A hydrocolloid polymer and sorbent article containing same are disclosed. The polymer is prepared from a reaction mixture that consists essentially of (a) about 80 to about 100 mole percent water-soluble alpha, beta-monoethylenically unsaturated monocarboxyly monomer containing a chain of three carbon atoms, (b) zero to about 20 mole percent water-soluble copolymerizable monoethylenically unsaturated monomer, (c) zero to about 3 percent of a copolymerizable polyethylenically unsaturated cross-linking agent, and (d) about 10 to about 25 percent by weight glycerol based upon the ethylenically unsaturated species present. The sorbent article comprises a water-insoluble fibrous web matrix having the hydrocolloid polymer coated thereon. The polymer and polymer-coated web exhibit improved water sorption and flexibility.
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RELATIVELY SOFT PLIABLE WATER-SWELLABLE POLYMER

Description

Technical Field

The present invention relates to highly water absorbent polymers suitable for use in sorbent products, such as incontinent pads, disposable diapers, sanitary napkins, tampons and the like. More particularly the invention relates to relatively soft, pliable hydrocolloid polymers, sorbent products containing such polymers and a method of producing such polymers.

Background Art

A variety of hydrophilic polymers that are useful in the manufacture of water sorbent (absorbent and/or adsorbent) particles, films and fibers are known in the art. Such polymers can be incorporated within various disposable sorbent products; i.e., incontinent pads, disposable diapers, sanitary napkins, tampons, adult incontinent systems, medical-surgical supplies and the like to enhance the absorbency of the product.

Generally, in each of these products, a fibrous batt or web is included to retain exuded liquids. However, such fibrous batts, although somewhat efficient, do not themselves hold sufficient liquid and leak, thereby causing a problem to the user. Hydrocolloids, sometimes referred to as hydrogels or superabsorbents, have been introduced into fibrous batt structures and used in the products mentioned above to increase their absorptive efficiency.

Hydrocolloid polymers are comprised of polymers or copolymers formed of various monomers. Typically, such polymers must be extruded or otherwise formed into film, fiber or particulate form. A number of such polymeric materials exhibit a relatively high \( T_g \) (glass transition temperature), making products containing such a polymer hard, brittle and stiff. Such
hard polymer films or particles can be uncomfortable to wear and actually can puncture the skin, thereby detracting from the sorbent product containing the same.

Polymerized acrylate/acrylic acid monomers are known in a variety of multi-component polymer/copolymer superabsorbents. In some compositions, the acrylic acid-containing polymer is grafted onto a hydrophilic substrate such as cellulose or a cellulose derivative, whereas in other compositions the acrylic acid-containing polymer is a copolymer free of such grafts. U.S. Patents No. 4,105,003, No. 4,134,863 and No. 4,340,057 describe exemplary graft homo- and copolymers, whereas U.S. Patents No. 4,167,464 and No. 4,178,221 describe water-absorbing acrylic acid-containing copolymers.

In addition, PCT/US 80/01567 (International Publication No. WO 81/01850) describes a cross-linked acrylic acid/acrylate polymer that contains 20-99.9 weight percent acrylic acid, 50-100 percent of whose carboxyl groups are neutralized prior to polymerization, and 0.1-80 weight percent of a polyfunctional cross-linking agent. Useful cross-linking agents are said to contain two or more ethylenically unsaturated groups that can be copolymerized by UV light with acrylic acid. Those monomers are photopolymerized as dispersions in 0.01-5 percent of an anionic, amphoteric or nonionic surface active agent.

Additional monomers that are typically present at less than 5 weight percent but as high as 15 weight percent can also be present prior to polymerization. Those monomers are said to be alpha, beta-monoethylenically unsaturated nitriles or amides.

The disclosed polymers are said to swell in water, blood and urine, and are said to be useful in diapers, bandages and the like. The polymers are also
said to be useful as flocculants in water treatment, in ore benefications and flotation, and the like.

Glycolic components are also known in various multi-component polymers, and are typically incorporated in homopolymer and copolymer systems to provide specific characteristics. For example, U.S. Patent No. 4,167,464 describes polymers that contain (a) 50-90 weight percent acrylic acid of which 70-100 percent of the carboxyl groups are neutralized prior to polymerization; (b) 2-25 weight percent acrylic or methacrylic ester in which the alcohol portion of the ester contains a C\textsubscript{10}-C\textsubscript{30} alkyl group; and (c) 5-30 weight percent acrylic ester in which the alcohol portion of the ester contains a lower C\textsubscript{1}-C\textsubscript{8} alkyl group, the latter ester being capable of replacement by 0-50 weight percent of acrylic or methacrylic nitrile or amide. Less than 5 weight percent of alpha, beta-monoethylenically unsaturated nitriles can also be included. Those monomers are polymerized by photoinitiation as dispersions in anionic, amphoteric, nonionic or mixed surfactants.

U.S. Patent No. 4,167,464 also discloses that glycols can be utilized to improve wicking of the polymerized compositions; i.e., the rate of liquid absorption. Those glycols can be present at 1 to 10 weight percent of the monomer mixture. Of those glycols, no more than about 50 weight percent can be polyols such as trimethylol propane or glycerol.

Allyl group-containing cross-linking agents are also disclosed as providing greater gel strength and an improved ability for the copolymers of U.S. Patent No. 4,167,464 to swell under a confining pressure. Such cross-linking agents are said to be useful at 0-15, and preferably 1-10 weight percent.

Polymers of the above patent are said to be useful as a sorbent in disposable diapers as well as in
the form of a film between the outer impermeable web of a disposable diaper and the inner a sorbent layer. The copolymers are further said to be useful as floculants in water treatment, ore beneficiation and flotation and the like.

U.S. Patent No. 4,178,221 discloses water-soluble acrylic polymers prepared by a sequential photopolymerization process. Exemplary acrylic polymers are said therein to include polymers prepared from acrylamide and alkali metal acrylates that can be present at about 20 to about 60 percent by weight of an aqueous monomer solution. In addition to the monomers and a photoinitiator, the prepolymerization mixture may also contain a free-radical transfer agent or polymerization modifier such as isopropanol or glycerol present at about 0.1 to 6 percent relative to the monomers.

U.S. Patent No. 3,872,063 describes a method of polymerizing acrylic monomers such as acrylic acid and acrylamide by use of a catalyst system based upon a bisulfite and a polyhydric alcohol such as sorbitol, manitol, glycerol or a long chain fatty acid ester of such a polyl. The catalyst is said to be present at from 0.001 to 5 percent, based on the weight of monomers present.

Another group of disclosures describes the post-polymerization use of a polyhydric alcohol along with a water-swellable polymer. For example, U.S. Patent No. 2,798,053 describes the preparation of polycarboxylic acid polymers that are substantially insoluble in water and organic solvents. Those polymers, cross-linked with a polyalkenyl polyether of a polyl containing at least 4 carbon atoms and three hydroxyl groups present at 0.10 to 1.0 weight percent, are said to have mucilaginous uses after neutralization.
As such, a disclosed final mucilage composition could contain 1.5 parts of a 75 percent neutralized polymer, 2 parts sodium sulfate or sulfonate, 50 parts of 40 percent aqueous glycerol, 25 parts of calcium dihydrogen phosphate dihydrate and 25 parts of sodium phosphate.

U.S. Patent No. 4,066,583 describes polymers polymerized from a monomer mixture that contained an unsaturated carboxylic acid, a C_{10}-C_{30} alkyl acrylate, and at least one of a C_{1}-C_{5} alkyl acrylate or acrylic or methacrylic nitrile or amide, and an optional, small amount of cross-linker. The polymer is neutralized after preparation in Freon 113. An aliphatic glycol containing 2 to 10 carbon atoms is used as a post polymerization plasticizer in an amount of greater than 30 parts per 100 parts of copolymer up to 125 parts per 100 parts copolymer. Sorbitol is said not to be useful, whereas other polyols with greater than two hydroxyls are said to be useful only in an admixture with a diol, and then only in an amount up to about 50 weight percent of a total mixture of glycol and polyol. The glycol is said to provide flexible film strips, fibers and the like to the polymer compositions which have a rapid and high ultimate absorption and retention of water and ionic solutions.

U.S. Patent No. 4,413,995 describes a sorbent panel that consists of a substrate coated on at least one surface with a reactive composition containing from 10 to 40 parts by weight liquid polyhydroxy organic compound such as glycerol, propylene glycol or ethylene glycol and 90 to 60 parts of a particulate water-insoluble, water-swellable absorbent polymer having a gel capacity of at least 10. The two components of the reactive composition are said to react and adhere to the substrate to form the sorbent panel.
Brief Summary of the Invention

The present invention contemplates a water-swellable, but substantially water-insoluble hydrocolloid polymer exhibiting a relatively low glass transition temperature ($t_g$) a sorbent article comprising a polymer-coated web that exhibits improved pliability and liquid sorption.

A hydrocolloid polymer of the invention is prepared by polymerization preferably using an electron beam, of an aqueous reaction mixture that consists essentially of (a) about 80 to about 100 mole percent water-soluble alpha, beta-monoethylenically unsaturated monocarboxy monomer containing a chain of three carbon atoms (preferably acrylic acid), (b) zero to about 20 mole percent water-soluble copolymerizable monoethylenically unsaturated monomer, (c) zero to about 3 mole percent of a copolymerizable polyethylenically unsaturated cross-linking agent, and (d) about 10 to about 25 weight percent glycerol based upon the total weight of ethylenically unsaturated species present. The hydrocolloid polymer when substantially free of water, but containing the above amount of glycerol exhibits a $t_g$ of about 150 to about 250 degrees C.

In preferred practice, about 50 to about 95 mole percent of the acid groups are neutralized with a monovalent cation. The polymer is preferably prepared from an aqueous reaction mixture that contains about 45 to about 70 weight percent copolymerizable ethylenically unsaturated species plus glycerol, with the remainder being distilled or deionized water.

A sorbent article of the invention comprises a water-insoluble fibrous web having a coating of the before-described hydrocolloid polymer thereon present at a weight add-on of 200 to about 1500 percent of the
weight of the matrix. The fibrous web matrix has a dry bulk recovery of at least about 30 percent, an initial dry bulk of at least 20 cubic centimeters per gram (cc/g) and a weight of less than about 2 ounces per square yard (oz/yd²).

The hydrocolloid polymer can coat the web matrix by being added thereto in polymerized, dry or damp form. Preferably, the polymer is coated onto the fibrous web matrix by being polymerized in situ.

The polymer-coated web can be used alone, but is preferably used in conjunction with one or more webs in the ultimately-produced sorbent article. For a disposable diaper, the additional webs can include one or more wicking layers disposed against the polymer-coated web, a water-impermeable outer layer on an outside surface and a water-permeable layer on the other outside surface. The polymer-coated web and one or more wicking layers are preferably compressed form for use in diapers. When so compressed, the relatively low $t_g$ value of the polymer and relatively greater pliancy of a polymer-coated web made therefrom can provide increased comfort to the wearer.

**Brief Description of the Drawing**

In the drawing forming a portion of this disclosure, the sole figure is a graph that illustrates the dependence of glass transition temperature ($t_g$) on the water content of two hydrocolloid polymers prepared from acrylic acid/potassium hydroxide. Data for one polymer, ARASORB 10 SH, available from Grain Processing Co. are shown in open circles. Data for a polymer of the present invention polymerized in the presence of 12.4 weight percent glycerol are shown as open squares. The ordinate is in $t_g$ temperature in degrees C, whereas
the abscissa is in the measured weight percentage of water measured in appropriate polymer samples.

The present invention provides several benefits and advantages.

One benefit is that relatively soft, pliable hydrocolloids can be prepared.

Another benefit is that such relatively soft hydrocolloids can be prepared that exhibit improved sorbencies of both deionized or distilled water and one percent aqueous sodium chloride solution as compared to similar polymers that are not prepared as is a polymer of the present invention.

An advantage of the invention is that the relatively soft hydrocolloid polymers can be prepared in situ on a fibrous matrix to form a sorbent web or batt.

Still another advantage of the invention is that the relatively soft hydrocolloid polymers in a single step polymerization process.

Still further benefits and advantages will be apparent to those skilled in the art from the detailed description that follows.

**Detailed Description of the Invention**

The present invention contemplates a relatively soft, pliable, substantially water-insoluble hydrocolloid polymer. The hydrocolloid polymer contains a relatively narrow range of glycerin or glycerol, which terms are used interchangeably herein, a portion of which may be reacted into the polymer itself and another, larger portion of which is chemically free but substantially homogeneously dispersed within the hydrocolloid when in dry or semi-dry (e.g. containing up to about 15 percent by weight water) form.

The hydrocolloid polymer is polymerized from an aqueous solution containing monomers and glycerol,
and it is unknown what percentage, if any, of the originally present glycerol is chemically incorporated into the hydrocolloid. As a result of this lack of knowledge, a hydrocolloid of this invention is described as a product of its method of preparation and one or more physical properties that the hydrocolloid exhibits.

In many instances, the characterization of a polymer on the basis of the monomers used in its preparation can be inaccurate because of the presence of relatively large amounts of unreacted monomers. Here, however, it is believed that a characterization of the polymerized hydrocolloid based upon the monomer mixture and glycerol used for its preparation is accurate because substantially all of the monomeric materials originally present are converted into the polymer; i.e., these hydrocolloids contain relatively low amounts of residual monomers.

A hydrocolloid polymer of this invention is prepared by polymerization, preferably by electron beam irradiation, of an aqueous reaction mixture. That aqueous reaction mixture consists essentially of (a) about 80 to about 100 mole percent of a partially neutralized water-soluble alpha,beta-monoethylenically unsaturated monocarboxy monomer containing a chain of three carbon atoms; (b) zero to about 20 mole percent water-soluble copolymerizable monoethylenically unsaturated monomer, (c) zero to about 3 mole percent of a copolymerizable water-soluble polyethylenically unsaturated cross-linking agent, and (d) about 10 to about 25 percent by weight, and more preferably about 10 to about 15 weight percent, glycerol based upon the total weight of ethylenically unsaturated monomer and cross-linking agent.

Acid group-containing monomers can be utilized and polymerized in free acid form. It is preferred,
however, to use and polymerize partially neutralized forms of acid group-containing monomers. In view of that preference, most of the following discussion will concern partially neutralized acid group-containing monomers.

The monoethylenically unsaturated monomers preferably contain about 5 to about 50 mole percent free acid groups and about 50 to about 95 mole percent acid groups neutralized with a monovalent, water-soluble cation. The monomers, cross-linking agent (when present) and glycerol constitute about 45 to about 70 weight percent, and more preferably about 55 to about 65 weight percent, of the aqueous reaction mixture. A resulting preferred partially neutralized hydrocolloid when substantially free of water but containing the originally present amount of glycerol (free and polymerized) exhibits a glass transition temperature, $T_g$, of about 250 degrees C or less to about 150 degrees C.

The principal monomeric constituent of a hydrocolloid of this invention is a water-soluble alpha,beta-monoethylenically unsaturated monocarboxy compound containing a three carbon atom chain. The phrase "monocarboxy monomer" is utilized herein to mean the above monomer that contains a single carboxy functionality. That single carboxy functionality is itself preferably a mixture of the free acid and monovalent cation salt forms of the free acid, as is discussed in further detail hereinafter. The phrase "monocarboxy monomer" is thus used herein as a short-hand phrase for the partially neutralized mixture of free acid and salt forms of the water-soluble alpha,beta-monoethylenically unsaturated monocarboxy monomer containing a chain of three carbon atoms.
The monocarboxy monomer and all of the other monomeric species discussed herein are referred to as being "water-soluble". That phrase is utilized herein to mean that whatever monomeric species is discussed is soluble in the aqueous mixture of monomeric species used for polymerization at the concentration utilized herein. To that end, the monocarboxy monomer and other monomers form clear, as compared to translucent or opaque, solutions in the aqueous reaction mixture at the concentration of use. Put differently, a water-soluble monomer forms a single phase when admixed with any other monomers and cross-linker mixture in water at the concentration at which that monomer or cross-linker is utilized herein. Similarly, a salt of a monocarboxy monomer with a monovalent cation is also water-soluble.

Exemplary monocarboxy monomers useful herein contain a chain of three carbon atoms that includes the monoethylenic unsaturation, and are exemplified by acrylic acid, methacrylic acid and cyanoacrylic acid. Mixtures of these monocarboxy monomers can also be used. Acrylic acid is particularly preferred.

The monocarboxy monomer constitutes about 80 to about 100 mole percent of the prepolymerized aqueous monomeric reaction mixture and polymerized monomers. More preferably, that monomer is present at about 95 to about 99.97 mole percent, and still more preferably, only the monocarboxy monomer and cross-linking agent are present in the monomer mixture and in the polymerized hydrocolloid. Most preferably, the monocarboxy monomer is the only polymerizable species present.

As noted earlier, the monocarboxy monomer is itself preferably a mixture of free acid and monovalent cation salt forms. The monovalent cation salt is formed from an alkali metal or monoamine. Alkali metal salts are preferred, with sodium and potassium salts being
particularly preferred. Ammonium salts prepared from ammonia and monoamines are also useful but such salts are preferably salts of sterically hindered, non-nucleophilic primary or secondary amines or, more preferably, tertiary amines such as tri-C\textsubscript{1}-C\textsubscript{4} alkylamines such as trimethylamine, triethylamine and tributylamine, or triethanolamine.

Polyvalent cation salts of the monocarboxy monomers are not utilized and are thus substantially absent from the monomer mixture and polymerized hydrocolloid. Polyvalent metal ions such as calcium, magnesium, aluminum and iron and polyvalent ammonium salts such as N,N,N',N'-tetramethylethylenediamine can cross-link the monomer mixture and resulting polymerized hydrocolloid.

The free acid form of the monocarboxy monomer typically constitutes about 5 to about 50 mole percent of the monocarboxy monomer mixture, more preferably constitutes about 10 to about 40 mole percent, and most preferably constitutes about 25 to about 40 mole percent. The monovalent cation salt therefore constitutes about 95 to about 50 mole percent, more preferably about 90 to about 60 mole percent of the monocarboxy monomer, and most preferably about 75 to about 60 mole percent, of the monocarboxy monomer. The water-soluble alpha,beta-monoethylenically unsaturated monocarboxy monomer is thus partially neutralized, with about 50 to about 95 mole percent, more preferably about 60 to about 90 mole percent, and most preferably about 60 to about 75 mole percent, of the acid groups neutralized with a monovalent cation.

Use of a partially neutralized water-soluble alpha,beta-monoethylenically unsaturated monocarboxy monomer saves the subsequent step of neutralization after polymerization, which step can be somewhat
difficult to carry out due to the gelatinous nature of aqueous compositions of the polymerized material. In addition, polymerization of a partially neutralized monocarboxy monomer whose degree of neutralization is substantially that desired in a sorbent product that is ultimately made facilitates the preparation of hydrocolloid polymer-coated webs for use in such products inasmuch as such webs are typically somewhat more difficult to manipulate than is the polymerized hydrocolloid itself.

One or more additional copolymerizable, water-soluble monoethylenically unsaturated monomers can also be present in the monomer mixture and polymerized hydrocolloid. Such monomers are familiar to those skilled in the hydrocolloid art and include methacrylamide, acrylamide, N-mono- and N,N-di-C₁₋₄ alkyl acrylamides and methacrylamides such as N-methyl acrylamide, and N,N-dipropyl methacrylamide, N- and N,N-(2-hydroxy)ethyl acrylamides and methacrylamides such as N-(2-hydroxy)ethyl acrylamide and N,N-di-(2-hydroxy)ethyl methacrylamide, methyl acrylate and methacrylate, (2-hydroxy)ethyl acrylate and methacrylate, acrylonitrile and the like.

The additional copolymerizable, water-soluble monoethylenically unsaturated monomers can also include acid group-containing monomers and their water-soluble monovalent cation salts. Included among these monomers are crotonic acid, itaconic acid, maleic acid, maleic anhydride (which readily hydrolyzes to the acid), C₁₋₆ alkyloxy mono- and di(2-hydroxy)ethyl mono-amides of maleic acid, sulfonic acid compounds such as styrenesulfonic acid, 2-vinyl-4-ethylbenzene-sulfonic acid, 2-sulfoethyl-methacrylic acid, 2-acrylamido-2-methylpropane-sulfonic acid, and vinylsulfonic acid, and
phosphate-containing monomers such as methacryloxy ethyl phosphate.

A copolymerizable monoethylenically unsaturated monomer or a mixture thereof can be present at zero to about 20 mole percent of the reaction mixture and polymerized hydrocolloid. More preferably, such monomer or monomers is present at about 5 to about 10 mole percent. Most preferably, the copolymerizable monoethylenically unsaturated monomer is absent.

When present, the water-soluble copolymerizable monoethylenically unsaturated monomer is preferably selected from the group consisting of acrylamide, methacrylamide, N-(2-hydroxy)ethyl acrylamide, N-(2-hydroxy)ethyl methacrylamide, 2-sulfoethylmethacrylic acid, and 2-acrylamido-2-methylpropanesulfonic acid.

Inasmuch as an aqueous solution of the above-mentioned copolymerizable acid group-containing monoethylenically unsaturated monomer and previously discussed monocarboxy monomer equilibrates rapidly to distribute the monovalent cations among the acid groups that are in accordance with the $pK_a$ values of the various acid groups and the pH value of the solution, admixture of the free acid form of one monomer and a salt form of that or another monomer provides a complex admixture in which it is not possible to ascertain which cation or proton originated from any given monomer. Consequently, the before-mentioned degree of partial acid group neutralization is to be understood to be the degree of neutralization of all of the acid groups present in the reaction mixture and resulting, polymerized hydrocolloid when acid group-containing monomers in addition to the monocarboxy monomer are present in the monomer mixture or in polymerized form.

Since the monocarboxy monomer and the additional
copolymerizable monomers that can be present are 
monoothelylenically unsaturated, the degree of 
neutralization of all of the acid group-containing 
monomers can be referred to in terms the neutralization 
of monoethylenically unsaturated monomers in their 
polymerized or unpolymerized forms.

The before-described monocarboxy monomer and 
copolymerizable water-soluble monoethylenically 
unsaturated monomer that can also be present can be 
grouped together for purposes of discussion. When so 
grouped, those monomers are collectively referred to as 
"monoethylenically unsaturated monomers."

A third element of a reaction mixture and 
resulting polymer of this invention that can be present 
is a copolymerizable, water-soluble cross-linking agent 
or cross-linker. A wide variety of cross-linker 
molecules is useful herein.

Exemplary of such cross-linkers are compounds 
that contain two or three moieties that contain acrylic-
type unsaturation as well as those that contain two 
moieties of allylic-type unsaturation. Such cross-
linking agents can be referred to as bis- or tris-
acryloyl or bis-methacryloyl and bis-allyl compounds, 
respectively.

A first, bis- or tris-acryloyl or bis- or 
tris-methacryloyl, cross-linker has a structure that 
corresponds to the formula:

\[
\begin{array}{c}
\text{O} \quad \text{R} \\
\text{A}(-\text{C}-\text{C}=\text{CH}_2)_n
\end{array}
\]

wherein R is hydrogen or C₁-C₄ alkyl, n is 2 
or 3, and A is a divalent or trivalent radical that 
contains a chain of 3 to about 30 atoms free from
copolymerizable unsaturation that is terminated by oxygen or nitrogen atoms; i.e., A is bonded to each 
\[ \;
\begin{array}{c}
O \; R \\
\parallel \\
-C-C=CH_2
\end{array} \] (acyrloyl) group through an oxygen or nitrogen atom. The A radical is preferably divalent; i.e. n preferably is 2.

A second, bis-allyl cross-linker, has a structure that corresponds to the formula:

\[ \;
H_2C=CH-CH_2-B-CH_2-CH=CH_2
\]

wherein B is a divalent radical that is an allylimino radical or contains a chain of 4 to about 10 atoms free from copolymerizable unsaturation that is terminated by oxygen or nitrogen atoms.

Di- or tri-valent radicals A and divalent B radicals above, while generally being different in structure, share the properties of "containing a chain of 3 (or 4) to about 30 (or 10) atoms" being "free from copolymerizable unsaturation" and being "terminated by oxygen or nitrogen atoms." These phrases are utilized herein as follows.

The phrase "free from copolymerizable unsaturation" is used to mean that although some unsaturation can be present in either radical, that unsaturation does not take part in a polymerization reaction contemplated herein. Exemplary of such unsaturation is that found in a benzene ring.

The phrase "contains a chain of 3 (or 4) to about 30 (or 10) atoms" is meant to indicate a lower limit of chain length of 3 or 4 atoms in a straight or branched chain radical whose longest axis contains at least 3 or 4 atoms, respectively, and is the axis that joins the two acryloyl or allylic portions of the molecule, and which axis can be as long as 30 or 10
atoms, respectively. The phrase is also meant to encompass the presence of one or more rings whose axial length between the two acryloyl or allylic portions of the molecule cannot be defined in terms of whole numbers of atoms. The enumerated number of atoms in the phrase is still further intended to encompass the terminal oxygen or nitrogen atoms, that are discussed below.

The phrase "terminated by oxygen or nitrogen atoms" is meant to indicate that the two or three acryloyl portions of the first cross-linker are present as esters or amides, respectively, whereas the two allyl portions can be present as ethers (oxygen atom-terminated), or amides, or amines (nitrogen atom-terminated), respectively. Thus, where A or B is cyclic and may therefore not strictly speaking contain termini, such cyclic radicals are considered herein to have termini that are defined by the atoms that bond the A or B radicals to the acryloyl or allylic portions. The phrase is also meant to indicate that the terminal atoms of the divalent or trivalent radicals are the same atom, which can be either oxygen or nitrogen. Thus, the first cross-linker is, for example, a tris- or bis-acrylate, a tris- or bis-methacrylate, a tris- or bis-acrylamide or a tris- or bis-methacrylamide. The water-soluble allyl derivatives that constitute the second cross-linker are bis-compounds, except for triallyl amine as is discussed hereinafter.

Exemplary useful water-soluble first cross-linkers formed from a preferred divalent A radical include methylenebisacrylamide, methylenebis-methacrylamide, trimethylenebisacrylamide, a polyethylene glycol (PEG) diacrylate or methacrylate that contains an average of one to about 9 PEG units per molecule such as ethyleneglycol dimethacrylate, tetraethyleneglycol diacrylate [that can also be named
polyoxyethylene (4) diacrylate or PEG-4 diacrylate], and polyoxyethylene (9) diacrylate [that can also be named nonaethyleneglycol diacrylate or polyethyleneglycol (9) diacrylate], meta-xylylenyl bisacrylamide (the bisamide formed between two moles of acrylic acid and one mole of meta-xylylenediamine), 1,6-hexanediol diacrylate, 1,4-butanediol diacrylate, 1,3-butanediol diacrylate, and the like. Exemplary tris-acrylates and methacrylates include trimethylolpropane triacylate (TMPTA) and trimethacrylate, respectively, as well as pentaerythritol triacrylate or trimethacrylate.

Of the above first cross-linkers, methylenebisacrylamide (MBA) and PEG diacrylates containing an average of 1 to 9 PEG units per molecule are preferred, with MBA being particularly preferred.

Exemplary useful second cross-linkers include water-soluble di- or bisamides of an allylamine and dicarboxylic acids such as those formed from carbonic acid, oxalic acid, malonic acid, succinic acid, malic acid and tartaric acid, which can be named diallyl urea, diallyl oxalldiamide, diallyl malondiamide, diallyl succindiamide, diallyl maldiamide and diallyl tartardiamide. Exemplary diallyl diamines include N,N'-diallylpyperazine, N,N'-diallylethylene diamine and the like.

Also included in the second group are di- or bis-ethers of an allyl alcohol and a polyhydric alcohol (polyol) having a chain length of 2 to about 10 atoms. Exemplary diethers include the polyethylene glycol (PEG) derivatives that include an average of 1 to 3 PEG repeating units per molecule such as ethyleneglycol diallyl ether, diethyleneglycol diallyl ether and triethyleneglycol diallyl ether. Further diallyl ethers include those compounds formed from 1,3- butanediol, 1,2,3-trihydroxybutane, 2,3,4-trihydroxy butyric acid,
the aldo- and ketotetroses such as erythrose and erythulose, respectively, the aldo- and ketopentoses such as ribose and xyloketose, respectively, the aldo- and keto-hexoses such as glucose and fructose, respectively, as well as from a saccharide such as sucrose or maltose. (It is to be understood that although diallyl ethers are referred to as reaction products of allyl alcohol and a polyhydric alcohol, those ethers are most frequently prepared by a Williamson-type synthesis from an allyl halide and a strongly alkaline aqueous solution of polyhydric alcohol. It is to be further understood that mixtures of positional isomers are often obtained by such reactions. Additionally, mixtures are obtained that contain more or less than one mole of allyl group per molecule ether, but contain an average of about two moles of allyl groups per molecule of ether.) Particularly preferred second cross-linkers are diallyl tartardiamide (DATDA) and a diallyl PEG ether that contains an average of one to three PEG repeating units per molecule.

A further useful second cross-linker is triallylamine. It is well known that diallyl group-containing compounds wherein the allyl groups are separated by three atoms such as in diallylamine and diallyl ether form cyclic compounds when polymerized. As a consequence, such compounds do not contribute well to cross-linking, but rather tend to co- or homopolymerize. A particular example of this phenomenon is diallylamine, which when protonated during polymerization as would be the case here, forms six- and/or seven-membered ring, straight chain homopolymers. Triallylamine is useful herein because it can form cross-links in addition to cyclizing. It is noted that the minimum chain length of the before-mentioned bis- or
di-allyl second cross-linkers is at least three atoms as to avoid the cyclopolymerization route.

Each of the before-described cross-linkers can be used alone in an amount discussed hereinafter, or can be used mixed with another of the cross-linkers. In preferred practice, a cross-linker of the first type is mixed with a cross-linker of the second type, and the resulting mixture is utilized as the cross-linking agent. In such an embodiment, the two cross-linkers are preferably present at a mole ratio to each other of about 1:1.5 to about 1:15, more preferably at about 1:4 to about 1:10, and most preferably at a ratio of about 1:5 to about 1:7, of first cross-linker to second cross-linker.

A before-described cross-linking agent can be present at zero to about 3 mole percent of the total copolymerizable ethylenically unsaturated species present in the reaction mixture (monoethylenically unsaturated monomers plus cross-linking agent), and can therefore be absent as where the preferred electron beam radiation utilized to polymerize the monomers is used in addition to cross-link the hydrocolloid. More preferably, however, an externally-provided cross-linker as described hereinabove is not utilized, and is absent. When present, the cross-linker is present in an amount of up to about 3 mole percent, more preferably in an amount of about 1 to about 0.03 mole percent, and most preferably in an amount of about 0.1 to about 0.05 mole percent. Mixtures of one or more of the before-recited cross-linking agents can also be utilized.

In reviewing the before-discussed ethylenically unsaturated components (species) of the reaction mixture, it is seen that the water-soluble alpha,beta-monoethylenically unsaturated monocarboxy monomer containing a chain of three carbon atoms is
always present, and is most preferably acrylic acid. The reaction mixture can also be substantially free of the water-soluble copolymerizable monoethylenically unsaturated monomer, as well as being substantially free of that monomer and the water-soluble polyethylenically unsaturated cross-linking agent.

One further component that is always present is glycerin, also known as glycerol. Glycerol is present at about 10 to about 25, and more preferably at about 10 to about 15, weight percent of the total monoethylenically unsaturated monomers (the monocarboxy monomer and additional monomer, if present) and cross-linking agent if present; i.e., copolymerizable ethylenically unsaturated species present.

Other glycols or polyols such as ethyleneglycol or its polymers, propylene glycol, sorbitol and the like are substantially absent. Put differently, the reaction mixture and resulting hydrocolloid polymers are substantially free of glycols and polyols other than glycerol.

The reason that glycerol is a singularly useful material is not known. However, one or more characteristics of glycerol may set it apart from other glycols and polyols in this instance. Although not wishing to be bound by theory, some of these distinguishing features are discussed below in regard to other glycols and polyols that might, at first glance, seem similarly useful.

As noted earlier, a portion of the glycerol of the reaction mixture may be incorporated into the hydrocolloid polymer. The amount, if any, of that reacted portion relative to the amount of glycerol in the unpolymerized mixture is unknown, but is not thought to be more than about one-half of the glycerol originally present.
That reaction of glycerol and its possible incorporation into the polymer could be due to the activity of glycerol as a chain transfer agent or polymerization modifier as recited in U.S. Patent No. 4,178,221 that utilized about one-half or less of the lowest amount and herein, and also recites that isopropyl alcohol is useful for that purpose. Glycerol and isopropanol act as chain transfer agents through their respective hydrogen atoms bonded to the carbon atom bearing the secondary hydroxyl group in each compound.

Isopropanol is not useful herein if only because of its relatively low boiling point and relatively high vapor pressure relative to glycerol. Thus, little, if any, free isopropanol would remain after a hydrocolloid polymer is prepared and dried for an ultimate use in a sorbent product.

Glycols such as ethylene glycol and the polyethylene glycols or trimethylolpropane do not contain a similarly bonded hydrogen atom and do not function similarly as chain transfer agents. Propylene glycol does possess a similarly bonded hydrogen atom, and therefore may act as a chain transfer agent. However, propylene glycol boils at a temperature about 100 degrees below that of glycerin and has a vapor pressure at 25 degrees C that is about fifty times the vapor pressure of glycerin at 50 degrees C (0.133 vs. 0.0025). As a consequence, significant amounts of propylene glycol can be lost during the drying process.

Polyhydroxy compounds such as glucose, sucrose and sorbitol contain more than one hydrogen atom bonded to a secondary alcohol and may therefore also act as chain transfer agents. However, these compounds are all solids at room temperature and could therefore add to the hard, brittle characteristics of the dried
hydrocolloid that are sought to be avoided herein. In
addition, polyhydroxy compounds such as glucose, sucrose
and sorbitol and liquids such as polypropylene glycols
contain a plurality of potential chain transfer sites
per molecule that can thereby provide polymers having
molecular weights that are too low to be useful herein.

Still further, none of the before-mentioned
compounds has the water holding capacity of glycerin,
which capacity also aids in the performance of sorbent
products made from a hydrocolloid of this invention.
Thus, glycerol (glycerin) is alone in its use herein.

Glycerol is present in a reaction mixture and
polymerized hydrocolloid in an amount of about 10 to
about 25 weight percent of the total monomeric species
(monethylenically unsaturated monomers and
polyethylenically unsaturated cross-linker). More
preferably, glycerol is present at about 10 to about 15
weight percent.

Below about 10 weight percent, the desired $t_g$-
lowering effect is not noted appreciably. At a level of
about 12 weight and higher, increasing incompatibility
between the hydrocolloid and glycerol is noted in $t_g$
measurements by differential scanning calorimetry (DSC)
of water-free hydrocolloids, although hydrocolloid
polymers containing 25 weight percent glycerol are still
useful.

The presence of the glycerin in the reaction
mixture can permit glycerin to react through chain
transfer and become a part of the hydrocolloid, thereby
lowering the average molecular weight of the
hydrocolloid produced and incorporating alkylene
hydroxyl groups into the polymer backbone. That
presence also permits unreacted glycerin to be
substantially evenly distributed throughout the polymer
so that the resulting hydrocolloid is substantially homogeneous in its glycerin content.

Thus, a hydrocolloid of the present invention and its method of preparation are further distinguished from those teachings wherein glycerol is admixed after polymerization and is typically utilized in relatively larger quantities than are utilized herein. Such post-polymerization admixtures typically cannot achieve the homogeneity of dispersion in the polymer matrix as are obtained herein without substantial physical mixing and dissolution of the polymer as in the case of a mucilage prepared in U.S. Patent No. 2,798,053. A hydrocolloid of the present invention is substantially water-insoluble, as compared to a mucilage that is soluble.

The monoethylenically unsaturated monomer, polyethylenically unsaturated cross-linking agent (when present) and glycerin constitute a total of about 45 to about 70 weight percent of the aqueous reaction mixture, with the remaining about 35 to about 30 weight percent being substantially only distilled or deionized water. More preferably, those constituents are present at about 55 to about 65 weight percent of the total aqueous reaction mixture, with the remaining about 55 to about 65 weight percent being substantially only deionized or distilled water.

The aqueous reaction mixture has a pH value that is dictated by the degree of neutralization of the acid groups present. As noted earlier, the aqueous reaction mixture can contain a complex mixture of free acid and acid salt, although most are carboxylic acids and their salts. As a result, the aqueous reaction mixture behaves as a buffer over the range of acid group neutralization levels contemplated. The pH value of the reaction mixture is typically about 7 to about 9. It is noted that the pH value observed after polymerization
can be different from that of the reaction mixture if only because the $pK_a$ values of polymerized ethylenically unsaturated acids typically broaden and differ from those monomeric species that contain ethylenic unsaturation, and also because of proximity effects of the polymeric polyanionic material formed.

The reaction mixture is typically and preferably polymerized using standard electron beam polymerization techniques that are described in detail hereinafter. Polymerization is carried out in a manner such that substantially all of the mono- and polyethylenically unsaturated components of the reaction mixture are polymerized. Thus, conversion is substantially 100 mole percent. The quantity of residual monomer (measured after drying) is typically below about 500 parts per million (ppm) of polymer, and is usually in the range of about 100 to about 200 ppm.

A hydrocolloid polymer of the present invention is substantially water-insoluble, as noted previously. Most of the glycerol originally present in the reaction mixture can be extracted from the polymer. However, once polymerization is completed, most of the polymerized, previously unpolymerized ethylenically unsaturated components of the reaction mixture are not solubilizable in water and cannot be extracted with water regardless of the state of neutralization of any acid groups present.

In terms of a dried hydrocolloid of the invention, about 10 to about 40 weight percent can be extracted, which values include glycerol. More usually, about 20 to about 30 weight percent of the dry weight of such a hydrocolloid can be extracted using a method discussed hereinafter.
Once the polymerization is completed, the resulting hydrocolloid polymer is dried by any of a number of well known techniques.

That drying can be to what can be called "bone" dryness at which substantially no water is left in the hydrocolloid as determined by a Karl-Fisher titrator. More preferably, however, the hydrocolloid polymer is dried sufficiently to contain about 10 to about 15, and most preferably about 5 to about 10 weight percent water by the above test. Thus, a dried hydrocolloid can contain about zero to about 15 weight percent water.

One of the benefits of the present invention is that its hydrocolloid polymers are relatively soft and pliable as compared to the relatively hard, brittle hydrocolloid polymers that are prepared from a reaction mixture containing the same amounts of the same copolymerizable ethylenically unsaturated species but missing the glycerin used in the polymerization of a hydrocolloid polymer herein. Put differently, a hydrocolloid polymer of the present invention exhibits a relatively lower \( T_g \) than does such a similar polymer that contains the same amount of water, particularly for hydrocolloid polymers containing up to about 15 weight percent water. That lowering of \( T_g \) is at least about 50 degrees below the value obtained from a reaction mixture containing the same constituents except glycerin and polymerized by the same procedure.

This generalized lowering of \( T_g \) values is shown in the sole Figure that is a part of this disclosure. That Figure shows a graph of \( T_g \) values versus water content for a polymer of this invention and a similar, typically used hydrocolloid polymer sold under the Trademark ARASORB 10SH (available from Grain Processing Co. of Muscatine, Iowa).
As can be seen from that Figure, the presence of glycerol, there at 12.4 weight percent, lowers the \( t_g \) value of a hydrocolloid polymer of this invention as compared to the similar polymer used as a control. That lowering of \( t_g \) values is usually about 70 to about 100 degrees C for the range of water percentages usually encountered in sorbent products; i.e. about zero to about 15 weight percent.

The \( t_g \) values for the hydrocolloid of this invention shown in the Figure are typical of such values for polymers of this invention. This is particularly the case at bone dryness. Thus, one property that can be used to distinguish a polymer of this invention is a \( t_g \) at substantial dryness of about 250 to about 150 degrees C. The \( t_g \) values of a polymer-coated web are measured after removing the polymer from the web.

Another surprising property of a polymer of this invention is its improved ability to sorb water or saline in a standard test. Several standardized tests are utilized to compare hydrocolloid polymers and sorbent products made therefrom. Some tests measure sorption over a short time period of a few minutes, others examine equilibrium values at which the hydrocolloid is permitted to soak in an excess of the test liquid over a period of days or more, whereas other assays fall somewhere in between.

One intermediate time period assay is carried out for a time period of two hours and is referred to herein as a maximum absorbent capacity (MAC) assay, the details of which are provided hereinafter. In one such assay, two sorbent webs were prepared using the same mixture of monomer and polymerization conditions. The only difference between the two samples was that the web containing a hydrocolloid polymer of this invention also had about 10 weight percent glycerol in that polymer.
The specifics for this preparation are discussed hereinafter in regards to stiffness for webs.

Using the MAC assay with deionized water, the control web sorbed 44 milliliters per gram (ml/g) of web, whereas the web of this invention sorbed 73 ml/g. When a one percent by weight sodium chloride solution was used in place of deionized water, the results were 17 and 21 g/ml, respectively.

An assay known as a gravimetric absorbent test (GAT) measures the sorption of a web that is compressed by a force of one pound per square inch over a period of hours. Here the above webs performed similarly, providing sorption values of about 10 and 9.4 g/ml, respectively.

The polymerization reaction utilized to form a hydrocolloid of the invention can be by any known means by which such polymerization reactions can be ordinarily carried out. Polymerization is typically and preferably carried out using standard electron beam polymerization procedures, particularly where sorbent articles containing a polymer are prepared by in situ polymerization of the polymer on a supporting fibrous web matrix as is discussed hereinafter.

Exemplary means of polymerization include the particularly preferred electron beam method described in detail hereinafter as well as other radiative processes such as by the use of gamma radiation and actinic light, preferably in the presence of a photosensitizer. Additional means include use of a free radical initiator and heat such as azobisisobutyronitrile, or sodium or potassium thiosulfate, peroxide initiators such as t-butyl hydoperoxide or benzoyl peroxide; and oxidation-reduction (redox) polymerization utilizing a redox couple such as hydrogen peroxide and ascorbic acid. The polymerizations can be carried out in water, as is
preferred, or an appropriate mixed solvent such as a water-methanol mixture. The polymerization reaction can also be carried out using so-called inverse phase polymerization techniques that utilize an organic solvent such as hexane as the continuous phase, an appropriate water-in-oil surfactant and an aqueous solution of all of the monomers.

More specifically, the utilization of a free radical-initiating catalyst in an aqueous solution to effectuate polymerization of monomers is described in U.S. Patent No. 3,686,024 to Nankee et al. Photoinduced polymerization processes are described in U.S. Patents No. 4,167,464 to George; No. 4,178,221 to Boutin et al. and No. 4,308,148 to Boutin et al. The use of ionizing radiation to effect polymerization is described in U.S. Patents No. 3,764,502 to Restaino; No. 4,192,727 to Ward; and No. 4,411,754 to Kaetsu et al. The use of electron beam ionizing radiation to effect polymerization as described in U.S. Patent No. 4,192,727 is particularly preferred herein. The disclosures of the above-listed patents are herein incorporated by reference.

A hydrocolloid polymer of the invention is typically utilized as a sorbent in an article of manufacture such as a sanitary napkin, a surgical or wound dressing, a diaper, a wipe or the like. In such an article of manufacture, the hydrocolloid polymer is contained in and on a supporting fibrous web matrix and constitutes a portion of what is commonly referred to as an absorbent layer (or sorbent layer since both absorption and adsorption can occur) because most such products contain a plurality of layers that each serve a particular function. The use of a polymer of this invention in such a product provides a more pliable
product, particularly where the polymer is polymerized in situ as discussed hereinafter.

The hydrocolloid polymer is often utilized in a sorbing article in the form of a powder that is typically prepared by drying and then pulverizing the polymerized material, or, more preferably, the hydrocolloid polymer is prepared in situ on a supporting web that is thereafter dried as a unit. The sorbent layer comprising a supporting fibrous web matrix and hydrocolloid polymer, however applied, can be referred to as a "polymer-containing web", a "hydrocolloid-containing web" or a "polymer-coated web".

More specifically, the hydrocolloid polymer is distributed within a water-insoluble fibrous matrix web that comprises a substantially high loft, resilient fibrous web layer, and is present in an amount of about 200 to about 1500 percent by weight add-on to the matrix based upon the weight of fibrous matrix. Most preferably, the hydrocolloid polymer is present at about 500 to about 1000 percent weight add-on. Thus, the matrix plus hydrocolloid polymer constitute a hydrocolloid polymer-containing web or sorbing layer.

Frequently, one or more additional webs are placed adjacent to or disposed on one or both surfaces defined by the hydrocolloid polymer-containing web to form a sorbent laminate. Such additional webs can constitute a so-called "wicking layer" that functions to transport the liquid to be sorbed to the hydrocolloid polymer. An additional web can also constitute a water-impermeable membrane that provides an outside surface to the article such as a diaper, or a water-permeable layer that constitutes an inner layer of the article.

Where a powdered form of the hydrocolloid polymer is utilized, it can be sprinkled onto and into the interstices of a fibrous web matrix, and thereby
form a coating on the web matrix. It is often desirable to slightly moisten either the web or hydrocolloid polymer powder prior to causing contact therebetween so that the fibers of the web adhere to the powdered polymer as well as physically entrapping the powder.

More preferably, the hydrocolloid is prepared in situ on the resilient fibers of the fibrous web matrix. Here, the web is sprayed or submerged or otherwise coated with an aqueous solution of the appropriate, partially neutralized monomer and cross-linkers, and the polymer thereafter formed. Preferably, the polymer is formed by use of irradiation such as electron beam irradiation.

The hydrocolloid polymer coating is present arrayed around, between and on the resilient fibers of the fibrous web matrix of the sorbing layer in an intermittently dispersed form. The hydrocolloid polymer is in the form of particles that can be in the shape of fibers, spheres, bits of film when added as a pre-formed dry powder. When polymerized in situ, the hydrocolloid polymer provides globules and bits of film-like particles that are adhered to and around the fibers of the fibrous web. As a consequence, a polymer-containing web made by in situ polymerization can be distinguished from a similar web made by adding the pre-formed dry powder.

Sorbent layers comprising a web matrix coated with hydrocolloid polymer are most preferably prepared by electron beam irradiation, as noted previously. Here, in a laboratory preparation, a web matrix is coated in an aqueous solution of copolymerizable ethylenically unsaturated species, as described before, placed into a polyethylene bag so that the plane of the web is parallel to the major plane defined by the sides of the bag, and the bag is sealed. The bag and its
contents are then irradiated. The bag is thereafter turned over and irradiated again. Powder samples are similarly prepared except that the bags are free of the matrix, and are not turned over.

The amount of irradiation used to polymerize the monomers and cross-linkers is expressed in megarads (Mrads) per side of the irradiated bag and sorbent layer. Thus, the expression 2-2 is used to indicate that each side of the bag and sorbent layer therein was irradiated with 2 Mrads. Similarly, the expression 2-2, 8-8 indicates that a single irradiation of 2 Mrads was used for each side, and was followed by single irradiations of 8 Mrads on each side.

Add-on of hydrocolloid to a fibrous web matrix to form a sorbent layer is determined by weighing a known area of dried sorbent layer subtracting the weight of a similar area of starting web matrix and dividing the resulting number by the weight of that area of starting web matrix, and multiplying by 100 percent. Add-on is thus expressed as a ratio of the hydrocolloid polymer weight relative to the weight of the starting web matrix.

It is of some import to the function of the sorbing layer formed by the resilient fibrous web matrix and hydrocolloid polymer to have that polymer present in a quantity that is sufficient to sorb a desired amount of liquid, and spaced on and within the web in a manner such that gel blocking does not substantially occur. Gel blocking occurs when hydrocolloid polymer is present in a sufficient quantity and spaced so closely together that as the particles imbibe liquid and swell, a layer of gel is formed that blocks further penetration of liquid into the layer. The in situ polymerization technique described herein, when used to provide about 200 to about 1500 percent add-on of hydrocolloid
polymer, provides a sufficient amount of liquid sorbency while exhibiting a relatively minimal amount of gel blocking, if any.

In particularly preferred practice, a sorbent laminate comprised of the supporting fibrous web matrix that contains the hydrocolloid polymer (sorbing layer), and one or more adjacent webs such as wicking layers are compressed as a composite after polymerization and before drying, with the fibrous web layer being maintained in the compressed state by the dried hydrocolloid polymer. The sorbent laminate is compressed to substantially reduce its thickness. For example, such a structure is compressed sufficiently to reduce the thickness of the laminate structure by at least 50 percent and the pressure utilized in conjunction with drying is sufficient to cause the composite to remain compact after the pressure is released. The compression utilized should not be so high as to substantially crimp or crease the resilient fibers of the fibrous layer. Upon wetting the polymer-containing web, the hydrocolloid becomes wet so that the fibrous layer expands from its compressed state due to the inherent resilience of the fibers of that layer, and thereby facilitates swelling of the hydrocolloid polymer. Where a hydrocolloid-containing compressed sorbent web is utilized for a sorbent article, the starting fibrous web matrix (prior to the addition of hydrocolloid polymer) has an initial dry bulk recovery of at least about 30 percent, and more preferably at least about 60 percent, an initial dry bulk of at least about 20 cubic centimeters per gram (cc/g), and a weight of less than about 2 oz/yd - (about 68 gm/m²).

The initial dry bulk is the area times thickness of the layer under the load of 0.01 pounds per square inch calculated in cubic centimeters. This value
is divided by the weight in grams in order to provide the measurement in cubic centimeters per gram.

The dry bulk recovery is obtained by subjecting the web to a load of 1.75 pounds per square inch (psi) for five minutes, removing the load and allowing the web to rest for one minute, subjecting the web to a load of 0.01 psi for one minute and then measuring the final dry bulk under the 0.01 psi load. The dry bulk recovery is the final bulk divided by the initial bulk expressed in percent.

If the fibrous web can provide this dry bulk recovery and has an initial dry bulk of at least 20 cc/gm with a web weight of less than 2 oz/yd², the fibrous web meets the requirements of the sorbing layer.

When the fibrous web matrix has these requirements, it can retain hydrocolloid polymer up to at least 1,500 percent of the dry basis weight of the web. It is preferable that the web contain 200 percent to 1,500 percent by weight dry basis hydrocolloid, relative to the dry basis weight of the web.

A suitable fibrous web for a sorbing layer has a substantially high loft, and has a tendency to return substantially to its original thickness on compression followed by release. The resulting resiliency of the fibrous web typically permits a sorbing layer containing a hydrocolloid polymer to regain at least about 75 percent of its original thickness when it is released from its compressed state as liquid penetrates the sorbent product.

Such webs are typically formed from synthetic staple fibers such as polyethylene, polypropylene, polyester, nylon, bicomponent fibers and the like are particularly desirable. Cellulosic fibers such as rayon can also be used.
The fibrous web can be formed by carding, dry laying or wet laying fibers so as to provide a low density structure, as is well known in the art. In one preferred embodiment, staple polyester fibers are air laid with a minor portion of fusible fibers to form a web whose fibers are lightly bonded by passing hot air through the web fibers making the fusible fibers tacky so as to stick to each other and the staple fibers to provide further integrity to the web structure.

The wicking layer is comprised of substantially uniformly disposed, frictionally engaged particles of hydrophilic fibers, such as rayon fibers, cellulosic fibers, or peat moss, or mixtures thereof. The cellulosic fibers include wood pulp fibers, cotton linters, and the like. The wood pulp fibers generally are those that are used to form the fluff or fibrous batt layer in conventional sorbent products such as disposable diapers, sanitary napkins, etc. Other cellulosic fibers that can also be used are rayon fibers, flax, hemp, jute, ramie, cotton and the like. The particles of fibers or peat moss or mixtures thereof are placed in such a way as to form a layer in which the particles are spaced sufficiently close to one another so as to promote rapid movement of liquid (wicking) in the plane of the layer. Typically, there is a transition zone between the sorbent web and wicking layer that comprises portions of the engaged wicking layer particles that extend into the hydrocolloid polymer and become integral therewith so that those particles are in intimate contact with the hydrocolloid polymer.

An exemplary compressed, composite useful in a diaper can be prepared as follows.

The sorbent composite is made by four steps.

First, a fibrous web structure is made by blending
polyester fiber T-375W manufactured by DuPont and fusible BICO 1040 fiber, made by BASF, in a ratio of 67/33 percent by weight. This blend is carded into a high bulk non-woven web structure of approximately 1.20 oz/yd² (about 40.7 g/m²) weight and passed through an air bonder at a temperature of 325°F (about 163°C) for a duration of 5.6 seconds and at a pressure differential of 0.25 inches (0.64 cm) of water. This heat process bonds the web by partially melting the BICO fiber.

The second step consists of applying to that web a coating of potassium acrylate solution and glycerol at a concentration of about 65 percent solids and about 60 percent neutralized monocarboxy monomer. The monomer is added by suction coating to a desired level of 12.0 oz/yd² (about 40 g/m²) of dry coating weight. The thus applied coating is polymerized and cross-linked into a hydrocolloid polymer by multiple electron beam irradiations of 2 Mrads and 2 Mrads with an ESI 300 KV electron accelerator.

Pulp wicking layers are attached as the third step. Prior to this, the polymer is adjusted to a 25 percent moisture content. It is passed through the suction zone of a Hammermill where pulp is defiberized and deposited at a weight of 4.8 oz/yd² (about 162.75 g/m²). The use of vacuum causes at least some of the deposited fibers to migrate into the polymer-containing web and become integral therewith. Pulp is applied to the other side similarly. In other embodiments, pulp layers of about 50 g/m² are used. The entire composite is lightly sprayed with water to provide a moisture content of the pulp of about 10 percent by weight. The resulting web is thereafter compressed to a thickness of 0.143 inches (about 0.36 cm), and then dried for use. A useful sorbent layer can also be prepared in compressed form having a single wicking layer or no wicking layer.
Upon release of pressure, the pulp has formed into a high density layer with a capillary size suitable for liquid wicking and the resilient fiber layer remains compressed. Upon use of the resulting dry structure, when a significant amount of liquid contacts the surface and migration of liquid into the sorbent layer takes place, the hydrocolloid polymer becomes soft and releases the resilient fibers so that the thickness of the structure increases markedly. This increase in thickness provides a volume for storage of liquid.

Further details concerning compressed composite sorbing products as discussed above, and their sorbing layers can be found in U.S. Patents No. 4,500,315; No. 4,537,590; No. 4,540,454; and No. 4,573,988, all to Pieniak et al., whose disclosures are incorporated herein by reference.

It is noted that when a hydrocolloid polymer of the invention is employed as a portion of a sorbent layer of a sorbing article and polymerized in situ by an electron beam as described before, the liquid sorbing properties of the polymer are reduced as compared to the same properties of a similar polymer prepared separately. The reason for the difference in properties is thought to reside in the fact that the dose of radiation utilized for an in situ polymerization process is generally greater than that required for formation of a hydrocolloid prepared free in an aqueous medium. The liquid sorption properties of webs so produced are however improved over the same properties obtained utilizing no glycerol.

**Best Mode For Carrying Out The Invention**

**A. Testing Procedures**

Several testing procedures have been utilized to analyze the hydrocolloid polymers of the present
invention and to compare them with other hydrocolloid polymers. Details of those testing procedures are described hereinbelow.

1. Residual Monomer

Residual monomer levels are determined by high-performance liquid chromatography (HPLC). The monomers assayed are acrylic acid and its ester dimer.

Glacial acrylic acid, in an amount of about 500 milligrams (mg) is weighed to the nearest 0.1 mg into a 100 milliliter (ml) volumetric flask and is diluted to volume with 0.01 N sulfuric acid to form Solution A. Acrylic acid ester dimer (at least 95 percent pure) in an amount of about 100 mg is weighed to the nearest 0.1 mg into a second 100 ml flask, and is diluted to volume with 0.01 N sulfuric acid to form Solution B. Each of Solutions A and B is mixed thoroughly.

Solution A (10 ml) and Solution B (10 ml) are pipetted into a third 100 ml volumetric flask and diluted to volume with 0.01 N sulfuric acid to form Working Standard I (WS I). Working Standard II (WS II) is prepared similarly using 1 ml of each of Solutions A and B. Each Working Sample solution is mixed thoroughly.

Duplicates of each WS I and WS II are prepared. Portions of each of the four standards are placed into autosampler vials and capped.

A powder sample of hydrocolloid polymer of about 125 mg, weighed to the nearest 0.1 mg, is weighed into 50 ml centrifuge tube. (Powdered hydrocolloid polymers discussed herein are sized to pass through a 20 mesh sieve, U.S. Standard Sieve series.) Twenty-five ml of 0.1 N sulfuric acid are added to the tube and the tube is capped. The capped tube is shaken on a
mechanical wrist shaker for 20 minutes. An aliquot is removed, filtered through a 0.45 micron disposable filter, placed into an autosampler vial, and the vial is capped to provide an acid extract sample. A duplicate sample is similarly prepared.

A generally similar procedure is utilized for sorbent layers comprised of a web matrix coated with hydrocolloid polymer except that approximately 1.0 gram (g) of the coated web, weighed to the nearest 0.1 mg, is weighed into a 30 ml serum vial. The above amount of sulfuric acid is added and the vial is capped and sealed. Where sorbency is too great to permit ready extraction, 30 ml of 0.1 N sulfuric acid are used with a larger serum vial.

A Waters Associates HPLC equipped with a model M-590 pump, a model M-481 ultraviolet detector (set at 214 nm) and an autosampler is used. The HPLC uses an Amine\textsuperscript{2} HPX-87H ion exchange (Bio-Rad) column and a guard column. Sulfuric acid (0.01 N) is used as the mobile phase.

In a typical analytical assay, instrumental settings are:

- **Flow rate:** 0.80 ml/minute
- **Injection volume:** 20 microliters (ul)
- **Wavelength:** 214 nm
- **Column heater temperature:** 40°C
- **Range:** 0.05 AUFS

Retention times typically found are:
- **Acrylic acid:** 14.6 minutes
- **Ester dimer:** 17.7 minutes
The HPLC is run for about 30 minutes prior to use or until a stable baseline is obtained. Samples of WS I and WS II are injected. Duplicate samples of WS I and WS II are injected and the areas/mg of both runs for each sample determined. The values of area/mg should agree within +2 percent of their averages or the runs are repeated. Response factors for each sample are also calculated.

An aliquot of each sample extract to be assayed is injected once. The results for each pair of duplicate samples should agree within +3 percent or the duplicate samples are reassayed.

The amounts of acrylic acid and its ester dimer present in the sample are thereafter calculated from the areas of the HPLC chart, the response factor, the dilution factor and sample weight using a standard equation, and are expressed in parts per million of the original sample.

2. Percentage Extractables

Percentage extractables are determined in a manner generally similar to the manner of determining residual monomer. In this case, however, a standard of polyacrylic acid (PAA) of a molecular weight of about 80,000 is utilized.

More specifically, approximately 200 mg of PAA, weighed to the nearest 0.1 mg, are weighed into a 100 ml volumetric flask and diluted to volume with 0.2 molar (M) Na₂SO₄ as mobile phase. Glacial acryllic acid (GAA; 500 mg) weighed as before into a 500 ml volumetric flask and diluted to volume with the mobile phase serves as a GAA standard solution. Aliquots (10 ml and 1 ml) of the GAA standard solution are each diluted with
mobile phase to 100 ml in separate 100 ml volumetric flasks serve as working standards.

The powder sample of hydrocolloid polymer (150 mg) weighed as before is placed into a 50 ml centrifuge tube to which 25 ml of 0.2 M Na₂SO₄ are added. The tube is capped and shaken on a mechanical wrist shaker for 25 minutes, filtered as before into an autosampler vial, and the vial is capped. If the filtrate is not clear, the cloudy filtrate is returned to the centrifuge tube, the tube is centrifuged and the supernatant filtered as above. The sorbent layer samples are prepared as discussed previously, and assayed as discussed above. The standards and samples are prepared as in duplicate.

The HPLC is run as described before. Typical instrument settings are:

Flow rate: 10 ml/minute
Injection volume: 20 µl
Wavelength: 214 nm
Column heater temperature: 40°C
Range: 0.2 AUFS

Retention times typically found are:

PAA 6.7 minutes
Acrylic acid 9.9

A size exclusion stationary phase (3000 PW) is used with a Toyo Soda TSK guard column.

The working standards of PAA and GAA are injected separately and their retention times are determined. Duplicates of each standard are run. The areas/mg for each of the two injections should agree within ±5 percent of their average for each standard, or
the stanardization procedure is repeated. The response factors are calculated for the standards.

Each sample to be assayed is injected once. The results for each pair of duplicate samples should agree within ±5 percent of their average, or the samples are run again.

Both high and low molecular weight polymers are extractable. The high molecular weight percentage extractables is related to the 80,000 molecular weight standard using the response factor for that polymer, whereas the low molecular weight percentage extractables is related to the monomer standard using the response factor for the monomer.

The percentage extractables for high and low molecular weight polymers are calculated separately, each using the appropriate peak areas and response factors, as well as the dilution factor, and sample weight. The individual extractables percentages are then summed to provide the extractables percentage.

3. Fluid Sorption (MAC Assay)

Fluid sorption by a hydrocolloid polymer is determined as follows. A powder sample is dried in a vacuum oven for about 18 hours at a temperature of 40°C. An aliquot of about 100 mg, weighed to the nearest 0.1 mg, is added to 200 ml of deionized water, and permitted to sorb the water for a time period of 2 hours.

A filter paper is soaked with deionized water and allowed to drain until no further drops of water appear. The wet filter is thereafter weighed.

The mixture of hydrocolloid polymer and water is thereafter filtered through the wet filter paper. After no further drops of water are apparent, the combined wet filter paper and swollen hydrocolloid are
weighed to provide a total weight. Subtraction of the weight of dried hydrocolloid polymer powder and wet filter paper from the total weight provides the weight of sorbed deionized water, which is expressed as a percentage of the original weight of the dried hydrocolloid polymer weight, or in milliliters of deionized water sorbed per gram of dry hydrocolloid polymer.

A similar procedure is utilized for sorbent layers comprised of a web matrix coated with a hydrocolloid polymer. In both cases, the study is carried out at ambient room temperature, without stirring. Sorption studies of 1 percent sodium chloride (saline) solutions are carried out similarly except that 1 percent sodium chloride in deionized water is used in place of the deionized water.

B. Comparative Web Stiffness

A polymer of the present invention can provide sorbent webs that are relatively less stiff than are similarly prepared webs that are prepared from a substantially same reaction mixture that lacks the requisite amount of glycerol. One way to assay such stiffness is by the use of a stiffness testing machine such as a V-5 Stiffness Tester Model 150-B manufactured by Taber Instruments. A stiffness assay is normally carried out both in the machine direction (MD) and in the cross direction (CD) of the web.

The webs utilized were prepared using 2-2, 8-8 electron beam in situ polymerization using an aqueous bath containing acrylic acid neutralized to about 60 mole percent with potassium hydroxide at a solids level of about 65 percent as described before.

A stiffness assay using a Taber V-5 Model 150-B stiffness tester was carried out as follows.
The web to be tested was cut into sample pieces 3" x 1" (about 7.62 x 2.54 cm), with the 3" (7.62 cm) dimension in the test direction. The machine direction was marked on each sample. The samples (web pieces) were dried to a known, and predetermined moisture content.

Using the above-named instrument, the "Driving Disc" was set to zero by pressing the operating switch. The jaws were exactly centered in reference to the three lines located above the jaws prior to zeroing. The instrument was leveled by adjusting the tips on the two front legs until the line inscribed on top of the pendulum was directly in line with zero.

One end of the sample was secured into the upper clamp, with the other end in the lower clamp. The sample was centered using center lines on the back of the clamp as a guide. The direction of the material to be read [either machine direction (MD) or cross direction (CD)] was placed in a vertical direction.

The sample was centered between the rollers by moving the left roller toward the sample until contact was made, but caused no deflection of the pendulum from zero. The right roller was positioned against the sample until finger tight, and then backed-off one-quarter turn. The sample was then ready for measurement.

The operating switch was deflected to "R" (right) and held continuously until the inscribed mark on the pendulum reached 15° on the "Driving Disc". The operating switch was released immediately upon the pendulum reaching the 15° mark, and the reading in stiffness units was recorded.

The above procedure was repeated by deflecting the operating switch to "L" (left), and the reading in stiffness units was again recorded.
The above procedure was repeated for five samples for each web. The ten readings in stiffness units were thereafter averaged to provide the stiffness value, which is in units of gram-centimeters.

A second set of 5 samples was prepared from the web with their longest (test) dimension at 90° to the longest dimension of the first set of samples. Stiffness values were then similarly obtained. Use of stiffness values obtained by the above procedures provided values for MD and CD, which are at 90° to each other.

Some of the samples were also assayed twice. The results are shown in Table 1 below.

The results shown in Table 1 were obtained using the webs described above that contained a control polymer and a hydrocolloid polymer of this invention. Comparisons were made with bone dry polymers as well as with polymers containing 15 weight percent water. The webs containing 15 weight percent water were thereafter retested.
### Table 1

**Taber Stiffness**

<table>
<thead>
<tr>
<th></th>
<th>Stiffness</th>
<th>10% Control</th>
<th>Glycerol</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Direction</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>First Test @ 15% H₂O</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MD</td>
<td>70</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>CD</td>
<td>10</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td><strong>Retest @ 15% H₂O</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MD</td>
<td>50</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>CD</td>
<td>6</td>
<td>2</td>
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<tr>
<td><strong>Bone Dry</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>MD</td>
<td>147</td>
<td>106</td>
<td></td>
</tr>
<tr>
<td>CD</td>
<td>14</td>
<td>9</td>
<td></td>
</tr>
</tbody>
</table>

1Taber stiffness measured as discussed above in units of gram-centimeters.

2MD = machine direction; CD = cross direction.

As can be seen from the data above, a sorbent web prepared in accordance with this invention using a hydrocolloid of this invention provided much less stiffness and greater flexibility in both directions of flex than did the control web. That improvement was also noted on retesting a previously tested sample wherein the initially observed values were degraded by that first assay.

The percentage of extractables for the above webs were determined and found to be 12.4 percent for the control web and 25.2 percent for the web prepared from a glycerin-containing monomer mixture. That latter extractables amount included glycerin. Residual monomer
levels in parts per million were 92 and 100, in the order mentioned.

The present invention has been described with respect to preferred embodiments. It will be clear to those skilled in the art that modifications and/or variations of the disclosed subject matter can be made without departing from the scope of the invention set forth herein.
WHAT IS CLAIMED IS:

1. A water-swellable, but substantially water-insoluble hydrocolloid polymer prepared by polymerization of an aqueous reaction mixture consisting essentially of (a) about 80 to about 100 mole percent water-soluble alpha, beta-monoethylenically unsaturated monocarboxy monomer containing a chain of three carbon atoms, (b) zero to about 20 mole percent water-soluble copolymerizable monoethylenically unsaturated monomer, (c) zero to about 3 mole percent of a copolymerizable polyethylenically unsaturated cross-linking agent, and (d) about 10 to about 25 percent by weight glycerol based upon the total weight of copolymerizable ethylenically unsaturated species present, said hydrocolloid polymer when substantially free of water but containing said amount of glycerol exhibiting a glass transition temperature of about 250 to about 150 degrees C.

2. The hydrocolloid polymer of claim 1 prepared from a reaction mixture that contains about 10 to about 15 percent by weight glycerol.

3. The hydrocolloid polymer of claim 1 wherein about 50 to about 95 mole percent of said acid groups are neutralized with a monovalent cation.

4. The hydrocolloid polymer of claim 1 prepared from a reaction mixture that is substantially free of copolymerizable monoethylenically unsaturated monomer.

5. The hydrocolloid polymer of claim 1 prepared from a reaction mixture that is substantially free of copolymerizable monoethylenically unsaturated monomer and copolymerizable polyethylenically unsaturated cross-linking agent.
6. The hydrocolloid polymer of claim 5 wherein said alpha, beta-monoethylenically unsaturated monocarboxy monomer is acrylic acid.

7. The hydrocolloid polymer of claim 1 wherein about 60 to about 90 mole percent of said acid groups are neutralized with a monovalent cation.

8. A water-swellable but substantially water-insoluble hydrocolloid polymer prepared by polymerization of an aqueous reaction mixture consisting essentially of a) partially neutralized acrylic acid, b) a cross-linking agent present at zero to about 3 mole percent based upon the total moles copolymerizable ethylenically unsaturated species present, and c) about 10 to about 15 weight percent glycerol based upon the total weight of copolymerizable ethylenically unsaturated species present, said partially neutralized acrylic acid containing about 5 to about 50 mole percent free acid groups and about 95 to about 50 mole percent acid groups neutralized with a monovalent cation, said hydrocolloid polymer when substantially free of water but containing said amount of glycerol exhibiting a glass transition temperature of about 250 to about 150 degrees C.

9. The hydrocolloid polymer of claim 8 wherein about 60 to about 90 mole percent of said acid groups are neutralized with said monovalent cation.

10. The hydrocolloid polymer of claim 8 wherein said aqueous reaction mixture is free of said cross-linking agent.

11. The hydrocolloid polymer of claim 8 wherein said copolymerizable ethylenically unsaturated species and glycerol constitute about 45 to about 70 weight percent of said aqueous reaction mixture.

12. A polymer-coated web comprising a water-insoluble fibrous web matrix having coated thereon a
water-swellable but substantially water insoluble hydrocolloid polymer, said web matrix having a dry bulk recovery of at least about 30 percent, an initial dry bulk of at least 20 cc/g and a weight of less than about 2 oz/yd², said hydrocolloid polymer being polymerized and coated on said matrix in an amount of about 200 to about 1500 percent weight add-on to said web matrix and prepared by polymerization of an aqueous reaction mixture that consists essentially of (a) about 80 to about 100 mole percent alpha,beta-monoethenically unsaturated monocarboxy monomer containing a chain of three carbon atoms, (b) zero to about 20 mole percent water-soluble copolymerizable monoethenically unsaturated monomer, (c) zero to about 3 mole percent water-soluble polyethenically unsaturated cross-linking agent, and (d) about 10 to about 15 percent by weight glycerol based upon the total weight of copolymerizable ethenically unsaturated monomer and cross-linking agent present, said hydrocolloid polymer when removed from said web and substantially free of water but containing said amount of glycerol exhibiting a glass transition temperature of about 250 to 150 degrees C.

13. The polymer-coated web of claim 12 wherein said coated hydrocolloid polymer of said web contains about 5 to about 15 weight percent water.

14. The polymer-coated web of claim 12 wherein said acid groups of said monoethenically unsaturated monomers of said aqueous reaction mixture are neutralized to about 50 to about 95 mole percent with a monovalent cation.

15. The polymer-coated web of claim 14 wherein said aqueous reaction mixture is substantially free of said water-soluble copolymerizable monoethenically unsaturated monomer.
16. The polymer-coated web of claim 14 wherein said aqueous reaction mixture is substantially free of said water-soluble copolymerizable monoethylenically unsaturated monomer and said polyethylenically unsaturated cross-linking agent.

17. The polymer-coated web of claim 16 wherein said alpha,beta-monoethylenically unsaturated monocarboxy monomer is acrylic acid.

18. The polymer-coated web of claim 17 wherein said glycerol is present at about 10 to about 15 weight percent.

19. A polymer-coated web comprising a water-insoluble fibrous web matrix having coated thereon a water-swellable but substantially water-insoluble hydrocolloid polymer, said web matrix having a dry bulk recovery of at least about 60 percent, an initial dry bulk of at least about 20 cc/g and a weight of less than about 2 oz/yd², said hydrocolloid polymer being present in an amount of about 400 to about 1200 percent weight add-on of said web matrix, and prepared by polymerization of an aqueous reaction mixture consisting essentially of a) partially neutralized acrylic acid, b) a cross-linking agent present at zero to about 3 mole percent based upon the total copolymerizable ethylenically unsaturated species present, and c) about 10 to about 15 weight percent glycerol based upon the total weight of ethylenically unsaturated species present, said partially neutralized acrylic acid containing about 60 to about 90 mole percent acid groups neutralized with a monovalent cation, said hydrocolloid polymer when removed from said web and substantially free of water but containing said amount of glycerol exhibiting a glass transition temperature of about 250 to about 150 degrees C.
20. The polymer-coated web of claim 19 wherein said aqueous reaction mixture is free of said cross-linking agent.

21. The polymer-coated web of claim 19 wherein said copolymerizable ethylenically unsaturated species and glycerol constitute about 45 to about 70 weight percent of said aqueous reaction mixture.

22. The polymer-containing web of claim 19 wherein said hydrocolloid coating is present in an amount of about 500 to 1000 weight percent of the weight of said matrix.

23. The polymer-containing web of claim 19 wherein said hydrocolloid polymer is polymerized in situ on the fibers of said fibrous matrix.

24. The polymer-containing web of claim 19 further including a wicking layer disposed on one surface defined by said web, said wicking layer comprising substantially uniformly disposed, frictionally engaged particles of hydrophilic fibers, peat moss or a mixture thereof that are placed in such a way as to form a layer in which said particles are spaced sufficiently close to one another so as to promote rapid movement of liquid in the plane of said layer, said polymer-containing web and said wicking layer together constituting a sorbent laminate.

25. The sorbent laminate of claim 24 further containing a transition zone between said said polymer-containing web and said wicking layer that comprises portions of said engaged wicking layer particles that extend into said hydrocolloid polymer such that said particles become integral with said hydrocolloid polymer and are in intimate contact therewith.

26. The sorbent laminate of claim 24 in a form compressed to substantially reduce its thickness.
**INTERNATIONAL SEARCH REPORT**

International Application No. PCT/US90/03296

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)

 According to International Patent Classification (IPC) or to both National Classification and IPC

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<th>INT. CL. (5): CO8F 2/54; B32B 9/04</th>
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II. FIELDS SEARCHED

**Minimum Documentation Searched**

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Documentation Searched other than Minimum Documentation to the extent that such documents are included in the fields searched

III. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>X</td>
<td>US, A, 4,192,727 (WARD) 11 MARCH 1980 See the entire document.</td>
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* 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
  
  "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.
  
  "Z" document member of the same patent family

IV. CERTIFICATION

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International Searching Authority: ISA/US

Signature of Author of Report: W.J. VanBalen