-15 lower- alkyl units. One such useful lanolin derivative is Lanexol AWS (PPG-12-PEG-50, Croda, Inc., New York, N.Y.). A useful poly(15-20)C2–C3-alkoxylate is PPG-5-Ceteth-20, known as Procetyl AWS (Croda, Inc.).

According to one embodiment of the present invention, the emollient material reduces undesirable tactile attributes, if any, of the wetting composition. For example, emollient materials, including dimethicone, can reduce the level of tackiness that may be caused by the ion-sensitive binder or other components in the wetting composition, thus serving as a detackifier.

Desirably, the wetting composition contains less than about 25 weight percent of emollients based on the total weight of the wetting composition. More specifically, the wetting composition may comprise less than about 5 weight percent emollient, and most specifically less than about 2% emollient. More desirably, the wetting composition may contain from about 0.01 weight percent to about 8 weight percent of emollients. Even more desirably, the wetting composition may contain from about 0.2 weight percent to about 2 weight percent of emollients.

In one embodiment, the wetting composition and/or pre-moistened wipes of the present invention comprise an oil-in-water emulsion comprising an oil phase containing at least one emollient oil and at least one emollient wax stabilizer dispersed in an aqueous phase comprising at least one polyhydric alcohol emollient and at least one organic water-soluble detergent, as disclosed in U.S. Pat. No. 4,559,157, issued Dec. 17, 1985 to Smith et al., the entirety of which is herein incorporated by reference.

Surface Feel Modifiers

Surface feel modifiers are used to improve the tactile sensation (*e.g.*, lubricity) of the skin during use of the product. Suitable surface feel modifiers include, but are not limited to, commercial debonders; and softeners, such as the softeners used in the art of tissue making including quaternary ammonium compounds with fatty acid side groups, silicones, waxes, and the like. Exemplary quaternary ammonium compounds with utility as softeners are disclosed in U.S. Pat. No. 3,554,862, issued to Hervey et al. on Jan.

12, 1971; U.S. Pat. No. 4,144,122, issued to Emanuelsson et al., Mar. 13, 1979, U.S. Pat. No. 5,573,637, issued to Ampulski et al. Nov. 12, 1996; and U.S. Pat. No. 4,476,323, issued to Hellsten et al., Oct. 9, 1984, the entirety of all of which is herein incorporated by reference. Desirably, the wetting composition contains less than about 2 weight percent of surface feel modifiers based on the total weight of the wetting composition. More desirably, the wetting composition contains from about 0.01 weight percent to about 1 weight percent of surface feel modifiers. Even more desirably, the wetting composition contains from about 0.01 weight percent to about 0.05 weight percent of surface feel modifiers.

Fragrances

A variety of fragrances may be used in the wetting composition of the present invention. Desirably, the wetting composition contains less than about 2 weight percent of fragrances based on the total weight of the wetting composition. More desirably, the wetting composition contains from about 0.01 weight percent to about 1 weight percent of fragrances. Even more desirably, the wetting composition contains from about 0.01 weight percent to about 0.05 weight percent of fragrances.

Fragrance Solubilizers

Further, a variety of fragrance solubilizers may be used in the wetting composition of the present invention. Suitable fragrance solubilizers include, but are not limited to, polysorbate 20, propylene glycol, ethanol, isopropanol, diethylene glycol monoethyl ether, dipropylene glycol, diethyl phthalate, triethyl citrate, Ameroxol OE-2 (Amerchol Corp.), Brij 78 and Brij 98 (ICI Surfactants), Arlasolve 200 (ICI Surfactants), Calfax 16L-35 (Pilot Chemical Co.), Capmul POE-S (Abitec Corp.), Finsolv SUBSTANTIAL (Finetex), and the like. Desirably, the wetting composition contains less than about 2 weight percent of fragrance solubilizers based on the total weight of the wetting composition. More desirably, the wetting composition contains from about 0.01 weight percent to about 1 weight percent of fragrance solubilizers. Even more desirably, the wetting composition contains from about 0.01 weight percent to about 0.05 weight percent of fragrance solubilizers.

Opacifiers

Suitable opacifiers include, but are not limited to, titanium dioxide or other minerals or pigments, and synthetic opacifiers, such as REACTOPAQUE® particles (available from Sequa Chemicals, Inc., Chester, South Carolina). Desirably, the wetting composition contains less than about 2 weight percent of opacifiers based on the total weight of the wetting composition. More desirably, the wetting composition contains from about 0.01 weight percent to about 1 weight percent of opacifiers. Even more desirably, the wetting composition contains from about 0.01 weight percent to about 0.05 weight percent of opacifiers.

pH Control Agents

Suitable pH control agents for use in the wetting composition of the present invention include, but are not limited to, malic acid, citric acid, hydrochloric acid, acetic acid, sodium hydroxide, potassium hydroxide, and the like. An appropriate pH range minimizes the amount of skin irritation resulting from the wetting composition on the skin. Desirably, the pH range of the wetting composition is from about 3.5 to about 6.5. More desirably, the pH range of the wetting composition is from about 4 to about 6. Desirably the overall pH of the wet wipe product; *i.e.*, the complete wet wipe product including the fabric portion and the wetting solution portion, is from about 4.5-5.5; preferably, about 5.0. Desirably, the wetting composition contains less than about 2 weight percent of a pH adjuster based on the total weight of the wetting composition. More desirably, the wetting composition contains from about 0.01 weight percent to about 1 weight percent of a pH adjuster. Even more desirably, the wetting composition contains from about 0.01 weight percent to about 0.05 weight percent of a pH adjuster.

Although a variety of wetting compositions, formed from one or more of the above-described components, may be used with the wet wipes of the present invention, in one embodiment, the wetting composition contains the following components, given in weight percent of the wetting composition, as shown in Table 1 below:

Table 1. Wetting Composition Components

Wetting Composition Component:	*Weight Percent:*
Deionized Water	about 86 to about 98
Insolubilizing compound	about 2 to about 20
Preservative	Up to about 2
Surfactant	Up to about 2
Silicone Emulsion	Up to about 1
Emollient	Up to about 1
Fragrance	Up to about 0.3
Fragrance solubilizer	Up to about 0.5
pH adjuster	Up to about 0.2

In another embodiment of the present invention, the wetting composition comprises the following components, given in weight percent of the wetting composition, as shown in Table 2 below:

Table 2. Wetting Composition Components

Class of Wetting Composition Component:	*Specific Wetting Composition Component:*	*Component Name:*	*Weight Percent:*
Vehicle	Deionized Water		about 86 to about 98
Insolubilizing compound	Sodium Chloride (Millport Ent., Milwaukee, WI)		about 2 to about 20
Preservative	Glycerin, IPBC and DMDM Hydantoin	Mackstat H-66 (McIntyre Group, Chicago, IL)	Up to about 2
Surfactant	Acyl Glutamate	CS22 (Ajinomoto, Tokyo, Japan)	Up to about 2
Silicone Emulsion (Detackifier/Skin Feel agent)	Dimethiconol and TEA Dodecylbenezene Sulfonate	DC1785 (Dow Corning, Midland, MI)	Up to about 1
Emollient	PEG-75 Lanolin	Solulan L- 575 (Amerchol, Middlesex, NJ)	Up to about 1
Fragrance	Fragrance	Dragoco 0/708768 (Dragoco, Roseville, MN)	Up to about 0.3
Fragrance solubilizer	Polysorbate 20	Glennsurf L20 (Glenn Corp., St. Paul, MN)	Up to about 0.5
pH adjuster	Malic Acid to pH 5 (Haarman & Reimer, Tetrboro, NJ)		Up to about 0.2

In another embodiment of the present invention, the wetting composition comprises the following components, given in weight percent of the wetting composition, as shown in Table 3 below:

Table 3. An Exemplary Wetting Composition

Class of Wetting composition Component:	*Specific Wetting composition Component:*	*Component Name:*	*Weight Percent:*
Vehicle	Deionized Water		about 93
Insolubilizing compound	Zinc Chloride		about 1
Preservative	Glycerin, IPBC and DMDM Hydantoin	Mackstat H-66	about 1
Surfactant	Acyl Glutamate	CS22/ECS 22P	about 1
Silicone Emulsion	Dimethiconol and TEA Dodecylbenezene Sulfonate	DC 1784/ DC1785	about 0.5
Emollient	PEG-75 Lanolin	Solulan L- 575	about 0.25
Fragrance	Fragrance	Dragoco Fragrance 0/708768	about 0.05
Fragrance solubilizer	Polysorbate 20	Glennsurf L20	about 0.25
pH adjuster	Malic Acid to pH 5		about 0.07

It should be noted that the above-described wetting compositions of the present invention may be used with any one of the above-described triggerable binder compositions of the present invention. Further, the above-described wetting compositions of the present invention may be used with any other binder composition, including conventional binder compositions, or with any known fibrous or absorbent substrate, whether dispersible or not.

Strength Properties

In one embodiment of the present invention, wet wipes are produced using the above-described wetting composition in Table 2 and an air-laid fibrous material comprising about 75 weight percent of bleached kraft fibers and 25 weight percent of any of the above-described ion-sensitive or triggerable binder compositions of the present invention, wherein the weight percentages are based on the total weight of the dry nonwoven fabric. The amount of wetting composition added to the nonwoven fabric, relative to the weight of the dry nonwoven fabric in these embodiments, is desirably about 180 percent to about 240 weight percent. In a further embodiment of the present invention, wet wipes are produced using the above-described wetting composition in Table 1 and an air-laid fibrous material comprising 80 weight percent of softwood fibers and 20 weight percent of an ion-sensitive binder of the present invention. The amount of wetting composition added to the nonwoven fabric, relative to the weight of the dry nonwoven fabric in these embodiments, is desirably about 180 percent to about 240 weight percent. In a further embodiment of the present invention, wet wipes are produced using the above-described wetting composition in Table 1 and an air-laid fibrous material comprising 90 weight percent of softwood fibers and 10 weight percent of an ion-sensitive binder of the present invention. The amount of wetting composition added to the nonwoven fabric, relative to the weight of the dry nonwoven fabric in these embodiments, is desirably about 180 percent to about 240 weight percent.

Desirably, the wet wipes of the present invention possess an in-use wet tensile strength of at least about 100 g/in when soaked with 10% to 400% by weight wet wipes solution containing more than 0.5% by weight monovalent and/or divalent salts, such as NaCl, $ZnCl_2$ and/or $CaCl_2$ or mixtures thereof, and a tensile strength of less than about 30 g/in after being soaked in soft water or hard water containing up to 200 ppm concentration of Ca^{2+} and/or Mg^{2+} for 24 hours or less, preferably after about one hour. For handsheet substrates, cross deckle wet tensile strength (CDWT) have been reported. Machine direction wet tensile strength (MDWT) has been reported for substrates made on a continuous former.

More desirably, the wet wipes of the present invention possess an in-use wet tensile strength of at least about 300 g/in when soaked with 10% to 400% by weight wet wipes solution containing more than 0.5% by weight monovalent and/or divalent salts, such as NaCl, $ZnCl_2$ and/or $CaCl_2$ or mixtures thereof, and a tensile strength of less than about 75 g/in after being soaked in soft water or hard water containing up to 200 ppm concentration of Ca^{2+} and/or Mg^{2+} for 24 hours or less, preferably after about one hour.

Most desirably, the wet wipes of the present invention possess an in-use wet tensile strength of > 300 g/in when soaked with 10% to 400% by weight wet wipes solution containing more than 0.5% by weight monovalent and/or divalent salts, such as NaCl, $ZnCl_2$ and/or $CaCl_2$ or mixtures thereof, and a tensile strength of less than about 30 g/in after being soaked in soft water or hard water containing up to 200 ppm concentration of Ca^{2+} and/or Mg^{2+} for 24 hours or less, preferably after about one hour.

Products with high basis weights than flushable wet wipes may have relatively higher wet tensile strength. For example, products, such as pre-moistened towels or hard-surface cleaning wipes, may have basis weights above 70 gsm, such as from 80 gsm to 150 gsm. Such products can have CDWT values of 500 g/in or greater, and after soaking values of about 150 g/in or less, more specifically about 100 g/in or less, and most specifically about 50 g/in or less.

Method of Making Wet Wipes

The pre-moistened wipes of the present invention can be made in several ways. In one embodiment, the triggerable polymer composition is applied to a fibrous substrate as part of an aqueous solution or suspension, wherein subsequent drying is needed to remove the water and promote binding of the fibers. In particular, during drying, the binder migrates to the crossover points of the fibers and becomes activated as a binder in those regions, thus providing acceptable strength to the substrate. For example, the following steps can be applied:

1. Providing an absorbent substrate that is not highly bonded (e.g., an unbonded airlaid, a tissue web, a carded web, fluff pulp, etc.).
2. Applying a triggerable polymer composition to the substrate, typically in the form of a liquid, suspension, or foam.
3. Drying the substrate to promote bonding of the substrate. The substrate may be dried such that the peak substrate temperature does not exceed about 100° to 220° C.
4. Applying a wetting composition to the substrate.
5. Placing the wetted substrate in roll form or in a stack and packaging the product.

Application of the triggerable polymer composition to the substrate can be by means of spray; by foam application; by immersion in a bath; by curtain coating; by coating and metering with a wire-wound rod; by passage of the substrate through a flooded nip; by contact with a pre-metered wetted roll coated with the binder solution; by pressing the substrate against a deformable carrier containing the triggerable polymer composition such as a sponge or felt to effect transfer into the substrate; by printing such as gravure, inkjet, or flexographic printing; and any other means known in the art.

In the use of foams to apply a binder or co-binder polymer, the mixture is frothed, typically with a foaming agent, and spread uniformly on the substrate, after which vacuum is applied to pull the froth through the substrate. Any known foam application method can be used, including that of U.S. Pat. No. 4,018,647, "Process for the Impregnation of a Wet Fiber Web with a Heat Sensitized Foamed Latex Binder," issued Apr. 19, 1977 to Wietsma, the entirety of which is herein incorporated by reference. Wietsma discloses a method wherein a foamed latex is heat-sensitized by the addition of a heat-sensitizer such as functional siloxane compounds including siloxane oxyalkylene block copolymers and organopolysiloxanes. Specific examples of applicable heat-sensitizers and their use thereof for the heat sensitization of latices are described in the U.S. Pat. Nos. 3,255,140; 3,255,141; 3,483,240 and 3,484,394, all of which are incorporated herein by reference. The use of a heat-sensitizer is said to result in a product having a very soft and textile-like hand compared to prior methods of applying foamed latex binders.

The amount of heat-sensitizer to be added is dependent on, inter alia, the type of latex used, the desired coagulation temperature, the machine speed and the temperatures in the drying section of the machine, and will generally be in the range of about 0.05 to about 3% by weight, calculated as dry matter on the dry weight of the latex; but also larger or smaller amounts may be used. The heat sensitizer can be added in such an amount that the latex will coagulate far below the boiling point of water, for instance at a temperature in the range of 35° C. to 95° C., or from about 35° C. to 65° C.

Without wishing to be bound by theory, it is believed that a drying step after application of the triggerable binder solution and before application of the wetting composition enhances bonding of a fibrous substrate by driving the binder to fiber crossover points as moisture is driven off, thus promoting efficient use of the binder. However, in an alternative method, the drying step listed above is skipped, and the triggerable polymer composition is applied to the substrate followed by application of the wetting composition without significant intermediate drying. In one version of this method, the triggerable polymer composition selectively adheres to the fibers, permitting excess water to be removed in an optional pressing step without a significant loss of the binder from the substrate. In another version, no significant water removal occurs prior to application of the wetting composition. In yet another alternative method, the triggerable polymer composition and the wetting composition are applied simultaneously, optionally with subsequent addition of salt or other insolubilizing compounds to further render the binder insoluble.

The present invention is further illustrated by the following examples, which are not to be construed in any way as imposing limitations upon the scope thereof. On the contrary, it is to be clearly understood that resort may be had to various other embodiments, modifications, and equivalents thereof which, after reading the description herein, may suggest themselves to those skilled in the art without departing from the spirit of the present invention and/or the scope of the appended claims.

As used herein, the "thickness" of a web is measured with a 3-in acrylic plastic disk connected to the spindle of a Mitutoyo Digimatic Indicator (Mitutoyo Corporation, 31-19, Shiba 5-chome, Minato-ku, Tokyo 108, Japan) and which delivers a net load of 0.05 psi to the sample being measured. The Mitutoyo Digimatic Indicator is zeroed when the disk rests on a flat surface. When a sample having a size at least as great as the acrylic disk is placed under the disk, a thickness reading can be obtained from the digital readout of the indicator. Water-dispersible substrates of the present invention can have any suitable thickness, such as from about 0.1 mm to 5 mm. For wet wipes, thicknesses can be in the range of 0.2 mm to about 1 mm, more specifically from about 0.3 mm to about 0.8 mm. Thickness can be controlled, for example, by the application of compaction rolls during or after web formation, by pressing after binder or wetting composition has been applied, or by controlling the tension of winding when forming a roll good.

The use of the platen method to measure thickness gives an average thickness at the macroscopic level. Local thickness may vary, especially if the product has been embossed or has otherwise been given a three-dimensional texture.

EXAMPLE 1

Cationic Polymer Synthesis

Cationic acrylate polymers were synthesized in Methanol, Ethanol or a 75/25 Acetone/Water mixture at 30%-40% total monomer solids. Vazo-52 (DuPont) was utilized as a free-radical initiator. A typical laboratory procedure is described below.

Acetone (VWR, Westchester, PA) 399 g and deionized (DI) water, 125 g, were charged into a 3 L four-neck round bottom flask. The flask was cooled in an ice bath and bubbled with nitrogen for 20 minutes to eliminate oxygen. The reaction flask was heated to reflux (approximately 60° C) prior to adding the monomer feeds and kept under nitrogen during reaction. ADAMQUAT MC-80 (Atofina Chemicals, Philadelphia, PA), 39.6 g, was diluted with 42.0 g of DI water and bubbled with nitrogen as it was fed into the reaction flask. Methyl acrylate (Atofina Chemicals, Philadelphia, PA), 267.7 g, and Vazo-

52, 0.6 g, were dissolved in 126.1 g of acetone. This solution was cooled in an ice bath and bubbled with nitrogen as it was fed into the reaction flask. Monomer solutions were fed into the reaction flask over a period of 4 hours using mechanical dosing pumps and held at reflux for an additional 2 hours. The acetone was removed by distillation over a period of approximately 5 hours, adding DI water as the acetone was removed. An aqueous solution with approximately 0.2% residual acetone at about 23% solids was obtained.

EXAMPLE 2

Polymer Synthesis

Polymers were synthesized by batch or semi-batch reactions as previously described in Example 1.

Sample Preparation

Two different basesheet materials were used to evaluate binder performance: UCTAD tissue and thermally-bonded air-laid nonwoven.

UCTAD Tissue

An uncreped through-air dried tissue substrate with a basis weight of approximately 33 gsm was used to evaluate binder samples at 15%-30% add-on. The UCTAD basesheet had no residual wet-strength in water. A uniform and consistent amount of each binder was applied to the substrate via a pressurized spray unit. This handsheet spray unit is designed to closely resemble the operation of a commercial airlaid machine using liquid or emulsion binders, but on a much smaller scale. The equipment is enclosed in a small-framed housing, which can be placed, under a laboratory hood. The unit has a stationary sample holder (10"x13") in the center of the unit and a moveable spray header directly over the sample holder. A vacuum box is installed under the sample holder section to help draw the binder into the web during the application process. The hand-sheet is placed on the vacuum box and the spray head is moved across the substrate as the binder is sprayed in a flat V-shaped pattern. The binder is contained in a pressurized storage vessel located outside of the spray cabinet and is delivered to the spray nozzles via high pressure flexible tubing. The spray header with its spray nozzle (Spraying Systems Company) assembly is moved over the sample by means of a belt driven slide assembly, providing the desired application uniformity and speed. The spray header could be operated at speeds close to 180 fpm and the spray atomization pressure could be set as high as 200 psig. The sample was manually removed and dried in a Werner Mathis, Model LTV Through-Air Dryer (TAD) at the indicated temperatures and for the indicated times. Final basis weight of the samples with binder was approximately 39-40 gsm.

Thermally-bonded Air-laid Nonwoven

A weak, thermally-bonded air-laid (TBAL) nonwoven test substrate was fabricated from Weyerhauser NF405 wood pulp and KoSA T-255 binder fibers. The binder fiber had a polyester core and a polyethylene sheath that melts at approximately 130 °C. The air-laid web was formed using approximately 4% binder fiber and thermally bonded above the melting temperature of the sheath. The TBAL basesheet had an average basis weight of 51 gsm and an average caliper of 1.0 mm. The TBAL substrate had a residual CD wet tensile strength of approximately 30 g/in. in water. Application and drying methods are as described for the UCTAD samples. Final basis weight of the samples with binder was approximately 63-64 gsm.

Tensile Testing

A SinTech 1/D tensile tester with Testworks 3.03 version software was used for all sample testing. A 100 Newton load cell with pneumatic grips was utilized. A gauge length of 2 in. and a crosshead speed of 12 in./min. were employed. The peak load values (in g/in.) of sample replicates were recorded and averaged and reported as machine-direction wet tensile strength (MDWT) or cross-deckle wet tensile strength (CDWT), depending on how the measurement was made.

The in-use strength of each sample was simulated by either 1) soaking the tensile sample in a salt solution of desired salt type and concentration or a formulated wetting solution containing salt, or 2) applying one of the afore mentioned solutions at a fixed add-on (typically 200%-300%). The samples were allowed to equilibrate for several hours before measuring the tensile strength. Disposal strength or dispersibility was assessed by transferring samples treated as "in-use" into an excess (typically 800 mL) of deionized water or hard water of specified hardness level (as metal ion) and allowing them to soak for the indicated amount of time before the tensile strength was measured.

Trigger Properties: UCTAD and TBAL Samples

Tables 4 through 16 below demonstrate the performance of a variety of cationic binders on TBAL and UCTAD basesheets. Entry numbers in the tables refer to a particular binder with the a/b suffix denoting application of the binder on a TBAL (a) or UCTAD (b) basesheet.

Table 4 and Table 5 demonstrate the triggerable tensile properties of cationic binders made under batch polymerization conditions and based upon 5-10 mole % of the cationic monomer MADQUAT with the predominant monomer in the polymer composition being either methyl acrylate or ethyl acrylate (6b). A triggerable cationic binder composed of a cationic acrylate or other cationic vinyl compound and alkyl acrylates or methacrylates with side chains containing four or more carbons (1a) and which triggers effectively in $ZnCl_2$ but not NaCl, is shown for comparison. Compared to 1a on a TBAL basesheet, all of the binders in Table 1 show greater in-use CDWTs in 4% NaCl, ranging from 160 to 290 g/in, with a triggered drop in CDWT after soaking in 200 ppm hard water after 1hour. These results are echoed in Table 5 for application of the binders on UCTAD with in-use CDWTs ranging from 100 to 351 g/in for 4% NaCl with a tensile loss upon transfer to 200 ppm hard water. These binders also show useful tensile properties when wetted with solutions containing salts other than NaCl, such as $ZnCl_2$, $CaCl_2$, or $MgCl_2$.

Table 4

Entry	Code	Binder Composition (Mole%)	Comments	Basesheet	Binder in Sheet (wt%)	Wetting Solution	CDWT in Wetting Solution (g/in)	CDWT after 1 h soak in 200 ppm hard water solution g/in)
1a	8394-064	20% MADQUAT, 80% butyl acrylate	Semi-Batch in methanol, 4 h teed. 2 h hold	TBAL	25	4% NaCl	41 ± 33	--
2a	8312-3	5% MADQUAT, 95% methyl acrylate	Batch conditions T = 60° C 23% solids in methanol, 0.2% Vazo-52	TBAL	20	4% NaCl	160 ± 7	48 ± 9
						4% $ZnCl_2$	451 ± 50	88 ± 21
3a	8312-14	5% MADQUAT, 5% 2-ethylhexyl acrylate, 90% methyl acrylate	Batch conditions T = 60° C 27% solids in methanol, 0.19% Vazo-52	TBAL	22	4% NaCl	290 ± 65	231 ± 59
4a	8312-15	4% MADQUAT, 96%methyl acrylate	Batch conditions T = 60° C 30% solids in methanol, 0.2% Vazo-52	TBAL	22	4% NaCl	278 ± 32	176 ± 5
5a	8312-16	5% MADQUAT, 10% butyl acrylate, 80% methyl acrylate	Batch conditions T = 60° C 29% solids in methanol, 0.19% Vazo-52	TBAL	23	4% NaCl	265 ± 16	136 ± 24
						4% $ZnCl_2$	380 ± 21	132 ± 26

Table 5

Entry	Code	Binder Composition (Mole%)	Comments	Basesheet	Binder in Sheet (wt%)	Wetting Solution	CDWT in Wetting Solution (g/in)	CDWT after 1 h soak in 200 ppm hard water solution g/in)
2b	8312-3	5% MADQUAT, 95% methyl acrylate	Batch conditions, T = 60° C 23% solids in methanol, 0.2% Vazo-52	UCTAD	20	4% NaCl	235 ± 47	
						4% $ZnCl_2$	478 ± 131	
						4% $CaCl_2$	285 ± 23	
						4% $MnCl_2$	178 ± 19	
6b	8312-7	10% MADQUAT, 7% 2-ethylhexyl acrylate, 83% methyl acrylate	Batch conditions, T = 60° C 30% solids, 0.17% Vazo-52	UCTAD	22	4% $ZnCl_2$l	318 ± 22	
						4% $CaCl_2$	100 ± 4	
						4% NaCl	100 ± 17	
3b	8312-14	5% MADQUAT, 5% 2-ethylhexyl acrylate, 90% methyl acrylate	Batch conditions, T = 60° C 27% solids in methanol, 0.19% Vazo-52	UCTAD	20	4% NaCl	269 ± 15	92 ± 4
						4% $ZnCl_2$	406 ± 48	113 ± 14
4b	8312-15	4% MADQUAT, 96% methyl acrylate	Batch conditions, T = 60° C 30% solids in methanol, 0.2% Vazo-52	UCTAD	22	4% NaCl	351 ± 31	152 ± 29
						4% $ZnCl_2$	482 ± 10	1412 ± 5
5b	8312-16	5% MADQUAT, 10% butyl acrylate, 85% methyl acrylate	Batch conditions, T = 60° C 29% solids in methanol, 0.19% Vazo-52	UCTAD	20	4% NaCl	311 ± 17	94 ± 8
						4% $ZnCl_2$	427 ± 31	97 ± 2

Table 6 and Table 7 show examples for binders synthesized via semibatch monomer addition methods which are preferable for large scale industrial practice. The binders in Table 6 provided in-use CDWTs in 4% NaCl on the TBAL basesheet ranging from 137 to 336 g/in, all with appreciable tensile decay over a 1 to 16 hour time period after transfer to 200 ppm hard water. Similar results were observed for the binders on UCTAD basesheets in Table 7.

Table 6

Entry	Code	Binder Composition (Mole%)	Comments	Basesheet	Binder in Sheet (wt%)	Wetting Solution	CDWT in Wetting Solution (g/in)	CDWT after 1 h soak in 200 ppm hard water solution g/in)
7b	8312-17	5% MADQUAT, 95% methyl acrylate	Batch conditions, T = 60° C 40% solids in methanol .2 n feed, 4 n hold, 0.2% Vazo-52	TBAL	22	4% NaCl	336 ± 40	127 ± 23
								105 ± 17 (6 h)
								169 ± 16 (16 h)
						4% ZnCl$_2$	461 ± 37	169 ± 14
8a	1408-019	5% MADQUAT, 95% methyl acrylate	Semibatch conditions in methanol	TBAL	25	4% NaCl	225 ± 34	57 ± 16
9a	8312-19	5% MADQUAT, 5% butyl acrylate, 90% methyl acrylate	Semibatch conditions T = 60° C 40% solids in methanol .2 n feed, 4 n hold, 0.2% Vazo-52	TBAL	22	4% NaCl	245 ± 27	87 ± 22
10a	8312-20	5% MADQUAT, 5% 2-ethylhexyl acrylate, 5% 2-methoxyethyl acrylate, 85% methyl acrylate	Semibatch conditions T = 60° C 40% solids in methanol .2 n feed, 4 n hold, 0.2% Vazo-52	TBAL	23	4% NaCl	137 ± 8	82 ± 10

Table 7

Entry	Code	Binder Composition (Mole%)	Comments	Basesheet	Binder in Sheet (wt%)	Wetting Solution	CDWT in Wetting Solution (g/in)	CDWT after 1 h soak in 200 ppm hard water solution g/in)
7b	8312-17	5% MADQUAT, 95% methyl acrylate	Seimbatch conditions, T = 60° C 40% solids in methanol .2 h feed, 4 h hold, 0.2% Vazo-52	UCTAD	20	4% NaCl	412 ± 24	88 ± 7
						4% ZnCl$_2$	598 ± 41	102 ± 11
8b	1408-019	5% MADQUAT, 95% methyl acrylate	Semibatch conditions in methanol	UCTAD	25	4% NaCl	395 ± 49	37 ± 5
9b	8312-19	5% MADQUAT, 5% butyl acrylate, 90% methyl acrylate	Semibatch conditions T = 60° C 40% solids in methanol .2 h feed, 4 h hold, 0.2% Vazo-52	UCTAD	20	4% NaCl	285 ± 16	92 ± 12
10b	8312-20	5% MADQUAT, 5% 2-ethylhexyl acrylate, 5% 2-methoxyethyl acrylate, 85% methyl acrylate	Semibatch conditions T = 60° C 40% solids in methanol .2 n feed, 4 n hold, 0.2% Vazo-52	UCTAD	20	4% NaCl	291 ± 15	93 ± 11

Table 8 and Table 9 demonstrate the influence of the cationic monomer counterion. Entries 11a/11b demonstrate the trigger properties for a binder based upon the cationic ADAMQUAT monomer with a chloride counterion while entries 12a/12b demonstrate trigger properties for the same polymer, except with a methyl sulfate counterion. As shown in both tables, the chloride ion containing-binders perform better than the methyl sulfate materials. While the methyl sulfate counterion was not as effective as the chloride, useful and triggerable strength properties were still obtained with methyl sulfate, particularly on the UCTAD basesheet.

Table 8

Entry	Code	Binder Composition (Mole%)	Comments	Basesheet	Binder in Sheet (wt%)	Wetting Solution	CDWT in Wetting Solution (g/in)	CDWT after 1 h soak in 200 ppm hard water solution g/in)
11a	1408-114	5% ADAMQUAT, (chloride), 95% methyl acrylate	Semibatch in methanol, 4 h feed, 2 h hold	TBAL	25	4% NaCl	325 ± 26	9 ± 15
12a	1408-111	5% ADAMQUAT, (chloride), 95% methyl acrylate	Semibatch in methanol, 4 h feed, 2 h hold	TBAL	25	4% NaCl	122 ± 8	12 ± 6

Table 9

Entry	Code	Binder Composition (Mole%)	Comments	Basesheet	Binder in Sheet (wt%)	Wetting Solution	CDWT in Wetting Solution (g/in)	CDWT after 1 h soak in 200 ppm hard water solution g/in)
11b	1408-114	5% ADAMQUAT, (chloride), 95% methyl acrylate	Semibatch in methanol	UCTAD	20	4% NaCl	514 ± 47	54 ± 25
12b	1408-111	5% ADAMQUAT, (methyl sulfate), 95% methyl acrylate	Semibatch in methanol	UCTAD	20	4% NaCl	285 ± 44	18 ± 2

Table 10 and Table 11 demonstrate the influence of changing the polymerization initiator level in the synthesis of a 5% ADAMQUAT/95% methyl acrylate binder composition. For similar polymerization conditions, decreasing the initiator level typically results in higher molecular weight. Entries 13a/13b, 14a/14b, and 15a/15b show an increase in in-use CDWT values with decreasing initiator level, suggesting that increased molecular weight is favorable for higher in-use strength. For the same samples, a parallel increase in residual tensile strength was observed after 1 hour soaks in 200 ppm hard water. However, this residual strength is kinetic in origin as shown in entries 13b, 14b, and 15a/15b where after 24 hours, the residual CDWT values dropped substantially.

Table 10

Entry	Code	Binder Composition (Mole%)	Comments	Basesheet	Binder in Sheet (wt%)	Wetting Solution	CDWT in Wetting Solution (g/in)	CDWT after 1 h soak in 200 ppm hard water solution g/in)
13a	1408-146	5% ADAMQUAT, 95% methyl acrylate	Semibatch conditions, 30% solids in acetone/water, 0.22% initiator, 4 h feed, 2 h hold	TBAL	25	4% NaCl	278 ± 25	47 ± 1
14a	1408-156	5% ADAMQUAT, 95% methyl acrylate	Semibatch conditions, 30% solids in acetone/water, 0.147% initiator, 4 h feed, 2 h hold	TBAL	25	4% NaCl	298 ± 23	103 ± 29
15a	1408-163	5% ADAMQUAT, 95% methyl acrylate	Semibatch conditions, 30% solids in acetone/water, 0.074% initiator, 4 h feed, 2 h hold	TBAL	25	4% NaCl	409± 15	245 ± 30 (1 h) 68 ± 3 (24 h)

Table 11

Entry	Code	Binder Composition (Mole%)	Comments	Basesheet	Binder in Sheet (wt%)	Wetting Solution	CDWT in Wetting Solution (g/in)	CDWT after 1 h soak in 200 ppm hard water solution g/in)
13b	1408-146	5% ADAMQUAT, 95% methyl acrylate	Semibatch conditions, 30% solids in acetone/water, 0.22% initiator, 4 h feed, 2 h hold	UCTAD	20	4% NaCl	505 ± 13	67 ± 15 (1 h)
14b	1408-156	5% ADAMQUAT, 95% methyl acrylate	Semibatch conditions, 30% solids in acetone/water, 0.147% initiator, 4 h feed, 2 h hold	UCTAD	20	4% NaCl	571 ± 16	221 ± 37 (24 h) 53 ± 18 (24 h)
15b	1408-163	5% ADAMQUAT, 95% methyl acrylate	Semibatch conditions, 30% solids in acetone/water, 0.074% initiator, 4 h feed, 2 h hold	UCTAD	20	4% NaCl	626 ± 36	461 ± 46 172 ± 10 68 ± 3 (24 h)

Table 12 shows the influence of increasing the monomer solids in the synthesis of a 5% ADAMQUAT/95% methyl acrylate binder composition at a fixed initiator level. Increased monomer solids typically results in improved monomer conversion as well as increased polymer molecular weight. Entries 16a and 17a demonstrate higher in-use strengths over 13a by ca. 100 g/in. with slightly higher residual CDWTs in hard water after 1 hour. However, these residual strengths drop significantly after 24 hours of hard water exposure.

Table 12

Entry	Code	Binder Composition (Mole%)	Comments	Basesheet	Binder in Sheet (wt%)	Wetting Solution	CDWT in Wetting Solution (g/in)	CDWT after 1 h soak in 200 ppm hard water solution g/in)
13a	1408-146	5% ADAMQUAT, 95% methyl acrylate	Semibatch conditions, 30% solids in acetone/water , 0.22% initiator, 4 h feed, 2 h hold	TBAL	25	4% NaCl	278 ± 25	47 ± 1
16a	1453-048	5% ADAMQUAT, 95% methyl acrylate	Semibatch conditions, 35% solids in acetone/water , 0.22% initiator, 4 h feed, 2 h hold	TBAL	25	4% NaCl	386 ± 30	99 ± 17 (1 h) 19 ± 8 (24 h)
17a	1453-082	5% ADAMQUAT, 95% methyl acrylate	Semibatch conditions, 40% solids in acetone/water , 0.22% initiator, 4 h feed, 6 h hold	TBAL	25	4% NaCl	370± 21	94 ± 17 (1 h) 0 ± 8 (24 h)

Table 13 demonstrates the influence on the tensile properties of the binder upon further modification of the polymer composition from the 5% ADAMQUAT/95% methyl acrylate composition. Compared to the 13a binder, changing the composition to 4% ADAMQUAT/96% methyl acrylate (18a) results in a relative increase in in-use CDWT as well as an initially higher residual CDWT in hard water (1 hour) that drops to acceptable levels after 24 hours. Similar binder performance to sample 18a is obtained through modification of the 13a composition by substitution of 15% of the methyl acrylate with methyl methacrylate. The change in properties of the 18a and 19a samples relative to sample 13a may be attributed to their more hydrophobic and/or more stiff (in the case of 19a) backbone structures. Comparatively, these binder compositions, 18a and 19a, perform similarly with regards to in-use strength and dispersibility to binder 15a. Similar results were also observed in Table 14 on the UCTAD basesheet comparing samples 13b with 18b.

Table 13

Entry	Code	Binder Composition (Mole%)	Comments	Basesheet	Binder in Sheet (wt%)	Wetting Solution	CDWT in Wetting Solution (g/in)	CDWT after 1 h soak in 200 ppm hard water solution g/in)
13a	1408-146	5% ADAMQUAT, 95% methyl acrylate	Semibatch conditions, 30% solids in acetone/water , 0.22% initiator, 4 h feed, 2 h hold	TBAL	25	4% NaCl	278 ± 25	47 ± 1
18a	1453-062	4% ADAMQUAT, 96% methyl acrylate	Semibatch conditions, 35% solids in acetone/water , 0.22% initiator, 4 h feed, 2 h hold	TBAL	25	4% NaCl	429 ± 23	237 ± 30 (1 h) 40 ± 20 (24 h)
19a	1453-054	5% ADAMQUAT, 15% methylmethacrylate, 80% methyl acrylate	Semibatch conditions, 35% solids in acetone/water , 0.22% initiator, 4 h feed, 2 h hold	TBAL	25	4% NaCl	408± 27	211 ± 26 (1 h) 56 ± 14 (24 h)

Table 14

Entry	Code	Binder Composition (Mole%)	Comments	Basesheet	Binder in Sheet (wt%)	Wetting Solution	CDWT in Wetting Solution (g/in)	CDWT after 1 h soak in 200 ppm hard water solution g/in)
13b	1408-146	5% ADAMQUAT, 95% methyl acrylate	Semibatch conditions, 30% solids in acetone/water , 0.22% initiator, 4 h feed, 2 h hold	UCTAD	20	4% NaCl	505 ± 13	47 ± 15 (1 h) 39 ± 4 (24 h)
18b	1453-082	5% ADAMQUAT, 95% methyl acrylate	Semibatch conditions, 35% solids in acetone/water , 0.22% initiator, 4 h feed, 2 h hold	UCTAD	20	4% NaCl	602± 8	298 ± 12 (1 h) 54 ± 12 (24 h)

Table 15 demonstrates again the influence of polymer composition on in-use strength and dispersibility. Modification of the binder composition 15a to that of 20a which contains 1% more of the hydrophilic ADAMQUAT monomer, resulted in a binder with decreased in-use CDWT and slightly faster dispersibility kinetics after a 1 hour soak in hard water, but similar final residual CDWT values after a 24 hour soak. The decrease in in-use CDWT can be attributed to the more hydrophilic structure of the 20a binder relative to the 15a binder.

Table 15

Entry	Code	Binder Composition (Mole%)	Comments	Basesheet	Binder in Sheet (wt%)	Wetting Solution	CDWT in Wetting Solution (g/in)	CDWT after 1 h soak in 200 ppm hard water solution g/in)
15a	1408-163	5% ADAMQUAT, 95% methyl acrylate	Semibatch conditions, 30% solids in acetone/water , 0.074% initiator, 4 h feed, 2 h hold	TBAL	25	4% NaCl	409 ± 15	245 ± 30 (1 h)
								68 ± 3 (24 h)
20a	1453-007	6% ADAMQUAT, 94% methyl acrylate	Semibatch conditions, 30% solids in acetone/water , 0.074% initiator, 4 h feed, 2 h hold	TBAL	25	4% NaCl	329± 11	156 ± 36 (1 h)
								66 ± 4 (24 h)

Table 16 demonstrates the wet-tensile decay properties of a TBAL handsheet containing 25% of a 5% ADAMQUAT/95% methyl acrylate binder. Introduction of the dry basesheet to either DI water or 200 ppm hard water resulted in a relatively slow CDWT decay from ca. 400 g/in to 70-100 g/in within 24 hours.

The tensile decay profile and ultimate tensile strength can be further tailored by choice of binder composition, binder add-on level and basesheet structure.

Table 16

Time (h)	MDWT in DI (g/in)	MDWT in 200 ppm HW (g/in)
0.0833	359 ± 24	452 ± 24
0.25	316 ± 13	345 ± 137
0.5	313 ± 29	278 ± 136
1	285 ± 40	306 ± 120
2	204 ± 91	251 ± 18
3	189 ± 39	227 ± 29
19	67 ± 7	127 ± 24
24	64 ± 14	100 ± 38

In addition to providing the necessary wet tensile strength and dispersibility with sodium chloride as the triggering agent, these new materials provide enhanced wettability of the basesheet or substrate due to the inherently more wettable nature of the short alkyl chains. This allows the wetting solution to be applied at a more rapid rate of operation and has positive implications for improving the rate of manufacturing operation.

EXAMPLE 3

Two binders provide comparative examples for the binder of the present invention. The first binder is a 75/25 (w/w) mixture of an ion-sensitive, sulfonate anion modified acrylic acid copolymer (SSB) disclosed in U.S. Patent No. 6,423,801 B1 (incorporated herein by reference) and a non-crosslinking ethylene-vinyl acetate latex, DUR-O-SET® -RB, manufactured by National Starch and Chemical Co. of Bridgewater NJ. This binder package, designated "SSB/RB" in the following discussion, is disclosed in U.S. Patent No. 6,429,261 B1 (incorporated herein by reference). It functions as an ion sensitive, triggerable binder for air-laid and other substrates, but suffers from a number of disadvantages compared to the present invention. These include: higher T_g (leading to higher dry basesheet stiffness) and low wettability or fluid absorption; higher sheet tackiness in the wet state, and poor pH control for the wetted product.

The second binder, DUR-O-SET® Elite-22, is a soft, self-crosslinking ethylene-vinyl acetate emulsion manufactured by National Starch and Chemical Co, of Bridgewater NJ. It provides high wet or in-use strength, but renders the basesheet non-dispersible. This binder is referred to as "Elite-22" in the following discussion.

Pre-formed Substrates

Evaluation of binder performance in prototype products was first investigated by applying the binders to the two different pre-formed basesheet materials as described above in Example 2: UCTAD tissue and thermally-bonded air-laid nonwoven basesheets.

Continuous Air-laid Basesheet Formation and Dry Basesheet Properties

Air-laid substrate materials were formed continuously on an experimental air-laid machine having a width of 24 inches. A DanWeb air-laid former with two forming heads was utilized to produce substrates with the physical properties listed in Table 17. Weyerhauser NF405 bleached softwood kraft fiber in pulp sheet form was fiberized in a hammermill and deposited onto a moving wire at 200-300 fpm. The newly formed web was densified to the desired level by heated compaction rolls and transferred to an oven wire, where it was sprayed on the top side with the desired binder formulation, applying approximately half of the desired binder solids relative to the dry fiber mass of the web.

Spray was applied via a series of Quick Veejet® nozzles, Nozzle type 600050, manufactured by Spraying Systems Co., Wheaton, IL, operating at approximately 100 psi. A spray boom over the web provided 5 such nozzles on 5.5 inch centers with a tip-to-wire distance of 8 inches. This arrangement yielded 100% overlap of the spray cones for the binder. Each binder was sprayed at approximately 15% binder solids with water as the carrier.

The wet web was carried through an oven section of approximately 30 feet in length, operating at 395 °F to dry the binder. The web was then turned over, transferred onto another wire and passed under a second spray boom to add the other half of the desired binder solids, for a total weight percent of 20% binder solids relative to the dry fiber mass of the web. The web was then passed through a second oven section as described above, to complete the drying of the substrate.

The center 12 inches of each code was slit in three 4 inch widths and was reserved for subsequent experiments.

The Comparative Binders, SSB/RB and Elite-22, were compared with a cationic, salt-sensitive binder composed of 95 mole percent methyl acrylate (M) and 5 mole percent [2-(acryloxy)ethyl] trimethyl ammonium chloride (U) was provided by Bostik Findley, Inc. under the product designation LX-7170-02. The polymer was prepared in acetone/water (75/25) at 30% total solids with 0.074% Vazo-52 initiator.

Preparation was at a larger scale, but was otherwise analogous to the methods described above. In the following discussion, this binder in accordance with the present invention is called MU-5.

Examination of Table 17 indicates that each code had a basis weight of approximately 60 gsm, a caliper of approximately 0.8 mm, and an MD dry tensile strength (MDDT) of approximately 2,000 g/in. Therefore, differences in other dry and wet basesheet properties are attributed to differences in performance of the respective binders.

Table 17 -- Dry Air-laid Basesheet Properties.

Code	Binder	Binder Add-On	Basis Weight (gsm)	Caliper (mm)	MDDT (g/in.)
202	SSB/RB	20%	60.8	0.76	2162
208	MU-5	20%	58.9	0.77	2010
213	Elite-22	20%	59.7	0.75	2013

Wet Product Conversion

The dry basesheet materials described above were converted into wet, coreless rolls by applying a wetting solution to a 4 inch slit of each code and winding it into a roll by methods such as those described in U.S. Patent No. 6,429,261 (incorporated herein by reference). Alternatively, the wetting solution was applied via a hand-held aerosol or pump-action sprayer to a sheet of the desired dimensions. Target add-on was typically approximately 100% to 400% relative to the weight of the dry basesheet. More typically, add-on was approximately 200% to 300% relative to the weight of the dry basesheet. In most cases for the experimental samples, solution add-on was 200%-250%.

Minimally, the aqueous wetting solution should contain a sufficient amount of salt necessary to provide adequate wet strength for the wipe.

In addition to salt, the formulated wetting solution can contain other ingredients, including but not limited to: surfactants, preservatives, fragrances, emollients, pH adjusters, buffering agents, skin care additives, and odor control additives. The components of an exemplary formulated wetting solution, designated "C01", appear in Table 18.

Table 18. -- Example of a Formulated Wetting Solution, C01

Component Class	Component	Supplier	Amount
Vehicle	Deionized Water	---	93.58
Triggering Agent	NaCl	Millport En., Milwaukee, WI	4.00
Surfactants and Preservatives	Mackendet EN64	McIntyre Group, Chicago IL	2.25
Fragrance	Cocoon Fragrance	Firmerich, Plainsboro, NJ	0.10
pH Adjuster	Malic Acid	Haarman & Reimer, Tetraboro, NJ	0.07

Wet Tensile Strength and Trigger Properties

A SinTech 1/D tensile tester with Testworks 3.03 version software was used for all sample testing. A 100 Newton load cell with pneumatic grips was utilized. A gauge length of 2 in. and a crosshead speed of 12 in./minute were employed. The peak load values (in g/in.) of sample replicates were recorded and averaged and reported as machine-direction wet tensile strength (MDWT) or cross-deckle wet tensile strength (CDWT), depending on how the measurement was made. For samples that were too weak to be handled and measured (typically less than 20 g/in.) a "0" was recorded for the peak load.

The in-use strength of each sample was simulated by applying a salt solution or formulated wetting solution at the desired add-on as described above. The samples were allowed to equilibrate for several hours before measuring the tensile strength. Disposal strength or dispersibility was assessed by transferring samples treated as “in-use” into an excess (typically 800 mL) of deionized water or hard water of specified hardness level (as metal ion) and allowed to soak for the indicated amount of time before the tensile strength was measured.

Handsheet Wet Strength and Dispersibility with NaCl Solution

Table 19 presents data for TBAL and UCTAD handsheet prototypes for the specified cationic binders. These data indicate that the TBAL handsheet yielded in excess of 300-400 g/in. of in-use tensile strength and decayed to <50g/in. of residual strength in hard water, depending on binder preparation and composition. The UCTAD tissue handsheet also yielded high levels of in-use tensile strength (500-600 g/in.) and decayed to approximately the same low levels of residual strength in hard water.

Table 19. -- CDWT for the TBAL and UCTAD Handsheets in NaCl Solutions at 200% Solution Add-on.

Entry	Code	Binder Composition (Mole%)	Comments	Basesheet	Binder in Sheet (wt%)	Wetting Solution	CDWT in Wetting Solution (g/in)	CDWT after 1 h soak in 200 ppm hard water solution g/in)
7a	8312-17	5% ADAMQUAT, 95% methyl acrylate	Semibatch conditions, 60°C, 40 % solids in methanol, 2 h feed, in hold, 02% Vazo-52	TBAL	25	4% NaCl	336 ± 40	127 ± 23 46 ± 16 (16 h)
18a	1453-062	4% ADAMQUAT, 96% methyl acrylate	Semibatch conditions, 35% solids in acetone/water, 0.22% initiator, 4 h feed, 2 h hold	TBAL	25	4% NaCl	429± 23	237 ± 30 (1 h) 40 ± 20 (24 h)
17a	1453-082	5% ADAMQUAT, 95% methyl acrylate	Semibatch conditions, 40% solids in acetone/water, 0.22% initiator, 4 h feed, 6 h hold	TBAL	25	4% NaCl	370± 21	94 ± 17 (1 h) 0 ± 8 (24 h)
13b	1408-146	5% ADAMQUAT, 95% methyl acrylate	Semibatch conditions, 30% solids in acetone/water, 0.22% initiator, 4 h feed, 2 h hold	UCTAD	20	4% NaCl	602± 8	298 ± 12 (1 h) 54 ± 12 (24 h)

Air-laid Wet Strength and Dispersibility with NaCl Solution

Table 20 details the MDWT of the dispersible air laid codes in NaCl solution from 0.5% to 4.0% by weight. Code 202 with the SSB/RB binder exhibits much lower in-use MDWT below 2% NaCl. At 2% or above, it stays roughly constant. After placing the wetted strips in DI water or hard water, the MDWT drops to essentially zero regardless of the percent NaCl present in the wetting solution. The MU-5 code, by contrast, still maintains a significant degree of in-use strength even as low as 0.5% NaCl. Also, at comparable salt level it gives increased in-use MDWT over the SSB/RB code. It is kinetically slower to disperse, and maintains a higher degree of residual strength in hard water versus DI water. The details of the effects are not completely understood at present, but may be due to a small amount of ester hydrolysis in the polymer backbone.

Table 20. -- MDWT for the Air-laid Codes in NaCl Solutions at 200% Solution Add-on

Code	Binder	Wetting Solution	MDWT (g/in.) In-use (T=0) and Soaks			
			Soak Solution	Time (hours)		
				0	1	5
202	SSB/RB	1% NaCl	---	63 ± 2	---	---
202	SSB/RB	2% NaCl	---	404 ± 33	---	---
202	SSB/RB	3% NaCl	---	440 ± 22	---	---
202	SSB/RB	4% NaCl	Hard Water (200 ppm)	387 ± 47	0	---
208	MU-5	0.5% NaCl	---	228 ± 18	---	---
208	MU-5	1% NaCl	DI water	477 ± 57	130 ± 30	21 ± 5
208	MU-5	2% NaCl	DI water	536 ± 61	159 ± 40	57 ± 8
208	MU-5	3% NaCl	DI water	520 ± 70	190 ± 19	85 ± 8
208	MU-5	4% NaCl	DI water	590 ± 48	230 ± 18	107 ± 10
208	MU-5	1% NaCl	Hard Water (200 ppm)	477 ± 57	190 ± 8	121 ± 10
208	MU-5	2% NaCl	Hard Water (200 ppm)	536 ± 61	234 ± 27	145 ± 22
208	MU-5	3% NaCl	Hard Water (200 ppm)	520 ± 70	242 ± 22	158 ± 13
208	MU-5	4% NaCl	Hard Water (200 ppm)	590 ± 48	256 ± 30	156 ± 3

Because of the low level of monovalent salt needed to produce trigger activity, the binders of the present invention may now maintain sufficient strength in the presence of urine, menses, and other biological fluids without the use of an external triggering agent. Therefore, they may be much more suitable for personal care applications beyond pre-wetted products.

Wet Strength and Dispersibility with Other Salt Solutions

Tables 21 and 22 detail the MDWT values of the MU-5 Code #208 in various salt solutions. These data indicate that the performance is similar to that of NaCl and a variety of divalent and monovalent salts function well as triggering agents for the MU-5. In-use strength is at least approximately 500 g/in. in 4% salt and at least approximately 400 g/in. in 2% salt. Dispersibility is kinetically slower and the samples maintain a slightly higher degree of residual strength in hard water versus DI water.

Table 21. -- MDWT for the Air-laid Codes in Various 4% Salt Solutions at 200% Solution Add-on

Code	Binder	Wetting Solution	Soak Solution	MDWT (g/in.) In-use (T=0) and Soaks		
				Time (hours)		
				0	1	5
208	MU-5	4% NaCl	DI water	590 ± 48	230 ± 18	107 ± 10
208	MU-5	4% NaCl	Hard Water (200 ppm)	590 ± 48	256 ± 30	156 ± 3
208	MU-5	4% Na_2SO_4	DI water	498 ± 35	255 ± 23	154 ± 9
208	MU-5	4% Na_2SO_4	Hard Water (200 ppm)	498 ± 35	239 ± 9	132 ± 4
208	MU-5	4% Na_2SO_4	DI water	528 ± 81	158 ± 17	63 ± 6
208	MU-5	4% Na_2O_4	Hard Water (200 ppm)	528 ± 81	209 ± 33	133 ± 22
208	MU-5	4% $CaCl_2$	DI water	507 ± 102	214 ± 6	120 ± 3
208	MU-5	4% $CaCl_2$	Hard Water (200 ppm)	507 ± 102	208 ± 33	145 ± 11
208	MU-5	4% $ZnCl_2$	DI water	613 ± 92	229 ± 9	126 ± 7
208	MU-5	4% $ZnCl_2$	Hard Water (200 ppm)	613 ± 92	251 ± 28	164 ± 12

Table 22. -- MDWT for the Air-Laid Codes in Various 2% Salt Solutions ~200% Solution Add-on

Code	Binder	Wetting Solution	Soak Solution	MDWT (g/in.) In-use (T=0) and Soaks Time (hours) 0	1	5
208	MU-5	2% NaCl	DI water	536 ± 61	159 ± 40	57 ± 8
208	MU-5	2% NaCl	Hard Water (200 ppm)	536 ± 61	234 ± 27	145 ± 22
208	MU-5	2% Na_2SO_4	DI water	399 ± 52	209 ± 20	120 ± 10
208	MU-5	2% Na_2SO_4	Hard Water (200 ppm)	399 ± 52	200 ± 16	129 ± 3
208	MU-5	2% $NaSO_4CH_3$	DI water	482 ± 79	128 ± 7	46 ± 4
208	MU-5	2% $NaSO_4CH_3$	Hard Water (200 ppm)	482 ± 79	202 ± 8	126 ± 10
208	MU-5	2% $CaCl_2$	DI water	480 ± 87	160 ± 9	73 ± 14
208	MU-5	2% $CaCl_2$	Hard Water (200 ppm)	480 ± 87	208 ± 23	139 ± 17
208	MU-5	2% $ZnCl_2$	DI water	518 ± 70	163 ± 9	93 ± 3
208	MU-5	2% $ZnCl_2$	Hard Water (200 ppm)	518 ± 70	200 ± 18	136 ± 14

Wet Strength and Dispersibility with C01 Solution

Table 23 details the MDWT of the air-laid codes in the formulated C01 wetting solution. On average, the MU-5 code showed approximately 25% higher strength than the SSB/RB code. The SSB/RB code was faster to disperse and the residual strength level was higher for the MU-5 code. However, there appeared to be little difference in the DI water and hard water dispersibility of the MU-5 code with the C01 solution. In hard water, the strength decayed to less than 70 g/in. after 24 hours.

Table 23. -- MDWT for the Air-laid Codes in C01
Wetting Solution at 225% Solution Add-on

Code	Binder	Wetting Solution	MDWT (g/in.) In-use (T=0) and Soaks						
			Soak Solution	*Time (hours)*					
				0	0.25	0.5	1	5	24
202	SSB/RB	C01	DI Water	453 ± 22	5 ± 1	0	0	0	0
202	SSB/RB	C01	Hard Water (200 ppm)	453 ± 22	5 ± 1	0	0	0	0
208	MU-5	C01	DI Water	569 ± 28	298 ± 7	264 ± 17	216 ± 7	132 ± 7	86 ± 9
208	MU-5	C01	Hard Water (200 ppm)	569 ± 28	298 ± 17	269 ± 16	234 ± 2	142 ± 4	67 ± 5
213	Elite-22	C01	---	1048 ± 38	---	---	---	---	---

Air-laid Basesheet Stiffness

As noted above, it is desirable for the basesheet to have a low stiffness both in the dry and wet state. In the dry state, it is desirable for the basesheet to remain more flexible for converting and handling, particularly with respect to wet-winding and fabrication of coreless rolls. Also, low product stiffness in the wet state is desirable. A more flexible wet product gives better feel and conformance to the body and hands when used. Also, a less stiff wiper sheet may be less resistant to turbulence and flow and be better able to clear household plumbing fixtures without clogging. Dry basesheet and wet product stiffness is characterized by a Cup Crush Test as described in the co-pending U.S. patent application Serial No. 09/900,698 assigned to Kimberly-Clark, which is incorporated herein by reference. Table 24 gives Cup Crush results for the three basesheet codes. In the dry state, Code 202 with the SSB/RB binder is stiffer than the other codes indicated by the higher Total Crush Energy and Peak Load values. The cationic MU-5 binder gave dry Total Crush Energy and Peak Load results which were similar to the low Tg, Elite-PE binder. In the wet state, the code with the Elite-PE binder gave the highest Total Crush Energy and Peak Load due to the cross-linking nature of the binder. The MU-5 and the SSB/RB codes gave values that are roughly comparable in the wet state.

Table 24. Total Cup Crush Energy Values for the Dry and Wet Air-laid Codes.

Code	Binder	Total Crush Energy, Dry (g*mm)	Std. Dev	Total Crush Energy, Wet (g*mm)	Std. Dev.	Peak Load Dry (g)	Std. Dev.	Peak Load Wet (g)	Std. Dev.
202	SSB/RB	3619	372	177.4	21.6	417.4	39.6	27.2	3.7
208	MU-5	1985	104	243.6	16.6	222.7	23.0	34.6	2.2
213	Elite-22	1790	313	404.5	32.8	210.9	32.1	50.3	5.3

Since cup crush is a measure of the softness and flexibility of the product, the lower the value, the softer and more flexible the wet wipe will be, and therefore the more desirable the product. In the dry state it is desirable to have a Peak Load of less than about 500 g and a Total Crush Energy of less than about 4000 g*mm. More desirably, the dry Peak Load would be less than about 400 g and a Total Crush Energy of less than about 3000 g*mm. Most desirably, the dry Peak Load would be less than about 300 g and a Total Crush Energy of less than about 2000 g*mm.

The wet wipes of the present invention desirably have a cup crush of less than about 40 g and a wet Total Crush Energy of less than about 450 g*mm. More desirably, the wet wipes have a cup crush of less than about 30 g and a wet Total Crush Energy of less than about 350 g*mm. Even more desirably, the wet wipes have a cup crush of less than about 20 g and a wet Total Crush Energy of less than about 250 g*mm.

Wettability

As noted above, it is desirable for the dry basesheet to have a high degree of wettability. This is especially important with respect to wet-winding and fabrication of coreless rolls. Poor wettability leads to poor control of the web in the wetting operation and a reduction in the rate of operation in the wet-winding process. A Drop Shape Analyzer (DSA-10), Kruss USA, Charlotte, NC, with an automatic drop-dosing system and a CCD camera was used to evaluate dry basesheet wettability. The DSA captures drop contact and absorption into porous substrates using high-speed photography. These images can be evaluated with the software provided by the manufacturer and used to measure contact angles and fluid intake times for nonwovens, such as the air-laid substrates in the present invention.

Table 25 indicates that the MU-5 code gives the best wettability, or shortest drop absorption time, for the basesheet codes with otherwise similar physical properties.

The short absorption time for the MU-5 indicates that it has the highest probability of running at a higher rate of operation in the wet-winding process.

Table 25. -- DSA Absorption Times for the Dry Air-laid Codes Using the C01 Wetting Solution

Code	Binder	DSA Absorption Time (ms)	Standard Dev.
202	SSB/RB	125	62
208	MU-5	65	13
213	Elite-22	120	16

For purposes of the present invention it is desirable that the basesheet have a DSA Absorption time of less than about 150 ms. Desirably, the basesheet has a DSA Absorption time of less than about 100 ms. More desirably, the basesheet has a DSA Absorption time of less than about 75 ms.

Tackiness

Low product tackiness or stickiness is another desirable attribute. Low tackiness provides good consumer feel and tactile properties, as well as ease of product dispensing. Sheet-to-sheet adhesion of basesheet samples wetted with the C01 wetting solution was measured with a Stable Microsystems TA-XT21 Texture Analyzer, Texture Technologies, Inc., Scarsdale, NY. A 5 kg load cell was used with a resolution of 0.1 g of force. The probe utilized was Texture Technologies TA-310 indexable Release Liner Rig for Tackiness and Adhesiveness of Flexible Materials. The bottom platen rig was not used, but was replaced with the platen rig from Texture Technologies TA-96 Double clamp set. In addition, a 0.25 cm thick stainless steel block was used as a material platform inside of the platen clamp rig. Each test rig was equipped with Plexiglas shims (approximately 2.5 cm x 4.4 cm by 0.25 cm) to provide maximum contact area with clamped testing material. The following test procedure was utilized.

Each sheet was sectioned (in the machine direction of the roll) into four 2.5 cm (1") wide sections. The samples were quickly cut, then returned to the sample container to prevent dry-out of the wetting solution. Before the first run of tests, the load cell was calibrated following the procedure outlined for the Texture Analyzer.

One strip of sheet was quickly draped lengthwise over the smooth edge of the stainless steel block (block used for this experiment had a rounded edge and a smooth edge). Each sheet was adjusted to be centered on the block. A small amount of tension was applied to the sheet by hand. One of the Plexiglas shims was placed at the lower portion of the strip near the base of the steel block. Tension was applied to the other side of the strip by sliding a second shim from the top surface of the block to the bottom surface. While maintaining tension, the block/sheet/shim apparatus was placed in the platen clamp. The assembly was centered and tightened into place with the clamp jaws contacting the Plexiglas shims.

A second strip of sheet was draped over and centered on the TA-310 probe. A small amount of sheet tension was applied by hand. One Plexiglas shim was slid between the strip and the tension screw, and then tightened down. A second shim was slid into the other side of the probe and tightened down. During this step, the sheet tension was maintained so as not to have any gaps between the strip and the probe. Additionally, the shims were maintained at the same distance from the probe end to maintain a constant pressure applied to the sheet during the test. The probe was then attached to the load cell. Fine adjustments were made to the platen rig to align the strips for testing. The above steps were completed in less than 3 minutes to ensure that the sheets did not dry out.

The Texture Expert Exceed software was used to produce the Tack Force versus distance curve using the following parameters in Table 26.

Table 26. -- Data Acquisition Parameters for Tackiness Testing.

Test Parameter	Description	Value
Test Type	Type of test performed	Adhesive
Pre-test Speed	Speed of tensile frame before trigger force is reached	1.0 mm/s
Test Speed	Speed of tensile frame after trigger force is reached	0.1 mm/s
Post-test Speed	Speed of tensile frame withdrawal after test time is reached	10 mm/s
Force	Force applied by tester	200 g
Time	Time that force is applied to sample (dwell time)	10 s
Withdrawal Distance	Withdrawal distance of probe after test is completed	30 mm
Trigger	Force necessary to begin test speed (see above)	0.5g
Data Acq. Rate	Rate at which data is acquired from test in points per second	500 pps

Peak Tack Force was determined using this method and the data appearing in Table 27. Code 202 with the SSS/RS binder had the highest Tack Force and was significantly higher than the MU-5 code. Code 213 exhibited the lowest tack force due to the non-dispersing, crosslinking nature of the binder.

Table 27. -- Peak Tack Force Data for the Air-laid Samples with C01 Solution (225%)

Code	Binder	Peak Tack Force (g)	Standard Dev.
202	SSB/RB	35.3	6.6
208	MU-5	7.1	1.2
213	Elite-22	1.8	0.6

For purposes of the present invention, it is desirable that the wet basesheet have a Peak Tack Force of less than about 50 g. Desirably, the wet basesheet has a Peak Tack Force of less than about 35 g. More desirably, the wet basesheet has a Peak Tack Force of less than about 10 g.

Product pH

It is also desirable to easily control the pH of the wetting solution that may be rendered or expressed from the product. The purpose is to provide the proper or optimum pH for skin contact with the product. The pH range for normal skin is approximately 4.5-5.5 and an optimal wetting solution should be formulated within this range to assure mild cleansing. Ideally, the pH of the expressed solution should remain close to the pH of the formulated solution. In other words, it is desirable to control the Expressed pH of the product solely by the pH of the wetting solution.

An Acumet® AR25 pH Meter with an Acufet® Solid State Electrode (Fisher Scientific, Pittsburgh, PA) was utilized to measure Expressed pH values for the air-laid codes wetted with the C01 wetting solution described above. Four 4 x 4.5 inch sheets were placed in a 60 mL syringe and the solution was squeezed from them into a clean polyethylene bag. This procedure was repeated twice more for each code. The pH for each sample was measured and the values were averaged. Theses values are listed in Table 28 below. The SSB/RB code gave a significant pH shift down. The SSB binder contains large amount of carboxylic acid residues in the polymer backbone that provide an inherent source of protons to the wetting solution, depressing the Expressed pH. The Elite-PE code gives a smaller, more moderate pH shift downward. The pH value for the MU-5 code gave a slight pH shift up, even though the binder pH was lower than SSB, as received. This indicates that the MU-5 had no inherent acid source and the Expressed pH was easily controlled by the wetting solution pH.

Table 28. -- Expressed pH Values for the Air-laid
Samples with C01 Solution (225%)

Code	Binder Type	Binder pH	Wetting Solution pH	Expressed pH	Δ pH
202	SSB/RB	4.2	5.0	3.7 ± 0.1	-1.3
208	MU-5	3.4	5.0	5.2 ± 0.1	+0.2
213	Elite-22	---	5.0	4.6 ± 0.1	-0.4

Temporary Wet Strength of the Dry Basesheet

As noted above, the MU-5 Air-laid code requires a low level of salt or triggering agent to produce trigger activity. Also, the binders of the present invention may be suitable for providing wet strength and/or temporary wet strength in the absence of added salt for dry tissues, towels, and other products due to their solubility characteristics. This is illustrated by Table 29 below. Table 29 shows the immediate wet tensile strength and tensile strength decay in various levels of hard water for the MU-5 air-laid code. Immediate wet tensile strength of approximately 400 g/in. was seen. After 24 hours or less, the wet tensile strength dropped to approximately 70-100 g/in., depending on water hardness level. The strength dropped to >20 g/in. in DI or soft water.

Table 29. -- Immediate Wet Tensile and Wet Tensile
Decay for the dispersible Air-laid Codes.

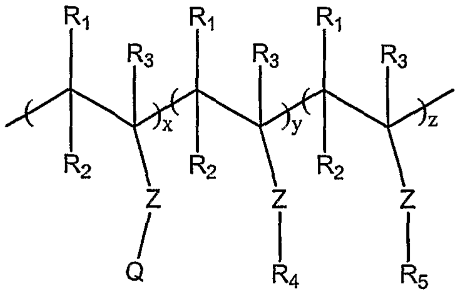
Code	Binder	Wetting Solution	MDWT (g/in.) of Dry Basesheet in Placed Water of Different Hardness Levels											
			Soak Solution Hardnes s (ppm)	Time (hours)										
				0	0.08	0.25	0.5	1	3	5	15	16	17	23
208	MU-5	None	0	462 ± 17	384 ± 17	316 ± 21	256 ± 16	208 ± 10	86.4 ± 11	26.3 ± 6.0	17.2 ± 5.4	---	---	---
208	MU-5	None	66	468 ± 8.1	426 ± 8.2	328 ± 4.3	271 ± 31	254 ± 18	164 ± 28	130 ± 26	---	---	---	73.1 ± 13
208	MU-5	None	125	388 ± 10	346 ± 46	306 ± 29	236 ± 15	210 ± 9.7	140 ± 15	119 ± 2.9	---	78 ± 1.9	---	---
208	MU-5	None	200	439 ± 51	378 ± 21	370 ± 11	311 ± 34	274 ± 18	185 ± 17	162 ± 17	---	---	124 ± 1.5	105 ± 11
202	SSB/RB	None	0	46 ± 4	---	---	0	---	---	----	---	---	---	---

It should be understood, of course, that the foregoing relates only to certain disclosed embodiments of the present invention and that numerous modifications or alterations may be made therein without departing from the spirit and scope of the invention as set forth in the appended claims.

CLAIMS

What is Claimed is:

1. A binder composition comprising a polymer having the structure:



wherein x = 1 to about 15 mole percent; y = about 60 to about 99 mole percent; and z = 0 to about 30 mole percent; Q is selected from C_1-C_4 alkyl ammonium, quaternary C_1-C_4 alkyl ammonium, and benzyl ammonium; Z is selected from –O-, -COO-, -OOC-, -CONH-, and –NHCO-; R_1, R_2, R_3 are independently selected from hydrogen and methyl; R_4 is C_1-C_4 alkyl; R_5 is selected from hydrogen, methyl, ethyl, butyl, ethylhexyl, decyl, dodecyl, hydroxyethyl, hydroxypropyl, polyoxyethylene, and polyoxypropylene.

2. A binder composition comprising the polymerization product of a vinyl-functional cationic monomer and one or more hydrophobic vinyl monomer with alkyl side chains of 1 to 4 carbon atoms.

3. The binder composition of Claim 2, wherein the vinyl-functional cationic monomer is selected from [2-(acryloxy)ethyl] dimethyl ammonium chloride, [2-(methacryloxy)ethyl] dimethyl ammonium chloride, [2-(acryloxy)ethyl] trimethyl ammonium chloride, [2-(methacryloxy)ethyl] trimethyl ammonium chloride, (3-acrylamidopropyl) trimethyl ammonium chloride, N,N-diallyldimethyl ammonium chloride, [2-(acryloxy)ethyl] dimethylbenzyl ammonium chloride, and [2-(methacryloxy)ethyl] dimethylbenzyl ammonium chloride.

4. The binder composition of Claim 2, wherein the vinyl-functional cationic monomer is selected from precursor monomers selected from vinylpyridine,

dimethylaminoethyl acrylate and dimethylaminoethyl methacrylate followed by quaternization of the polymer.

5. The binder composition of Claim 2, wherein the vinyl-functional cationic monomer is selected from [2-(acryloxy)ethyl] dimethyl ammonium chloride, [2-(acryloxy)ethyl] dimethyl ammonium bromide, [2-(acryloxy)ethyl] dimethyl ammonium iodide, and [2-(acryloxy)ethyl] dimethyl ammonium methyl sulfate.

6. The binder composition of Claim 2, wherein the vinyl-functional cationic monomer is selected from [2-(methacryloxy)ethyl] dimethyl ammonium chloride, [2-(methacryloxy)ethyl] dimethyl ammonium bromide, [2-(methacryloxy)ethyl] dimethyl ammonium iodide, and [2-(methacryloxy)ethyl] dimethyl ammonium methyl sulfate.

7. The binder composition of Claims 2, wherein the vinyl-functional cationic monomer is selected from [2-(acryloxy)ethyl] trimethyl ammonium chloride, [2-(acryloxy)ethyl] trimethyl ammonium bromide, [2-(acryloxy)ethyl] trimethyl ammonium iodide, and [2-(acryloxy)ethyl] trimethyl ammonium methyl sulfate.

8. The binder composition of Claims 2, wherein the vinyl-functional cationic monomer is selected from [2-(methacryloxy)ethyl] trimethyl ammonium chloride, [2-(methacryloxy)ethyl] trimethyl ammonium bromide, [2-(methacryloxy)ethyl] trimethyl ammonium iodide, and [2-(methacryloxy)ethyl] trimethyl ammonium methyl sulfate.

9. The binder composition of Claims 2, wherein the vinyl-functional cationic monomer is selected from (3-acrylamidopropyl) trimethyl ammonium chloride, (3-acrylamidopropyl) trimethyl ammonium bromide, (3-acrylamidopropyl) trimethyl ammonium iodide, and (3-acrylamidopropyl) trimethyl ammonium methyl sulfate.

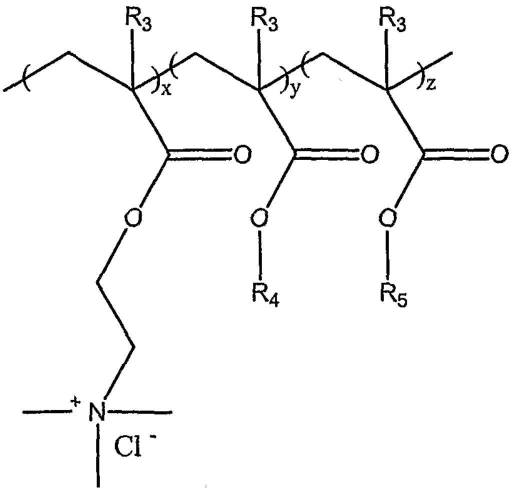
10. The binder composition of Claims 2, wherein the vinyl-functional cationic monomer is selected from N,N-diallyldimethyl ammonium chloride, N,N-diallyldimethyl ammonium bromide, N,N-diallyldimethyl ammonium iodide, and N,N-diallyldimethyl ammonium methyl sulfate.

11. The binder composition of Claims 2, wherein the vinyl-functional cationic monomer is selected from [2-(acryloxy)ethyl] dimethylbenzyl ammonium chloride, [2-(acryloxy)ethyl] dimethylbenzyl ammonium bromide, [2-(acryloxy)ethyl] dimethylbenzyl ammonium iodide, and [2-(acryloxy)ethyl] dimethylbenzyl ammonium methyl sulfate.

12. The binder composition of Claims 2, wherein the vinyl-functional cationic monomer is selected from [2-(methacryloxy)ethyl] dimethylbenzyl ammonium chloride, [2-(methacryloxy)ethyl] dimethylbenzyl ammonium bromide, [2-(methacryloxy)ethyl] dimethylbenzyl ammonium iodide, and [2-(methacryloxy)ethyl] dimethylbenzyl ammonium methyl sulfate.

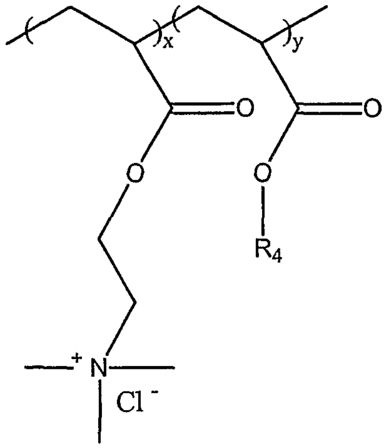
13. The binder composition of Claims 2, wherein the hydrophobic vinyl monomer is selected from branched or linear alkyl vinyl ethers, vinyl esters, acrylamides, and acrylates.

14. A binder composition that is the polymerization product of a cationic acrylate or methacrylate and one or more alkyl acrylates or methacrylates having the structure:



wherein x = 1 to about 15 mole percent; y = about 60 to about 99 mole percent; and z = 0 to about 30 mole percent; R_4 is C_1-C_4 alkyl; R_5 is selected from hydrogen, methyl, ethyl, butyl, ethylhexyl, decyl, dodecyl, hydroxyethyl, hydroxypropyl, polyoxyethylene, and polyoxypropylene.

15. A binder composition having the structure:



wherein x = 1 to about 15 mole percent; y = about 85 to about 99 mole percent and R_4 is C_1-C_4 alkyl.

16. The binder composition of Claim 15, wherein x = about 3 to about 6 mole percent, y = about 94 to about 97 mole percent and R_4 is methyl.

17. A nonwoven fabric comprising fibrous material and a binder material, said binder material comprising the binder composition of Claim 1.

18. A nonwoven fabric comprising fibrous material and a binder material, said binder material comprising the binder composition of Claim 2.

19. A nonwoven fabric comprising fibrous material and a binder material, said binder material comprising the binder composition of Claim 14.

20. A nonwoven fabric comprising fibrous material and a binder material, said binder material comprising the binder composition of Claim 16.

21. A fibrous substrate comprising:

fibrous material; and

a binder composition for binding said fibrous material into an integral web, said binder composition comprising the polymerization product of a vinyl-functional cationic monomer and one or more hydrophobic vinyl monomer with alkyl side chains of 1 to 4 carbon atoms.

22. The fibrous substrate of Claim 21, wherein the vinyl-functional cationic monomer is selected from [2-(acryloxy)ethyl] dimethyl ammonium chloride, [2-(methacryloxy)ethyl] dimethyl ammonium chloride, [2-(acryloxy)ethyl] trimethyl ammonium chloride, [2-(methacryloxy)ethyl] trimethyl ammonium chloride, (3-acrylamidopropyl) trimethyl ammonium chloride, N,N-diallyldimethyl ammonium chloride, [2-(acryloxy)ethyl] dimethylbenzyl ammonium chloride, and [2-(methacryloxy)ethyl] dimethylbenzyl ammonium chloride.

23. The fibrous substrate of Claim 21, wherein the vinyl-functional cationic monomer is selected from precursor monomers selected from vinylpyridine, dimethylaminoethyl acrylate and dimethylaminoethyl methacrylate followed by quaternization of the polymer.

24. The fibrous substrate of Claim 21, wherein the vinyl-functional cationic monomer is selected from [2-(acryloxy)ethyl] dimethyl ammonium chloride, [2-(acryloxy)ethyl] dimethyl ammonium bromide, [2-(acryloxy)ethyl] dimethyl ammonium iodide, and [2-(acryloxy)ethyl] dimethyl ammonium methyl sulfate.

25. The fibrous substrate of Claim 21, wherein the vinyl-functional cationic monomer is selected from [2-(methacryloxy)ethyl] dimethyl ammonium chloride, [2-(methacryloxy)ethyl] dimethyl ammonium bromide, [2-(methacryloxy)ethyl] dimethyl ammonium iodide, and [2-(methacryloxy)ethyl] dimethyl ammonium methyl sulfate.

26. The fibrous substrate of Claim 21, wherein the vinyl-functional cationic monomer is selected from [2-(acryloxy)ethyl] trimethyl ammonium chloride, [2-(acryloxy)ethyl] trimethyl ammonium bromide, [2-(acryloxy)ethyl] trimethyl ammonium iodide, and [2-(acryloxy)ethyl] trimethyl ammonium methyl sulfate.

27. The fibrous substrate of Claim 21, wherein the vinyl-functional cationic monomer is selected from [2-(methacryloxy)ethyl] trimethyl ammonium chloride, [2-(methacryloxy)ethyl] trimethyl ammonium bromide, [2-(methacryloxy)ethyl] trimethyl ammonium iodide, and [2-(methacryloxy)ethyl] trimethyl ammonium methyl sulfate.

28. The fibrous substrate of Claim 21, wherein the vinyl-functional cationic monomer is selected from (3-acrylamidopropyl) trimethyl ammonium chloride, (3-acrylamidopropyl) trimethyl ammonium bromide, (3-acrylamidopropyl) trimethyl ammonium iodide, and (3-acrylamidopropyl) trimethyl ammonium methyl sulfate.

29. The fibrous substrate of Claim 21, wherein the vinyl-functional cationic monomer is selected from N,N-diallyldimethyl ammonium chloride, N,N-diallyldimethyl ammonium bromide, N,N-diallyldimethyl ammonium iodide, and N,N-diallyldimethyl ammonium methyl sulfate.

30. The fibrous substrate of Claim 21, wherein the vinyl-functional cationic monomer is selected from [2-(acryloxy)ethyl] dimethylbenzyl ammonium chloride, [2-(acryloxy)ethyl] dimethylbenzyl ammonium bromide, [2-(acryloxy)ethyl] dimethylbenzyl ammonium iodide, and [2-(acryloxy)ethyl] dimethylbenzyl ammonium methyl sulfate.

31. The fibrous substrate of Claim 21, wherein the vinyl-functional cationic monomer is selected from [2-(methacryloxy)ethyl] dimethylbenzyl ammonium chloride, [2-(methacryloxy)ethyl] dimethylbenzyl ammonium bromide, [2-(methacryloxy)ethyl] dimethylbenzyl ammonium iodide, and [2-(methacryloxy)ethyl] dimethylbenzyl ammonium methyl sulfate.

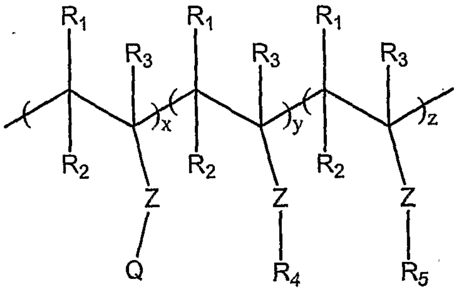
32. The fibrous substrate of Claim 21, wherein the hydrophobic vinyl monomer is selected from branched or linear alkyl vinyl ethers, vinyl esters, acrylamides, and acrylates.

33. A water-dispersible article comprising the fibrous substrate of Claim 21.

34. A *fibrous substrate comprising:*

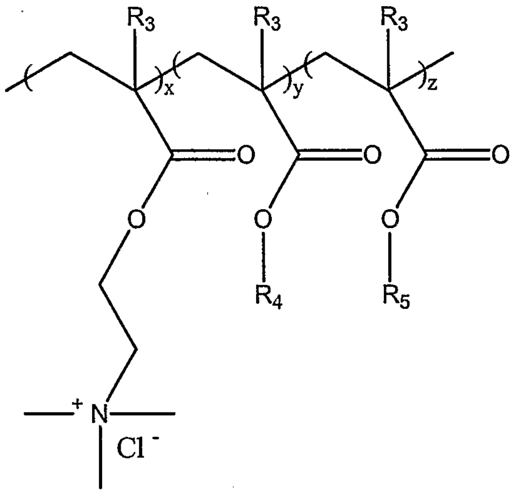
fibrous material; and

a binder composition for binding said fibrous material into an integral web, said binder composition comprising a composition having the structure:



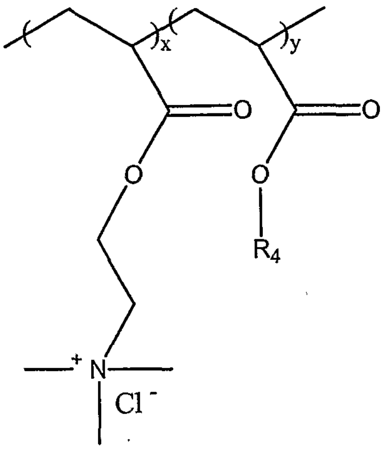
wherein x = 1 to about 15 mole percent; y = about 60 to about 99 mole percent; and z = 0 to about 30 mole percent; Q is selected from C_1-C_4 alkyl ammonium, quaternary C_1-C_4 alkyl ammonium and benzyl ammonium; Z is selected from –O-, -COO-, -OOC-, -CONH-,.and –NHCO-; R_1, R_2, R_3 are independently selected from hydrogen and methyl; R_4 is C_1-C_4 alkyl; R_5 is selected from hydrogen, methyl, ethyl, butyl, ethylhexyl, decyl, dodecyl, hydroxyethyl, hydroxypropyl, polyoxyethylene, and polyoxypropylene.

35. The fibrous substrate of Claim 34, wherein said composition is the polymerization product of a cationic acrylate or methacrylate and one or more alkyl acrylates or methacrylates having the structure:



wherein x = 1 to about 15 mole percent; y = about 60 to about 99 mole percent; and z = 0 to about 30 mole percent; R_4 is C_1-C_4 alkyl; R_5 is selected from hydrogen, methyl, ethyl, butyl, ethylhexyl, decyl, dodecyl, hydroxyethyl, hydroxypropyl, polyoxyethylene, and polyoxypropylene.

36. The fibrous substrate of Claim 34, wherein said composition has the structure:



wherein x = 1 to about 15 mole percent; y = about 85 to about 99 mole percent and R_4 is C_1-C_4 alkyl.

37. The fibrous substrate of Claim 36, wherein x = about 3 to about 6 mole percent, y = about 94 to about 97 mole percent and R_4 is methyl.

38. A water-dispersible article comprising the fibrous substrate of Claim 34.

39. A water-dispersible article comprising the fibrous substrate of Claim 35.

40. A water-dispersible article comprising the fibrous substrate of Claim 36.

41. A water-dispersible article comprising the fibrous substrate of Claim 37.

42. A wet wipe comprising:

a fibrous material;

a binder composition for binding said fibrous material into an integral web, said binder composition comprising the polymerization product of a vinyl-functional cationic monomer and one or more hydrophobic vinyl monomer with alkyl side chains of 1 to 4 carbon atoms; and

said fibrous material being wetted by a wetting solution containing a sufficient amount of an insolubilizing agent such that said binder composition is insoluble in said wetting solution.

43. The wet wipe of Claim 42, wherein the vinyl-functional cationic monomer is selected from [2-(acryloxy)ethyl] dimethyl ammonium chloride, [2-(methacryloxy)ethyl] dimethyl ammonium chloride, [2-(acryloxy)ethyl] trimethyl ammonium chloride, [2-(methacryloxy)ethyl] trimethyl ammonium chloride, (3-acrylamidopropyl) trimethyl ammonium chloride, N,N-diallyldimethyl ammonium chloride, [2-(acryloxy)ethyl] dimethylbenzyl ammonium chloride, and [2-(methacryloxy)ethyl] dimethylbenzyl ammonium chloride.

44. The wet wipe of Claim 42, wherein the vinyl-functional cationic monomer is selected from precursor monomers selected from vinylpyridine, dimethylaminoethyl acrylate and dimethylaminoethyl methacrylate followed by quaternization of the polymer.

45. The wet wipe of Claim 42, wherein the vinyl-functional cationic monomer is selected from [2-(acryloxy)ethyl] dimethyl ammonium chloride, [2-(acryloxy)ethyl] dimethyl ammonium bromide, [2-(acryloxy)ethyl] dimethyl ammonium iodide, and [2-(acryloxy)ethyl] dimethyl ammonium methyl sulfate.

46. The wet wipe of Claim 42, wherein the vinyl-functional cationic monomer is selected from [2-(methacryloxy)ethyl] dimethyl ammonium chloride, [2-(methacryloxy)ethyl] dimethyl ammonium bromide, [2-(methacryloxy)ethyl] dimethyl ammonium iodide, and [2-(methacryloxy)ethyl] dimethyl ammonium methyl sulfate.

47. The wet wipe of Claim 42, wherein the vinyl-functional cationic monomer is selected from [2-(acryloxy)ethyl] trimethyl ammonium chloride, [2-(acryloxy)ethyl] trimethyl ammonium bromide, [2-(acryloxy)ethyl] trimethyl ammonium iodide, and [2-(acryloxy)ethyl] trimethyl ammonium methyl sulfate.

48. The wet wipe of Claim 42, wherein the vinyl-functional cationic monomer is selected from [2-(methacryloxy)ethyl] trimethyl ammonium chloride, [2-(methacryloxy)ethyl] trimethyl ammonium bromide, [2-(methacryloxy)ethyl] trimethyl ammonium iodide, and [2-(methacryloxy)ethyl] trimethyl ammonium methyl sulfate.

49. The wet wipe of Claim 42, wherein the vinyl-functional cationic monomer is selected from (3-acrylamidopropyl) trimethyl ammonium chloride, (3-acrylamidopropyl) trimethyl ammonium bromide, (3-acrylamidopropyl) trimethyl ammonium iodide, and (3-acrylamidopropyl) trimethyl ammonium methyl sulfate.

50. The wet wipe of Claim 42, wherein the vinyl-functional cationic monomer is selected from N,N-diallyldimethyl ammonium chloride, N,N-diallyldimethyl ammonium bromide, N,N-diallyldimethyl ammonium iodide, and N,N-diallyldimethyl ammonium methyl sulfate.

51. The wet wipe of Claim 42, wherein the vinyl-functional cationic monomer is selected from [2-(acryloxy)ethyl] dimethylbenzyl ammonium chloride, [2-(acryloxy)ethyl] dimethylbenzyl ammonium bromide, [2-(acryloxy)ethyl] dimethylbenzyl ammonium iodide, and [2-(acryloxy)ethyl] dimethylbenzyl ammonium methyl sulfate.

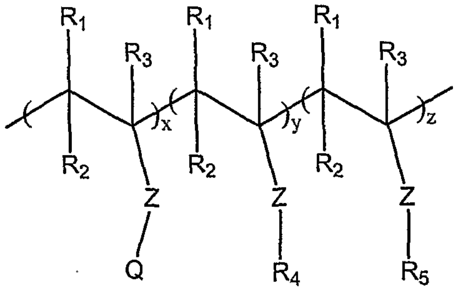
52. The wet wipe of Claim 42, wherein the vinyl-functional cationic monomer is selected from [2-(methacryloxy)ethyl] dimethylbenzyl ammonium chloride, [2-(methacryloxy)ethyl] dimethylbenzyl ammonium bromide, [2-(methacryloxy)ethyl] dimethylbenzyl ammonium iodide, and [2-(methacryloxy)ethyl] dimethylbenzyl ammonium methyl sulfate.

53. The wet wipe of Claim 42, wherein the hydrophobic vinyl monomer is selected from branched or linear alkyl vinyl ethers, vinyl esters, acrylamides, and acrylates.

54. A wet wipe comprising:

a fibrous material;

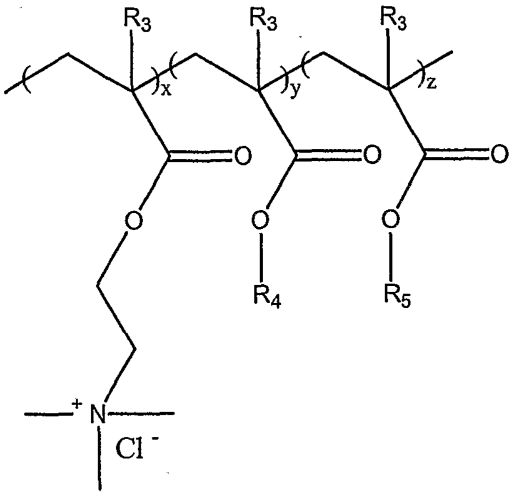
a binder composition for binding said fibrous material into an integral web, said binder composition comprising a composition having the structure:



wherein x = 1 to about 15 mole percent; y = about 60 to about 99 mole percent; and z = 0 to about 30 mole percent; Q is selected from C_1-C_4 alkyl ammonium, quaternary C_1-C_4 alkyl ammonium and benzyl ammonium; Z is selected from –O-, -COO-, -OOC-, -CONH-, and –NHCO-; R_1, R_2, R_3 are independently selected from hydrogen and methyl; R_4 is C_1-C_4 alkyl; R_5 is selected from hydrogen, methyl, ethyl, butyl, ethylhexyl, decyl, dodecyl, hydroxyethyl, hydroxypropyl, polyoxyethylene, and polyoxypropylene; and

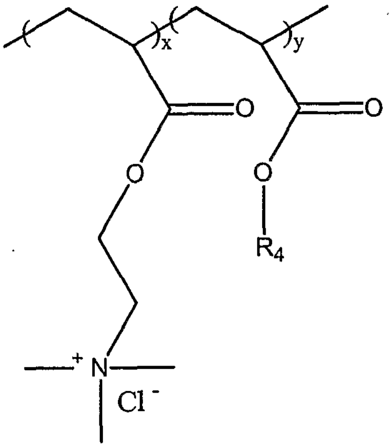
said fibrous material being wetted by a wetting solution containing a sufficient amount of an insolubilizing agent such that said binder composition is insoluble in said wetting solution.

55. The wet wipe of Claim 54, wherein said composition is the polymerization product of a cationic acrylate or methacrylate and one or more alkyl acrylates or methacrylates having the structure:



wherein x = 1 to about 15 mole percent; y = about 60 to about 99 mole percent; and z = 0 to about 30 mole percent; R_4 is C_1-C_4 alkyl; R_5 is selected from hydrogen, methyl, ethyl, butyl, ethylhexyl, decyl, dodecyl, hydroxyethyl, hydroxypropyl, polyoxyethylene, and polyoxypropylene.

56. The wet wipe of Claim 54, wherein said composition has the structure:



wherein x = 1 to about 15 mole percent; y = about 85 to about 99 mole percent and R_4 is C_1-C_4 alkyl.

57. The wet wipe of Claim 56, wherein x = about 3 to about 6 mole percent, y = about 94 to about 97 mole percent and R_4 is methyl.

INTERNATIONAL SEARCH REPORT

I[illegible]ational Application No
PCT/US 03/16512

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L33/14 C08L33/06 C08F220/34 D21H19/20 D04H1/64
C11D17/04 B05D7/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09D C08L C08F D21H B05D D04H C11D B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 02 077048 A (KIMBERLY CLARK CO) 3 October 2002 (2002-10-03) page 47; example 1; table 5	1-4,6-8, 13
X	page 52; example 2; table 11 claims 1-9,11,13,15	14
X	claims 10,12,14,16	17-19
X	claims 17,19	21-23, 25,27, 32,34,35
X	claims 21-24	33,38,39
X	claims 25,27,29,31 page 4, line 5 -page 10, line 34 --- -/--	42-44, 46,48, 53-55

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search 12 September 2003	Date of mailing of the international search report 22/09/2003
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Lindner, T

INTERNATIONAL SEARCH REPORT

I[illegible]ational Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 017, no. 135 (C-1037), 19 March 1993 (1993-03-19) & JP 04 309510 A (SUMITOMO CHEM CO LTD), 2 November 1992 (1992-11-02) page 5, paragraphs 13-15; example 4; table 1 ---	1-9, 11-15
X	EP 0 634 284 A (CANON KK ;DYNIC CORP (JP)) 18 January 1995 (1995-01-18) page 8, line 5 ---	1-3,5
X	EP 0 678 397 A (DAINIPPON PRINTING CO LTD) 25 October 1995 (1995-10-25) page 4, line 1-31 example 1 ---	2-4,6,13
X	EP 0 256 144 A (NAT STARCH CHEM CORP) 24 February 1988 (1988-02-24) page 7, line 17-29 page 7, line 45-47	2,13
X	page 8, line 43-51; example II; table II	1,4
X	page 10, line 15-31; example III; table IV ---	5,9
X	US 2001/055619 A1 (WEISBROD WOLFGANG ET AL) 27 December 2001 (2001-12-27) page 2, paragraphs 20,21 page 3, paragraphs 40,41 ---	1-3,8, 13,14
X	US 4 737 357 A (WEISBROD WOLFGANG ET AL) 12 April 1988 (1988-04-12) column 2, line 1 -column 3, line 48; examples 1,3,9-13 ---	1-3,7-9, 12-14
X	US 5 997 952 A (HARRIS JOHN K ET AL) 7 December 1999 (1999-12-07) column 11, line 66 -column 12, line 1; example 9; table 5 ---	1-3,8,14
A	US 4 133 684 A (TARUMI NORIYOSHI ET AL) 9 January 1979 (1979-01-09) * exemplary polymers A-1), A-3) and A-8) * ---	2,4,23, 44
A	US 5 954 921 A (DAHMEN KURT ET AL) 21 September 1999 (1999-09-21) column 1, line 66 -column 3, line 5 column 3, line 60-67 column 4, line 21-25; claim 9 ---	2-16, 21-32, 34-37
A	GB 1 549 032 A (SCHOELLER F) 1 August 1979 (1979-08-01) page 1, line 21-32 page 5, line 4-25 -----	1-4, 9-11, 14-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

I[illegible]national Application No
PCT/US 03/16512

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 02077048 A	03-10-2002	US 2003032352 A1	13-02-2003
		WO 02077048 A2	03-10-2002
JP 04309510 A	02-11-1992	JP 3341084 B2	05-11-2002
EP 0634284 A	18-01-1995	JP 3302792 B2	15-07-2002
		JP 7017129 A	20-01-1995
		DE 69403566 D1	10-07-1997
		DE 69403566 T2	22-01-1998
		EP 0634284 A1	18-01-1995
		ES 2105432 T3	16-10-1997
		US 5518821 A	21-05-1996
EP 0678397 A	25-10-1995	JP 3309172 B2	29-07-2002
		JP 7290845 A	07-11-1995
		DE 69510486 D1	05-08-1999
		DE 69510486 T2	23-03-2000
		EP 0678397 A1	25-10-1995
		US 5710096 A	20-01-1998
EP 0256144 A	24-02-1988	US 4710526 A	01-12-1987
		AU 571373 B2	14-04-1988
		AU 6005986 A	14-01-1988
		EP 0256144 A2	24-02-1988
		JP 61158851 A	18-07-1986
US 2001055619 A1	27-12-2001	DE 19809719 A1	09-09-1999
		BR 9901068 A	28-03-2000
		EP 0955041 A2	10-11-1999
		JP 11315017 A	16-11-1999
US 4737357 A	12-04-1988	DE 3438291 A1	24-04-1986
		AT 56143 T	15-09-1990
		CS 8507320 A2	15-07-1988
		DD 237611 A5	23-07-1986
		DE 3579558 D1	11-10-1990
		EP 0181515 A2	21-05-1986
		HU 38535 A2	30-06-1986
		JP 2030986 C	19-03-1996
		JP 7064756 B	12-07-1995
		JP 61100527 A	19-05-1986
US 5997952 A	07-12-1999	AT 243567 T	15-07-2003
		AU 7685398 A	11-12-1998
		DE 69815843 D1	31-07-2003
		EP 0983126 A1	08-03-2000
		JP 2002502449 T	22-01-2002
		TW 396197 B	01-07-2000
		WO 9852698 A1	26-11-1998
		US 6251485 B1	26-06-2001
US 4133684 A	09-01-1979	JP 1440142 C	30-05-1988
		JP 52113735 A	24-09-1977
		JP 62037390 B	12-08-1987
		JP 1210741 C	12-06-1984
		JP 52121325 A	12-10-1977
		JP 58045708 B	12-10-1983
		DE 2712579 A1	06-10-1977

INTERNATIONAL SEARCH REPORT

Information on patent family members

I[illegible]national Application No
PCT/US 03/16512

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5954921 A	21-09-1999	DE 4430069 A1	29-02-1996
		AT 164599 T	15-04-1998
		CA 2194602 A1	29-02-1996
		DE 59501788 D1	07-05-1998
		WO 9606119 A1	29-02-1996
		EP 0777692 A1	11-06-1997
		FI 970770 A	24-02-1997
		NO 970833 A	24-02-1997
GB 1549032 A	01-08-1979	DE 2528769 A1	30-12-1976
		BE 843485 A1	18-10-1976
		FR 2317686 A1	04-02-1977
		JP 52024529 A	24-02-1977