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3,705,053
HIGHLY ABSORBENT BONDED NONWOVEN FABRICS

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ABSTRACT OF THE DISCLOSURE

The present invention is concerned with new and improved binders for the production of nonwoven fabrics which have a high degree of absorbency, and retain their bonded character as well as absorbency through numerous wash-dry cycles. The fabrics are bonded by a novel self-crosslinking binder comprising a copolymer of (a) N-methylolamine or -amide units, (b) sulfonic acid units which contain no basic nitrogen atoms or group, and (c) certain acrylic units of neutral but mildly hydrophilic character which contain no basic nitrogen atoms or group.

It is already known to use N-methylol-acrylamide in copolymers to be used for bonding nonwoven fabrics and setting the binder in the fabric by heating the fabric impregnated therewith with a suitable acid catalyst to accelerate the crosslinking of the binder to insoluble condition on the fabric. When this is done, however, the bonded fabric generally becomes markedly less readily wettable than the fibrous mass that is used in making the bonded fabric. Hence, there is an undesirable water-repellency in the bonded mass which makes it relatively unsuitable for use as a wiping cloth or rag to remove and pick up liquids, as in washing furniture, as in kitchens in the home, or in washing cars.

Attempts have been made to overcome this disadvantage by selection of surfactant in the emulsion polymerization of the monomers to produce the binder and by the addition of a wetting agent to the impregnating medium by which the binder is applied to the nonwoven fabric. However, such expedients interfere with the removal of aqueous liquids when such fabrics are used for wiping wet surfaces, cause smearing of the liquid over the surface, and, in most instances, serve for one time use only because the surfactant or wetting agent is removed during the first use.

In accordance with the present invention, a binder copolymer itself is modified to incorporate a component which provides improved absorbency and at the same time remains in the binder so that it is not removed during use, rinsing, or washing of the cellular article or nonwoven fabric. The binder copolymer comprises a component (a), namely an N-methylol- or N-alkoxymethyl-substituted nitrogen-containing monoethylenically unsaturated monomer which imparts thermosetting qualities to the copolymer and may also serve to chemically bond the binder to the fibers of a nonwoven fabric. The binder also comprises a component (b) namely, an α,β-unsaturated monomer, which is copolymerizable with the nitrogen-containing monomer, contains a strong sulfur acid group having a pKa of 3.5 or less, but contains no basic nitrogen atom or group. This component serves to impart absorbency and rewettability. The balance (component (c)) of the binder copolymer, to make 100% by weight, may comprise one or more other α,β-ethylenically unsaturated monomers which contain no basic nitrogen atom or group and are at the most only moderately hydrophobic so that this component does not overcome the hydrophilicity of the second-

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mentioned component and thereby cause excessive reduction of absorbent and wettable characteristics.

By basic nitrogen atom, it is intended to refer to the nitrogen atom in an ordinary amine group (primary, secondary, or tertiary). Such groups are normally basic in character. This definition excludes the nitrogen atom of a carboxylic acid amide group and that of a ureido or carbamide group.

For the first component there may be used various monomers containing a nitrogen atom substituted with at least one methylol or methoxymethyl group. More specifically, the monomer that is useful here contains a carboxamido group, a ureido group, or an amino group in which the nitrogen atom is attached to a carbon atom in the ring of a 1,3,5-triazine. The nitrogen of the carboxamido, ureido or amino group is methylolated to attach at least one methylol group to the nitrogen atom, and, if desired, the N-methylol derivative is converted to the corresponding N-methoxymethyl-substituted derivative, all in conventional manner. Examples of monomers containing carboxamido groups are those derivatives of the amides of monoethylenically unsaturated monocarboxylic and dicarboxylic acids having a group of the formula $H_2C{=}C{<}$, such as the N-methylol- and N-methoxymethyl-substituted derivatives obtained from acrylamide, methacrylamide, maleimide, maleamic acid, itaconamic acid, crotonamide, fumarimide, fumaramic acid, acryloxypropionamide, and so on. Of these, the preferred monomers are those having a terminal group of the formula $H_2C{=}C{<}$, such as acrylamide and methacrylamide.

N-methylolated or N-methoxymethyl derivatives of ethylenically unsaturated monomers containing ureido groups are also useful. Examples of such ureido monomers are:

Compounds of the formula

$$H_2C{=}C(R)ZAN(R^3)CXNR'R^2 \qquad \text{(I)}$$

wherein

R is H or methyl,
Z is O, S,

$$-\overset{\overset{\displaystyle O}{\|}}{C}-O-$$

or

$$-\overset{\overset{\displaystyle O}{\|}}{C}-NH-$$

A is an alkylene group having 2 to 8 carbon atoms,
R^3 is selected from the group consisting of H, alkyl groups having 1 to 4 carbon atoms, hydroxyalkyl groups having 1 to 4 carbon atoms, and alkoxymethyl groups having 2 to 5 carbon atoms,
X is oxygen or sulfur,
R′ when not directly attached to R^2 is H, phenyl, methylbenzyl, benzyl, cyclohexyl or alkyl having 1 to 6 carbon atoms, hydroxyalkyl having 1 to 6 carbon atoms, N-alkoxyalkyl having 2 to 6 carbon atoms; R^2, when not directly attached to R′, is H, phenyl, methylbenzyl, benzyl, cyclohexyl or alkyl having 1 to 6 carbon atoms, and R′ and R^2, when directly connected together, may be the morpholino residue $-C_2H_4OC_2H_4-$, the piperidino residue

$$-(CH_2)_5-$$

or the pyrrolidino residue $-(CH_2)_4-$,

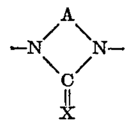
at least one of R′, R^2 and R^3 being methylol or methoxymethyl.

Examples of these compounds include:

N-methylol-β-ureidoethyl vinyl ether,
N-methylol-β-ureidoethyl vinyl sulfide,
N-methylol-β-thioureidoethyl vinyl ether,

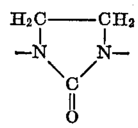
N-methylol-β-thioureidoethyl vinyl sulfide,
N-methylol-β-ureidoethyl acrylate,
N-methylol-β-thioureidoethyl methacrylate,
N-methylol-N′-(β-ureidoethyl)acrylamide,
N-methylol-N′-(β-ureidoethyl)methacrylamide,
N-methylol-N′-β-methacryloxyethyl-urea,
N-methylol-N′-methylol-N′-β-acryloxyethyl-urea,
N-methoxymethyl-N′-β-vinyloxyethyl-urea.

Among the ureido-containing monomers, those containing a cyclic ureido group of the following Formula II are also quite useful.



(II)

wherein A and X are as defined hereinbefore. The preferred cyclic ureido compounds are those which contain the group



(III)

which may be termed the cyclic N,N′-ethyleneureido group.

In II or III, one of the nitrogen atoms is connected to a polymerizable monoethylenically unsaturated radical and the substituent on the other nitrogen may be methylol or methoxymethyl.

Many other monoethylenically unsaturated monomers contain cyclic ureido groups and are useful for producing component (a) of the copolymer invention. Compounds of the following formulas wherein Y represents the group of Formula II above and R^4 is methylol or methoxymethyl are typical:

$$H_2C{=}CHYR^4 \qquad (IV)$$

$$H_2C{=}CHXAYR^4 \qquad (V)$$

wherein X and A are as defined hereinabove.

$$H_2C{=}C(R)\overset{O}{\overset{\|}{C}}ZAYR^4 \qquad (VI)$$

where R is selected from the group consisting of H and CH_3, Z is selected from the group consisting of —O— and NR^5, R^5 being selected from the group consisting of H, cyclohexyl, benzyl, and an alkyl group having 1 to 6 carbon atoms, and A is as defined hereinabove.

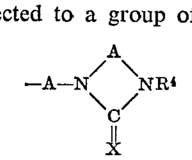
$$H_2C{=}C(R)\overset{O}{\overset{\|}{C}}NR^0CH_2YR^4 \qquad (VII)$$

wherein R, Y, and R^4 are as defined hereinabove and R^0 is H or alkyl having 1 to 12 carbon atoms;

$$H_2C{=}C(R)\overset{O}{\overset{\|}{C}}OCH_2\overset{O}{\overset{\|}{C}}NR^0AYR^4 \qquad (VIII)$$

wherein R, R^0, A, Y, and R^4 are as defined hereinabove.

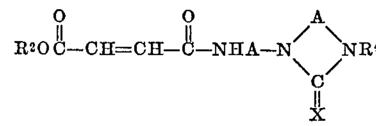
The N-[omega-(1,3-cyclodiazolidin-2-onyl)alkyl]-substituted unsaturated amic acids, their esters, and cyclic imides disclosed and claimed in U.S. Pat. 2,980,652, the disclosure of the patent being incorporated herein by reference are also useful. These compounds are not readily represented in generic scope by a single formula. The acids are those in which the nitrogen atom of maleamic acid, chloromaleamic acid, fumaramic acid, itaconamic acid, or citraconamic acid is substituted by, and directly connected to a group of the formula



(VIII-A)

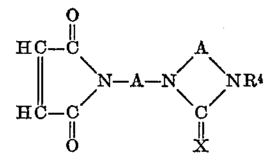
wherein A, X and R^4 are as defined hereinabove.

The N-substituted amic acid and esters derived from maleamic acid are typical and have the following generic formula



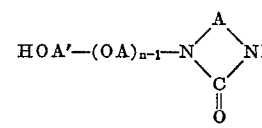
(IX)

in which A, R^4 and X are as defined hereinabove, and R^2 is an alkyl group having 1 to 12, preferably 1 to 4, carbon atoms. The internal cyclic imides derived from maleamic acid that are useful herein have the formula



(X)

The unsaturated dicarboxylic acid monoesters of a compound of the formula



(XI)

wherein A′ is a $(C_2–C_8)$alkylene group, n is an integer having a value of 1 to 4, and A and R^4 are as defined hereinbefore, derived from maleic, fumaric, chloromaleic, itaconic or citraconic acid. There may also be used the benzyl, cyclohexyl, and $(C_1–C_6)$alkyl esters of any of the monoesters just described which are disclosed in U.S. Pat. 3,194,792, and the specific compounds disclosed therein are incorporated herein by reference. Specific examples include:

Methylolated β-(N,N′-ethyleneureido)ethyl acid maleate,
Methylolated β-(N,N′-ethyleneureido)ethyl acid fumarate,
Methylolated methyl β-(N,N′-ethyleneureido)ethyl fumarate,
Methylolated β-(N,N′-ethyleneureido)ethyl fumarate.

Additional illustrative examples of carboxamide type include those of U.S. Pat. 3,274,164 having the general formula

$$H_2C{=}CHCH_2CH_2CON{-}(CH_2OR)_n \atop \quad\quad\quad\quad\quad\quad\quad\quad\quad |\atop \quad\quad\quad\quad\quad\quad\quad\quad\quad (H)_{2-n} \qquad (XII)$$

wherein R is selected from the group consisting of H and alkyl having 1 to 18 carbon atoms, and n is a number having an average value of about 0.8 to 2.0 and preferably having an average value of about 1.

Specific examples of the compounds represented by the several Formulas III to XII given above include:

(A) Formulas III and IV

N-vinyl-N′-methylol-N,N′-ethyleneurea
N-vinyl-N′-methoxymethyl-N,N′-ethyleneurea

(B) Formula V

N-vinyloxyethyl-N′-methylol-N,N′-ethyleneurea
N-vinyloxyethyl-N′-methoxymethyl-N,N′-ethyleneurea
N-vinylthioethyl-N′-methylol-N,N′-ethyleneurea.

(C) Formula VI

N-(β-methacrylamidoethyl)-N′-methylol-N,N′-ethyleneurea
N-(β-acrylamidoethyl)-N′-methoxymethyl-N,N′-ethyleneurea
N-(β-acryloxyethyl)-N′-methylol-N,N′-ethyleneurea
N-(β-methacryloxypropyl)-N′-methylol-N,N′-propyleneurea

N-(β-acryloxyethyl)-N'-methoxymethyl-N,N'-ethyleneurea

N-(β-acryloxyethyl)N'-methylol-N,N'-ethylenethiourea

(D) Formula VII

N-acrylamidomethyl-N'-methylol-N,N'-ethyleneurea

N-acrylamidomethyl-N'-methylol-N,N'-propyleneurea

(E) Formula VIII

N-[β-(α-acryloxyacetamido)ethyl]-N'-methylol-N,N'-ethyleneurea

N-[β-(α-methacryloxyacetamido)ethyl]-N'-methylol-N,N'-ethylenethiourea

N-[β-(α-methacryloxyacetamido)ethyl]-N'-methylol-N,N'-ethyleneurea

(F) Formulas IX, X, XI, and related compounds from other unsaturated dicarboxylic acids

N-[β-(β-carboxyacrylamido)ethyl]-N'-methylol-N,N'-ethyleneurea

N-[β-(β-carbomethoxyacrylamido)ethyl]-N'-methoxymethyl-N,N'-ethyleneurea

N-[β-(β-(ethylcarbonyl)acrylamido)ethyl]-N'-methylol-N,N'-ethyleneurea

N-[β-(β-carbomethoxyacrylamido)propyl]-N'-methylol-N,N'-propyleneurea

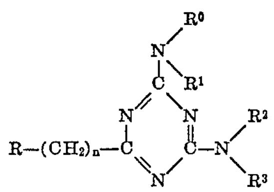
N-[β-(β-(methylcarbonyl)acrylamido)ethyl]-N'-methoxymethyl-N,N'-ethyleneurea.

Methylolated 1-[2-(β-trans-carbomethoxyacrylamido)-ethyl]-imidazolidinone-2 (see Ex. 5 of 2,986,652).

(G) Formula XII

The most useful of these compounds are N-methylol- and M-methoxymethyl-4-pentenamide.

N-methylol- or N-methoxymethyl-substituted amino-triazines in which the thus-substituted amino group is attached to a carbon atom of a 1,3,5-triazine ring containing an ethylenically unsaturated substituent having a group $H_2C{=}C<$ can also be used as component (a) of the copolymer. They may have the general formula



(XIII)

wherein

n is 0 or 1,

R^0 is selected from the group consisting of H, CH_2OH, and CH_2OCH_3,

R^1 is selected from the group consisting of H, CH_2OH, and CH_2OCH_3,

R^2 is selected from the group consisting of H, CH_2OH, and CH_2OCH_3,

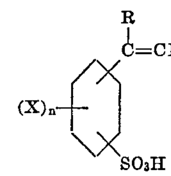
R^3 is selected from the group consisting of H, CH_2OH, and CH_2CH_3 at least one of R^0, R^1, R^2, and R^3 being methylol or methoxymethyl, and

R is an alkenyl group having 2 to 9 carbon atoms and a terminal group $H_2C{=}C<$. In other terms, the group R is an alkenyl group of the formula $-C_nH_{2n-1}$ in which n has a value of 2 to 9, which alkenyl group has a terminal group $H_2C{=}C<$. Examples in which n is zero include N-methylolacryloguanamine, N-methoxymethylacryloguanamine, N-methylol - 3 - butyroguanamine, and N-methylol-methacryloguanamine. When n is 1 and R has at least 3 carbon atoms, especially valuable monomers are embraced by the formula in which the double bond of the side chain substituent is in nonconjugated relationship in respect to the double bonds of the ring. Examples are N-methylol- or N-methoxymethyl-4-pentenoguanamine and the related compounds disclosed in U.S. Pat. 3,446,777.

Generally, it is undesirable to include in the copolymers of the present invention an amino compound that is moderately or strongly basic in character. However, the monomers which contain an amino group, the nitrogen atom of which is attached directly to a carbon atom in the ring of a 1,3,5-triazine is only weakly basic and does not interfere with the meritorious qualities of the resulting copolymers.

The amount of N-methylol- or N-methoxymethyl-substituted monomeric material required in the binder copolymer may be as low as about 0.2% by weight based on the weight of the copolymer, or it may be as high as about 10% by weight. Preferred copolymers contain about 0.5 to 4% by weight of such a monomer or mixture thereof.

The second component of the binder copolymer may also be derived from a wide range of monomers. Examples include ethylenesulfonic acid (vinylsulfonic acid), allylsulfonic acid, methallylsulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, 2-acrylamido - 2 - methylbutane-3-sulfonic acid, and the unsaturated aromatic sulfonic acids of U.S. Pat. 2,527,300, especially those of the formula



(XV)

wherein

R is hydrogen, methyl, or a halogen,

X is an alkyl group containing from 1 to 4 carbon atoms or a halogen atom,

n is zero or a whole number from 1 to 3, and the total number of carbon atoms in $(X)_n$ is not over 4.

Also useful are the sulfo-esters of α-methylene carboxylic acids of U.S. Pat. 3,024,221 or of U.S. Pat. 2,964,557 having the following formula

$$CH_2{=}\overset{R'}{\overset{|}{C}}O_2{-}Q{-}SO_3M \qquad \text{(XVI)}$$

wherein the symbol R' represents hydrogen, a halogen such as chlorine, or an organic radical such as an alkyl radical, the symbol —Q— represents a bivalent organic radical having 2 to 10 carbon atoms and having its valence bonds on two different carbon atoms, such as an alkylene or arylene radical, and M is a member of the group consisting of hydrogen, ammonium bases, and metals. The term "sulfo ester" of an α-methylene carboxylic acid is used herein to mean an ester corresponding to a carboxylate ester of an α-methylene carboxylic acid and a hydroxy organic compound, which latter compound has, as substituent on a carbon atom thereof, a sulfo group, i.e. a sulfonic acid group ($-SO_3H$) or a salt thereof such as a sodiosulfo ($-SO_3Na$) group.

In instances where —Q— is an aliphatic radical, the sulfo esters are representable by the formula

$$CH_2{=}\overset{R'}{\overset{|}{C}}{-}CO_2{-}(C_nH_{2n}){-}SO_3M \qquad \text{(XVII)}$$

wherein n is an integer, preferably from 2 to 4, including instances where $-C_nH_{2n}-$ is a straight chain. Another group of monomers useful for this component are those disclosed in copending application of William D. Emmons and Graham Swift, Ser. No. 134,905, entitled "Sulfonic Acid Monomers and Polymers," filed on Apr. 16, 1971, having the formula

$$H_2C{=}\overset{R}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}A{-}O{-}\overset{O}{\overset{\|}{C}}{-}X \qquad \text{(XVIII)}$$

wherein R is hydrogen or methyl.

A is an alkylene group having 2 to 6 carbon atoms, at least 2 of which extend in one chain between the oxygen atoms, and

X is an aromatic nucleus having 6 to 10 carbon atoms or an alkyl group having 2 to 10 carbon atoms, substituted by a sulfonic acid group and optionally one or more groups selected from sulfonic acid, carboxylic acid, and lower alkyl, such as methyl, ethyl, propyl, or butyl.

The proportion of monomeric component (b) in the copolymer may vary widely depending on its hydrocarbon content and also on the content and hydrophobicity of component (a) and of component (c), if any of the latter is present, after curing of the copolymer. There may be as little as about 0.2% by weight of monomeric component (b) in the copolymer and there may be as much as 45% by weight thereof in the copolymer, particularly when the hydrocarbon content or the content of the monomer other than hydrophilic groups is quite large. However, in most instances, a relatively lower proportion of monomer (b) is present; thus in preferred instances, there is from about ½ to 8 weight percent of monomeric component (b) and the balance of the copolymer units (c) to make 100%, may be composed of vinyl acetate, acrylonitrile, a lower alkyl acrylate or methacrylate in which the alkyl group has 1 to 4 carbon atoms and is preferably methyl or ethyl acrylate. As part of component (c) there may also be used a higher alkyl acrylate or methacrylate having 5 to 12 carbon atoms in the alkyl group in an amount of up to 30% by weight of the copolymer. There may also be present, in an amount of about 0.1 to 5 percent by weight, based on the copolymer weight, of one or more monomers having a reactive hydrogen atom. Such monomers include those having an amino group in which the nitrogen atom is attached to a carbon atom of a 1,3,5-triazine ring, amido, carboxylic acid, hydroxyl, and mercapto groups, such as acrylamide, methacrylamide, acrylic acid, methacrylic acid, itaconic acid, hydroxyethyl acrylate and mercaptoethyl methacrylate.

Specific examples of monomers of component (b) include:

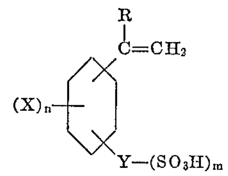
o-, m-, or p-styrene sulfonic acids
o-, m-, or p-isopropenylbenzene sulfonic acids
o-, m-, or p-alpha-chlorostyrene sulfonic acids
o-, m-, or p-alpha-bromostyrene sulfonic acids
2-vinyl-3-chlorobenzenesulfonic acid
2-vinyl-4-bromobenzenesulfonic acid
2-vinyl-5-fluorobenzenesulfonic acid
2-vinyl-6-chlorobenzenesulfonic acid
2-bromo-3-vinylbenzenesulfonic acid
3-vinyl-4-chlorobenzenesulfonic acid
3-vinyl-5-bromobenzenesulfonic acid
3-chloro-4-vinylbenzenesulfonic acid
2-fluoro-4-vinylbenzenesulfonic acid
2-isopropenyl-3-chlorobenzenesulfonic acid
2-bromo-3-isopropenylbenzenesulfonic acid
3-chloro-4-isopropenylbenzenesulfonic acid
2-vinyl-3-methylbenzenesulfonic acid
2-vinyl-4-ethylbenzenesulfonic acid
3-isopropenyl-4-methylbenzenesulfonic acid
3-ethyl-4-vinylbenzenesulfonic acid
2-vinyl-3,6-dichlorobenzenesulfonic acid
3-vinyl-4-methyl-5-chlorobenzenesulfonic acid
1-methoxy-4-sulfo-6-vinylnaphthalene
3-isopropenyl-1-naphthalenesulfonic acid
1-sulfo-3,6-dichloro-4-vinylnaphthalene

Also suitable for use in the preparation of the new copolymers are those unsaturated aromatic sulfonic acids in which the $CH_2{=}C<$ group is attached not directly to a nuclear carbon, as in the above-listed examples, but to an aliphatic carbon. Thus, allylbenzenesulfonic acids, methallylbenzenesulfonic acids, and haloallylbenzenesulfonic acids as, for example,

2-allylbenzenesulfonic acid
3-beta-methallylbenzenesulfonic acid
4-beta-bromallylbenzenesulfonic acid

may be used.

Aromatic sulfonic acids in which the sulfonic acid group is attached not to a nuclear carbon but to an aliphatic carbon atom are also suitable for use according to the present invention, including acids having the general formula



(XIX)

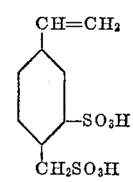
in which

X may be a halogen atom or an alkyl group having 1 to 4 carbon atoms,
R is hydrogen or methyl or a halogen atom,
Y is a divalent aliphatic, saturated hydrocarbon radical having from 1 to 4 carbon atoms,
m is 1 or 2, and
n is zero or a whole number from 1 to 3.

Some examples of such acids are:

o-, m-, or p-vinylphenylmethanesulfonic acids
o-, m-, or p-vinylphenylethanesulfonic acids
o-, m-, or p-isopropenylphenyl-n-butanesulfonic acids
o-, m-, or p-alpha-chlorovinylphenyl-n-propanesulfonic acids
2-vinyl-3-chlorophenylmethanesulfonic acid
2-vinyl-4-chlorophenylethanesulfonic acid
2-vinyl-5-bromophenyl-n-butanesulfonic acid
2-vinyl-3-methylphenylmethanesulfonic acid
2-vinyl-4-ethylphenyl-n-propanesulfonic acid
3-methyl-4-alpha-chlorovinylphenylmethanesulfonic acid
2-vinyl-4-ethyl-6-chlorophenyl-ethanesulfonic acid
1-[2-vinylphenyl]-n-butanedisulfonic acid-2,4
1-[4-vinylphenyl]-ethanesulfonic acid-1
4-[3-vinylphenyl]-2-butanesulfonic acid-2

Sulfonic acids containing sulfonic acid groups attached both to nuclear and aliphatic carbon atoms may also be used as, for example, 1-sulfo-3-vinylphenylmethanesulfonic acid,



It is preferred to use the aromatic sulfonic acids in the form of their alkali metal salts for copolymerization. The alkali metal sulfonate groups in the resinous copolymer product may be readily hydrolyzed to the free acid by treatment with acid as in the usual process for regeneration of exhausted cation exchange resins.

Heterocyclic sulfonic acids containing the necessary $CH_2{=}C<$ group are also operative in the preparation of copolymers of the present invention. A few examples of such acids are:

2-sulfo-5-allylfurane
2-sulfo-4-vinylfurane
2-sulfo-5-vinylthiophene

Aliphatic sulfonic acids suitable for use in the present invention include those represented by the general formula

$$CH_2{=}\underset{\displaystyle X}{\underset{|}{C}}{-}Y{-}(SO_3H)_n$$

in which X may be hydrogen or a group such as halogen, carboxyl, sulfo, cyano, carbamyl, nitro, aryl, i.e., phenyl, tolyl, xylyl, naphthyl, etc., saturated aliphatic hydrocarbon radicals having from 1 to 5 carbon atoms, i.e., methyl, ethyl, isopropyl, n-butyl, isobutyl, tert. butyl, n-amyl, tert. amyl, and the radicals —COOR, —COR, —$CONR_2$, —OR, and RCOO— in which R may be any organic hydrocarbon group, saturated aliphatic or aromatic, but is preferably an alkyl group of from 1 to 5 carbon atoms; Y is a divalent aliphatic saturated radical of from 1 to 4 carbon atoms, and n is 1 or 2.

Thus, there may be used, in addition to ethylenesulfonic acid itself,

1-bromoethylenesulfonic acid
1-cyanoethylenesulfonic acid
1-carbamylethylenesulfonic acid
1-nitroethylenesulfonic acid
1-phenylethylenesulfonic acid
1-isopropylethylenesulfonic acid
1-carbethoxyethylenesulfonic acid
1-carbophenoxyethylenesulfonic acid
1-acetylethylenesulfonic acid
1-naphthoylethylenesulfonic acid
1-amoxyethylenesulfonic acid
1-biphenyloxyethylenesulfonic acid
1-acetoxyethylenesulfonic acid
1-benzoxyethylenesulfonic acid
2-propenesulfonic acid
3-butenesulfonic acid
5-hexenesulfonic acid
2-sulfopropene-1
3-sulfobutene-1
2-methyl-4-pentenesulfonic acid
3-chloro-3-butenesulfonic acid
2-ethyl-3-butenesulfonic acid

Sulfonic acids containing more than a single acid radical, sulfonic or otherwise may also be used in the preparation of the new copolymers, i.e.

α-sulfoacrylic acid
α-sulfoethylenesulfonic acid
3-sulfo-4-pentenesulfonic acid
3-vinyl-5-sulfobenzoic acid
2-vinyl-1,5-benzenedisulfonic acid
2-vinyl-3-sulfophenylmethanesulfonic acid
3-vinyl-4-sulfomethylbenzoic acid

Instead of the sulfonic acids of the type disclosed as suitable for use in the present invention, derivatives thereof which are hydrolyzable to the acids may be copolymerized with component (a) and optionally (c) and the copolymer then hydrolyzed in order to provide free sulfonic acid groups. Alkali metal salts of the sulfonic acids may be used.

The following are also useful monomers for group (b):

2-sulfoethyl acrylate
2-sulfoethyl methacrylate
2-sulfoethyl α-ethylacrylate
2-sulfoethyl α-propylacrylate
2-sulfoethyl α-butylacrylate
2-sulfoethyl α-hexylacrylate
2-sulfoethyl α-cyclohexylacrylate
2-sulfoethyl α-chloracrylate
2-sulfo-1-propyl acrylate
2-sulfo-1-propyl methacrylate
1-sulfo-2-propyl acrylate and methacrylate
2-sulfo-1-butyl acrylate and methacrylate
1-sulfo-2-butyl acrylate and methacrylate
3-sulfo-2-butyl acrylate and methacrylate
2-methyl-2-sulfo-1-propyl acrylate and methacrylate
2-methyl-1-sulfo-2-propyl acrylate and methacrylate
3-bromo-2-sulfo-1-propyl acrylate
3-bromo-1-sulfo-2-propyl acrylate
3-chloro-2-sulfo-1-propyl acrylate
3-chloro-1-sulfo-2-propyl acrylate
1-bromo-3-sulfo-2-butyl acrylate
1-bromo-2-sulfo-3-butyl acrylate
1-chloro-3-sulfo-2-butyl acrylate
1-chloro-2-sulfo-3-butyl acrylate
3-bromo-2-sulfo-1-butyl acrylate
3-bromo-1-sulfo-2-butyl acrylate

3-chloro-2-sulfo-1-butyl acrylate
3-chloro-1-sulfo-2-butyl acrylate
1-chloro-2-methyl-3-sulfo-2-propyl acrylate
1-chloro-2-methyl-2-sulfo-3-propyl acrylate
1-chloro-2-(chloromethyl)-3-sulfo-2-propyl acrylate
1-chloro-2-(chloromethyl)-2-sulfo-3-propyl acrylate
3-methoxy-2-sulfo-1-propyl acrylate
3-methoxy-1-sulfo-2-propyl acrylate
2-sulfocyclohexyl acrylate
2-phenyl-2-sulfoethyl acrylate
1-phenyl-2-sulfoethyl acrylate
3-sulfo-1-propyl acrylate
3-sulfo-1-butyl acrylate
4-sulfo-1-butyl acrylate
Ar-sulfophenyl acrylate
Ar-sulfophenyl methacrylate
2-(Ar-sulfophenoxy)ethyl acrylate
Para-styrene sulfonic acid
Ortho-styrene sulfonic acid
Para-isopropenyl benzene sulfonic acid
Para-vinyl benzyl sulfonic acid
Ortho-isopropenyl benzyl sulfonic acid
Sodium para-styrene sulfonate
Potassium ortho-styrene sulfonate
Methyl para-styrene sulfonate
Ethyl para-vinyl benzyl sulfonate
Ortho vinyl benzene sulfonic acid
Isopropyl ortho-isopropenyl benzene sulfonate
n-Butyl ortho-styrene sulfonate
Tertiary butyl para-styrene sulfonate
2-chloro-4-vinylbenzene sulfonic acid
4-bromo-2-isopropenyl benzene sulfonic acid
3-vinyl toluene-6-sulfonic acid, sodium salt
2-ethyl-4-vinyl-benzene sulfonic acid
2,3-dichloro-4-vinyl benzene sulfonic acid
2,3,5-tribromo-4-vinyl benzene sulfonic acid
2-chloro-3-vinyl-toluene-6-sulfonic acid
2,3-diethyl-4-vinyl-benzyl sulfonate, sodium salt

Alkenyl sulfonic acid compounds:

Ethylene sulfonic acid
Sodium ethylene sulfonate
Potassium ethylene sulfonate
Methyl ethylene sulfonate
Isopropyl ethylene sulfonate
1-propene 3-sulfonic acid
1-propene 1-sulfonic acid, sodium salt
1-propene 2-sulfonic acid, ethyl ester
1-butylene 4-sulfonic acid, n-butyl ester
1-butylene 3-sulfonic acid
Tertiary butylene sulfonic acid

Sulfoalkylacrylate compounds:

Sulfomethylacrylate
2-sulfoethylacrylate
Sulfomethylmethacrylate, sodium salt
2-sulfoethylmethacrylate, methyl ester
2-sulfoethylmethacrylate, potassium salt

Examples of polymerizable sulfonic acid compounds of the Formula XVIII above include

Methacryloxyisopropyl acid sulfophthalate
Methacryloxyisopropyl sulfobenzoate
Methacryloxyisopropyl acid sulfosuccinate
Methacryloxyethyl sulfobenzoate
Methacryloxyisopropyl sulfopropionate

There may also be used styrene disulfonic acid, vinylnaphthalene-sulfonic acid, and β-sulfoethyl vinyl ether.

The sulfonic acid monomer may be polymerized either in its acid form or in the form of a salt of an alkali metal, ammonium hydroxide, or a volatile amine, such as trimethylamine, triethylamine, triethanolamine, diethanolamine, diethylamine, morpholine, and so on. The copolymer may be in the acid form or it may be fully neutralized or partially neutralized by a basic material, such as any of those mentioned above, and preferably by ammonium hydroxide, or by sodium, lithium, or potassium hydroxide. The copolymer is preferably in free acid form when used for impregnating a nonwoven fabric so that it serves as its own acidic catalyst for the curing operation, which then requires only the application of heat such as to temperatures of 50° C. to 150° C. for times of a quarter minute (at the higher temperatures) to several (3–10) minutes at lower temperatures.

The monomers can be polymerized in conventional ways using, for example, a free-radical catalyst. The polymerization may be effected as a solution polymerization, a suspension polymerization, an emulsion polymerization, or a precipitation polymerization. Any suitable free-radical catalyst may be employed, and especially water-soluble types when the polymerization is to be effected in aqueous media. Examples include hydrogen peroxide, ammonium persulfate, or an alkali metal persulfate; a redox system using such a persulfate with a reducing agent such as sodium hydrosulfite. In solution systems involving organic solvents for the monomers and polymers, a free-radical initiator soluble in the particular medium may be employed such as benzoyl peroxide, lauroyl peroxide, tert-butyl peroxide, or hydroperoxide. The usual amounts of initiator may be employed such as from 0.1% to 6% on the weight of the monomer, and in the redox system the persulfate may be employed in amounts of about 0.05 to 1% or so in conjunction with about 0.05 to 1% of sodium hydrosulfite.

Chain-transfer agents and other molecular weight regulators may be used.

NONWOVENS

The fibrous webs may be formed in any suitable manner such as by carding, garnetting, or by dry deposition from an air suspension of the fibers. The thin web or fleece obtained from a single card may be treated in accordance with the present invention, but generally it is necessary and desirable to superpose a plurality of such webs to build up the mat to sufficient thickness for the end use intended, particularly in the making of heat insulation. In building up such a mat, alternate layers of carded webs may be disposed with their fiber orientation directions disposed at 60° or 90° angles with respect to intervening layers.

The fibers from which the webs may be made include cellulosic fibers such as cotton, rayon, jute, ramie, and linen; also cellulose esters such as cellulose acetate; silk, wool, casein, and other proteinaceous fibers; polyesters such as poly-(ethylene glycol terephthalate); polyamides such as nylon; vinyl resin fibers such as the copolymer of vinyl chloride and vinyl acetate, polymers of acrylonitrile containing 70% to 95% by weight of acrylonitrile including those available under the trademarks Orlon and Acrilan; siliceous fibers such as glass and mineral wools.

An aqueous dispersion of the water-insoluble copolymer of the present invention may be applied to the web or mat of fibers in any suitable fashion such as by spraying, dipping, roll-transfer, or the like. The concentration may be from 5% to 60% by weight, and preferably from 5% to 25%, at the time of application as an aqueous dispersion.

The binder dispersion or powder may be applied to the dry fibers after the formation or deposition of the web or mat so as to penetrate partially into or completely through the interior of the fibrous products. Alternatively, the binder dispersion or powder may be applied to the fibers as they fall through the settling chamber to their point of deposition. This is advantageously obtained by spraying the binder dispersion or powder into the settling chamber at some intermediate point between the top and the bottom thereof. By so spraying the fibers as they descend to the point of collection, it is possible to effect a thorough distribution of the binder among the fibers before they are collected into the product. In the production of certain fibrous products wherein a hot molten mass of a polymer, such as nylon or a fused siliceous mass or glass, is disrupted by jets of heated air or steam, the binder dispersion or powder may be sprayed directly on the fibers while still hot and very shortly before their deposition so that quickly after deposition the binder is set and bonds the fibers in proper relationship. Preferably, however, application of the binder dispersion to the fibrous product is made at room temperature to facilitate cleaning of the apparatus associated with the application of the binder dispersion. The binder dispersion may be applied to one or both surfaces of the fibrous product or it may be distributed through the interior as well.

The binder of the present invention may be applied in conjunction with other binders, such as glue. Similarly, the use of potentially adhesive fibers within the fibrous product may also be resorted to in conjunction with the use of a binder of the present invention.

If desired, the aqueous dispersion of the polymer and condensate may also contain from about ½ to 3% by weight of a wetting agent to assist penetration of the fibrous web or mat to which it is applied, and it may contain either a foaming agent to provide the binder in a foamed condition in the final product or it may contain a defoamer when the ingredients of the aqueous dispersion have a tendency to give rise to foaming and in a particular case such foaming is undesirable. The conventional wetting agents, including the alkali metal salts of di(C_6–C_{12})alkyl sulfosuccinic acid, such as the sodium salt of dioctylsulfosuccinic acid, may be used. The wetting agent may also serve as the emulsifier in preparing the polymer latex or it may be added after production of the latex. Conventional foaming and defoaming agents may be employed, such as sodium soaps, including sodium oleate for foaming and octyl alcohol or certain silicones for defoaming.

An acid catalyst may be included in the aqueous dispersion at the time it is applied to the fibrous web or it may be applied to the fibrous web before or after the copolymer is applied. Examples of acidic catalysts that may be employed include oxalic acid, dichloroacetic acid, para-toluenesulfonic acid, and acidic salts such as ammonium sulfate or chloride and amine salts, such as the hydrochloride of 2-methyl-2-aminopropanol-1.

The proportion of the polymer that is applied to the web or mat is such as to provide 5 to 50% (or, in some cases, even up to 75%) by weight of copolymer based on the total weight of copolymer and fibers. After application of the aqueous dispersion of the water-insoluble copolymer to the fibrous web, the impregnated or saturated web is dried either at room temperature or at elevated temperatures. The web is subjected, either after completion of the drying or as the final portion of the drying stage itself, to a baking or curing operation which may be effected at a temperature of about 210° to 750° F. for periods which may range from about one-half hour at the lower temperature to as low as five seconds at the upper temperature. The conditions of baking and curing are controlled so that no appreciable deterioration or degradation of the fibers or copolymer occurs. Preferably, the curing is effected at a temperature of 260° to 325° F. for a period of 2 to 10 minutes.

It is believed that the curing operation in some way causes reaction of the polymer molecules to effect cross-linking thereof to a condition in which the binder is highly resistant to laundering and dry-cleaning. This reaction involves the N-methylol groups of some polymer molecules with the reactive hydrogen-containing groups of others of the polymer molecules. It is also believed that the curing causes some reaction between the N-methylol groups of the polymer molecules and reactive groups in the fibers such as the hydroxyl groups of the cellulose fibers. While the precise nature of the reaction and the products thereby obtained are not clearly understood, it is presumed that the resistance to laundering and dry-cleaning is the result of the reaction between binder polymer molecules to cross-link them and/or the reaction between the binder polymer molecules and reactive sites of the fiber molecules. However, it is not intended to limit the invention by any theory of action herein stated.

The bonded fibrous products of the present invention are characterized by softness, flexibility, resistance to discoloration on exposure to ultraviolet light, resistance to chlorinated hydrocarbon dry-cleaning fluids, and resistance to laundering. Because of the softness and flexibility and good draping qualities of the products of the present invention, they are particularly well adapted for use in garments where porosity, especially to moisture vapor, and soft hand and feel, make the products advantageous where contact with the skin of a wearer may be involved. In general, the products are quite stable dimensionally and have good resilience and shape-retention properties. They are adapted for use not only in garments but as padding or cushioning, and moisture-absorbing articles, such as bibs and diapers. They are also useful as heat- and sound-insulating materials and as filtration media, both for liquids and gases. They can be laminated with paper, textile fabrics, or leather to modify one or both surfaces of the latter materials. They may be adhered to films of cellophane, polyethylene, Saran, polyethylene glycol terephthalate (Mylar) or metallic foils, such as of aluminum, to improve the tear strength of such films and foils, to make the latter more amenable to stitching, and to modify other characteristics including strength, toughness, stiffness, appearance, and handle.

To assist those skilled in the art to practice the present invention, the following modes of operation are suggested by way of illustration, parts and percentages being by weight and the temperatures in degrees centigrade unless otherwise specifically noted.

In the following examples, the tests used with nonwoven fabrics are as follows:

(a) Absorbency test

A sample (4 in. x 4 in.) of the nonwoven is folded twice to give a 2 in. x 2 in. square which is then passed between steel rollers at 60 p.s.i. A paper clip is attached to weight the sample which is then placed on the top of a water bath in a beaker at ambient temperature. The time required by the nonwoven to become saturated is recorded as the "rewet" time and the time required for the sample to sink to the bottom of the beaker is recorded as the "sink" time.

(b) Tensile strength test

A strip 1 in. x 4 in. of each nonwoven is cut in the cross-machine direction, soaked in water, percholorethylene (PCE) or isopropanol (IPA) (each at room temperature) for 30 minutes, and with the ends of the strip clamped in the jaws of a tensile testing machine, it is then extended to the break.

(c) Washing

Sections of the nonwoven (10 in. x 10 in.) are washed in a conventional home laundry washing machine using terrycloth towels as ballast and ¼ cup of the commercial detergent Tide in 16 gals. of water at 140° F. using a 34 min. cycle (14 min. wash, 2 min. rinse, 2 min. spin).

(d) Wipe rate test

A 4 in. x 4 in. piece of the bonded cotton (about 8 oz./yd.^{2}) or nonwoven (about 0.5 oz./yd.^{2}) fabric is used to wipe up a 2 ml. water spill on a stainles steel surface. The sample's ability to wipe up the water is rated on a scale of 1 to 5 using the completeness of the wipe, whether a film of water was left or whether beads of water formed on the surface as criteria. A terrycloth towel would rank 1, i.e., the best, unbonded cotton is ranked 1–2, and if the water is not wiped up at all but smeared into a thin film the rank is 5.

(1) A solution of 180 parts sodium vinyl sulfonate (SVS) in 5049 parts deionized water is heated to 80° C. A solution of 31.5 parts sodium persulfate in 148.5 parts water is added. During a period of 150–160 min., while the temperature of the reaction mixture is maintained at 81±2° C., the following emulsified mixture is added:

	Parts
Deionized water	3215.7
Dicapryl sulfosuccinate (Na salt) (60%) in 50:50 mix of water and isopropanol	150.3
Methylolated acrylamide sol'n (50%)	360.0
Ethyl acrylate (EA)	8640.0

NOTE.—The methylolated acrylamide is essentially a mixture of N-methylolacrylamide and acrylamide in about a 1:1 ratio.

At the end of the addition, the mixture is heated to about 85° C. to complete the polymerization. Additional initiator may be added to complete polymerization if necessary. The product is cooled, filtered to remove small amounts of coagulum, if any, and packaged. The product is a milky-white dispersion of a copolymer of 96% ethyl acrylate, 2% sodium vinyl sulfonate, about 1.2% N-methylol acrylamide, and about 0.8% acrylamide with the following properties:

Percent T.S.	50.0±0.5
Viscosity ....cps	200±100
pH	2.6±0.3

(2)(a) A viscose nonwoven batt weighing about 0.5 oz./yd.^{2} is padded (one dip) through a bath containing 15% polymer solids (obtained by dilution of the dispersion made in (1)) and 0.5% NH_4Cl as catalyst and squeezed between rolls held with an air pressure of 30 p.s.i. (one nip) to give approximately 150% wet pickup. The saturated webs are air dried and then cured for 3 minutes at 300° F. in a laboratory oven. These webs are evaluated for absorbency and tensile strength by the tests described in (c) and (d) above.

(b) Pieces of cotton of the type used in surgery are also padded (one dip and one nip) through the same bath, air-dried and cured 3 minutes at 300° F. and used to evaluate the ability to wipe up a water spill.

(3) Procedure (1) is repeated except that 540 parts of sodium vinyl sulfonate and 8187 parts of ethyl acrylate is used and the 60% dicapryl sulfosuccinate is replaced with 60 parts of sodium lauryl sulfate. The resulting latex is an approximately 51% solids aqueous dispersion of a copolymer of 95% EA, 3% SVS, and about 1% each of acrylamide and methylolacrylamide.

(4) Procedure (3) is repeated except that the SVS is omitted, the amount of 50% methylolated acrylamide is raised to 720 parts and the amount of EA is increased to 8540 parts. The resulting approximately 51% solids dispersion contains a copolymer of 96% EA, about 2% N-methylolacrylamide, and 2% acrylamide.

(5) There is added to the dispersion obtained in (4) about 5 parts, per 100 parts of the dispersion, of dicapryl sulfosuccinate, sodium salt.

(6) Procedure (3) is repeated except that the SVS is omitted, the amount of EA is changed to 8410 parts, the amount of the 50% methylolated acrylamide is doubled to 720 parts, and 225 parts of itaconic acid (IA) is added. The resulting polymer is a copolymer of 93.5% EA, 2.5% IA, about 2% acrylamide, and about 2% N-methylolacrylamide.

Table I summarizes the results of absorbency tests (a) on the bonded fabrics made according to procedure (2)(a) or (b) with the polymers of procedures (1), (3), (4), (5) and (6) before and after washing one or more times according to wash test (c). It also lists the tensile strength in ounces per inch width when soaked in water and perchloroethylene (PCE). The table shows that (4), (5), and (6) which are in effect controls lack the absorbency and/or rewettability of the products of (1) and (3) made from copolymer of the present invention.

TABLE I

	Absorbency (seconds)						Water wipe rating	Wet tensile strength (oz./in.)	
	Initial		After 1 wash		After 10 washings				
	Rewet	Sink	Rewet	Sink	Rewet	Sink		H_2O	PCE
Polymer:									
(1)	<1	2	5	5	<1	4	1–2	5.5	4.8
(3)	1	2	1	5	<1	3	1	6.0	9.6
(4)	315	>600	>300	>300	>300	>300	5	8.3	7.1
(5)	1	3	141	141	>300	>300	4	6.1	7.2
(6)	395	>600	530	>600	----------	----------	5	6.8	9.2

Polymers of (4) and (5) are in effect controls since they lack component (b) in the copolymer but are otherwise similar to those of (1) and (3) above. Polymer of (6) shows that use of the weaker carboxylic acid, itaconic acid, cannot produce the absorbency and wiping characteristics of the copolymers of the present invention.

(7) Procedure (1) above is used to prepare an aqueous dispersion of a copolymer of 92% of EA, about 1.6% of acrylamide, about 2.4% of N-methylol-acrylamide, and 4% of the sodium salt of 2-acrylamido-2-methyl-propanesulfonic acid.

(8) Procedure (1) is used to prepare an aqueous dispersion of a copolymer of 92% (EA), about 1% acrylamide, about 1% N-methylolacrylamide and 6% of the sodium salt of methacryloxyisopropyl acid sulfophthalate.

(9) Procedure (3) is used to produce an aqueous dispersion of a copolymer of 89% EA, 4% of itaconic acid, about 2% acrylamide, about 2% N-methylolacrylamide, and 3% of the 1:1 mole ratio adduct of butylene glycol dimethacrylate and sodium bisulfite.

(10) The dispersions obtained in Procedures (7), (8), and (9) are used to bond a viscose rayon nonwoven as in (2)(a) above and to bond a piece of surgical cotton in (2)(b) above and then the products are tested with the results set out in Table II. In this instance, the wet tensile strength is determined in water and isopropanol (IPA) instead of water and perchloroethylene.

TABLE II

	Absorbency (seconds)						Water wipe rating	Wet tensile strength (oz./in.)	
	Initial		After 1 wash		After 10 washings				
	Rewet	Sink	Rewet	Sink	Rewet	Sink		H_2O	IPA
Polymer:									
(7)	<1	3	1	4	1	2	1–2	6.4	4.6
(8)	<1	3	8	15	1	24	1–2	5.5	3.8
(9)	<1	5	----------	----------	1	6	1–2	6.5	10.1

(11) The procedure of (1) above is repeated replacing the SVS with 180 parts of sodium α-sulfoethyl acrylate. When the resulting copolymer dispersion is used for bonding a nonwoven fabric or a piece of surgical cotton in accordance with (2)(a) and (2)(b) hereinabove, the results are similar to those obtained with the copolymer of (1) (see Table I).

(12) The procedure of (1) above is repeated replacing the SVS with 450 parts of sodium allylsulfonate. When the resulting copolymer dispersion is used for bonding a nonwoven fabric or a piece of surgical cotton in accordance with (2)(a) and (2)(b) hereinabove, the results are similar to those obtained with the copolymer of (1) (see Table I).

(13) The procedure of (1) above is repeated except the SVS is omitted, 320 parts of potassium styrenesulfonate (PSS) is included in the emulsified mixture, and the EA is replaced with 8500 parts of methyl acrylate (MA), resulting in an aqueous dispersion of a copolymer of about 94.5% MA, about 3.5% PSS, about 1% of N-methylolacrylamide, and about 1% of acrylamide. When the resulting copolymer dispersion is used for bonding a nonwoven fabric or a piece of surgical cotton in accordance with (2)(a) and (2)(b) hereinabove, the results are similar to those obtained with the copolymer of (1) (see Table I).

(14) The procedure of (13) above is repeated replacing the PSS with 550 parts of ammonium acryloxyethyl sulfopropionate (AESP) and the MA with a mixture of 600 parts of acrylonitrile (AN), 70 parts of acrylic acid (AA), 4200 parts of MA and 3400 parts of EA, resulting in an aqueous dispersion of a copolymer of about 6.1% AESP, about 6.7% AN, about 0.8% AA, about 1.0% N-methylolacrylamide, about 1.0% acrylamide, about 46.6% MA, and 37.8% EA. When the resulting copolymer dispersion is used for bonding a non-woven fabric or a piece of surgical cotton in accordance with (2)(a) and (2)(b) hereinabove, the results are similar to those obtained with the copolymer of (1) (see Table I).

(15) The procedure of (13) above is repeated replacing the PSS with 880 parts of sodium acryloxyethyl o-sulfobenzoate (AESB), and the methylolated acrylamide with 800 parts of a 50% aqueous solution of N-methylol-4-pentenoguanamine (MPG), and the MA with 7720 parts EA, resulting in an aqueous dispersion of a copolymer of about 9.8% AESB, 4.5% MPG, and 85.7% EA. When the resulting copolymer dispersion is used for bonding a non-woven fabric or a piece of surgical cotton in accordance with (2)(a) and (2)(b) hereinabove, the results are similar to those obtained with the copolymer of (1) (see Table I).

(16) The procedure of (1) above is repeated replacing the SVS with 660 parts of the sodium salt of acryloxyethyl acid 3,5-disulfophthalate (AEDSP), the methylolated acrylamide with 260 parts of N-methylol-β-ureidoethyl acrylate (MUA), and the EA with a mixture of 7600 parts of EA and 480 parts of β-hydroxyethyl acrylate (HEMA), resulting in an aqueous dispersion of a copolymer of about 7.3% AEDSP, 2.9% MUA, 5.3% HEMA, and 84.5% EA. When the resulting copolymer dispersion is used for bonding a nonwoven fabric or a piece of surgical cotton in accordance with (2)(a) and (2)(b) hereinabove, the results are similar to those obtained with the copolymer of (1) (see Table I).

(17) The procedure of (1) above is repeated replacing the SVS with 810 parts of the sodium salt of 8-acryloxyoctyl acid 3,5-disulfophthalate (AODP), the methylolated acrylamide with 360 parts of an aqueous solution containing 80 parts of N-methylolmethacrylamide and 100 parts of N-methylol-4-pentenamide (MPA), and the EA with a mixture of 3600 parts of isopropyl acrylate (iPA) and 4400 parts of MA, resulting in an aqueous dispersion of a copolymer of about 9% AODP, about 0.9% N-methylolmethacrylamide, about 1.1% MPA, 40% iPA, and 49.0% MA. When the resulting copolymer dispersion is used for bonding a nonwoven fabric or a piece of surgical cotton in accordance with (2)(a) and (2)(b) hereinabove, the results are similar to those obtained with the copolymer of (1) (see Table I).

(18) The procedure of (1) above is repeated replacing the SVS with 1000 parts of the ammonium salt of acryloxyethoxyethoxyethyl acid 4 - sulfophthalate (AE3EOSP), the methylolated acrylamide with 400 parts of an aqueous solution containing 50 parts of N-methylolallylguanamine (AMG) and 150 parts of N-methoxymethyl-4-pentenoguanamine (MOMPG) and the EA with a mixture of 4600 parts of propyl acrylate (PA) and 3300 parts of EA, resulting in an aqueous dispersion of a copolymer of about 11% AO3EOSP, 0.5% MAG, 1.6% MOMPG, 50.5% PA, and 36.4% EA. When the resulting copolymer dispersion is used for bonding a nonwoven fabric or a piece of surgical cotton in accordance with (2)(a) and (2)(b) hereinabove, the results are similar to those obtained with the copolymer of (1) (see Table I).

(19) Procedure (3) is repeated except that the sodium lauryl sulfate is replaced with 150 parts of sodium diocytl sulfosuccinate (60% in a 50:50 mixture of water and isopropanol).

A portion of the resulting latex is used to bond a nonwoven fabric and cotton wadding by Procedures (2)(a) and (b) with results similar to those obtained with polymer (3) as shown in Table I.

(20) Procedure (1) is repeated except that the SVS is replaced by 210 parts of 2-acrylamido-2-methyl-3-butanesufonic acid and the surfactant solution is replaced with 130 parts of a 50% solution in a 50:50 mix of water and isopropanol of the sodium salt of di-dodecyl sulfosuccinate.

A portion of the resulting latex is used to bond a nonwoven fabric and cotton wadding by Procedures (2)(a) and (b) with results similar to those obtained with polymer (3) as shown in Table I.

We claim:

1. As an article of manufacture, a nonwoven fabric bonded by at least 5% by weight, based on the weight of fibers in the fabric, of a copolymer of

(a) 0.2 to 10% by weight of at least one α,β-monoethylenically unsaturated monomer containing an amino group in which the nitrogen atom is attached to a carbon atom of a 1,3,5-triazine ring, a carboxylamide group, or a ureido group, the nitrogen atom of such amino, carboxylamido, or ureido group being substituted by a methylol or methoxymethyl group,

(b) 0.2 to 11% by weight of at least one α,β-monoethylenically unsaturated monomer, in acid or salt form, having a sulfur-containing acid group and containing no basic nitrogen atom and

(c) the balance to make 100% by weight, of at least one other α,β-monoethylenically unsaturated monomer which contains no sulfur-containing acid group, or salt thereof, and no basic nitrogen atom.

2. As an article of manufacture, a nonwoven fabric according to claim 1 wherein the copolymer comprises from about 0.5 to 4% by weight of monomeric material (a), and from about 0.5 to 8% by weight of monomeric material (b).

3. A nonwoven fabric according to claim 1 wherein the fabric is formed of cotton or rayon fibers.

4. A nonwoven fabric according to claim 2 wherein the fabric is formed of cotton or rayon fibers.

References Cited

UNITED STATES PATENTS

2,971,935	2/1961	Floria	260—79.3 MU
3,007,887	11/1961	Essig	117—161 UN
3,090,704	5/1963	Collins et al.	117—138.8 F
3,123,589	3/1964	Vanderkool et al.	260—79.3 MU
3,213,053	10/1965	Kendrick	117—161 UT
3,457,209	7/1969	Mikofalvy	117—140 A

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