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(54) **Water-absorbent nonwoven fabric and process for producing same.**

(57) A nonwoven fabric having an excellent water absorption, a satisfactory softness and hand feeling, and a superior processability and wet mechanical strength, comprises synthetic fibers and water-absorbent cellulosic fibers intertwined with each other, the water-absorbent cellulosic fibers comprising cross-linked carboxymethyl cellulose fibers having a carboxymethyl group-substitution degree of 0.35 to 1.6, and being produced by forming a precursory nonwoven web from the synthetic fibers and cellulose fibers intertwined with each other, and carboxy methylating and cross-linking separately or simultaneously the cellulose fibers in the precursory nonwoven fabric by using a carboxymethylating agent and a cross-linked agent, to convert the precursory nonwoven web to a water-absorbent nonwoven fabric.

## BACKGROUND OF THE INVENTION

## 1. Field of the Invention

5 The present invention relates to a water-absorbent nonwoven fabric and a process for producing the same. More particularly, the present invention relates to a water-absorbent nonwoven fabric comprising synthetic fibers and water-absorbent cellulosic fibers intertwined with each other, having a high water-absorption similar to that of conventional high water-absorbent resins, and exhibiting a satisfactory softness, hand feeling, processability and an excellent mechanical sheet strength even after absorbing water therein, and a process for  
10 producing the same.

## 2. Description of the Related Art

15 Recently, as water-absorbent material capable of absorbing water and an aqueous solutions containing salts, for example, an aqueous common salt solution, a group of resinous materials, which are referred to as high water-absorbent resins, are known. Basically, the water absorbent resinous materials are produced by slightly cross-linking water-soluble polymeric materials to convert them to water-insoluble and water-absorbent materials. As examples of the high water-absorbent materials, starch derivatives which are produced by graft-copolymerizing acrylonitrile with starch and hydrolyzing the graft-polymerized product; cross-linked starch derivatives which are produced by graft-copolymerizing acrylic acid metal salts with starch; cross-linked acrylic acid copolymers which are produced by copolymerizing acrylic acid with a copolymerizing cross-linking agent; and methyl methacrylate-vinyl acetate copolymer derivatives which are produced by hydrolyzing methyl methacrylate-vinyl acetate copolymers, are known and some of these are now used in practice. Almost all of the conventional water-absorbent materials are supplied in the form of a fine powder or grains. Therefore, when  
20 they are practically utilized, they are usually not used alone but used together with a suitable supporting material, to form a composite article. For example, in the production of disposable diapers, usually the water-absorbent resin powder is evenly distributed between a pair of fluff pulp mats. In the production of other water-absorbent articles, the water-absorbent resin powder is employed by being interposed between a pair of sheet materials, for example, paper sheets, nonwoven fabrics or synthetic resin sheets.

25 In the production of the above-mentioned composite articles, a desired amount of the water-absorbent resin powder must be evenly sprinkled on or in the supporting material and the sprinkled water-absorbent resin powder must be fixed on or in the supporting material so as to prevent the dropping-off of the water-absorbent resin powder. This production is complicated and difficult. Also, when the water-absorbent article is used, sometimes, the resultant water-absorbed resin gel particles move to the outside of the article and/or are disconnected from the article. Further, the conventional composite article is disadvantageous in that when fluff pulp mats or paper sheets, which are most popular as a supporting material for the water-absorbent resin powder, are used, the resultant composite article exhibits a reduced mechanical strength and is easily deformed after absorbing water therein.

30 Various attempts were made to eliminate the above-mentioned disadvantages. For example, Japanese Unexamined Patent Publication (Kokai) Nos. 57-21,549 and 63-159,440 disclose a method in which a high water-absorbent resin is formed into fibers, and then the water-absorbent fibers are formed into a sheet; Japanese Examined Patent Publication (Kokoku) No. 55-50,074 discloses a method in which a water-absorbent resin powder is dispersed in a binder resin solution to provide a coating liquid and the coating liquid is coated on a surface of a supporting material; and Japanese Unexamined Patent Publication (Kokai) Nos. 59-204,975, 60-149,609, 63-10,638, 63-105,044, 2-111,484, and 61-194,300 disclose a method in which a supporting sheet,  
35 for example, fluff pulp sheet, paper sheet or nonwoven fabric, is impregnated with a water-soluble monomer solution containing a cross-linking monomer, and the impregnated monomer is polymerized together with the cross-linking monomer to provide a cross-linked water-absorbent polymer fixed to the supporting sheet. Other attempts were also made to eliminate the above-mentioned disadvantages. For example, Japanese Examined Patent Publication (Kokoku) No. 59-45,695 and Japanese Unexamined Patent Publication (Kokai) Nos. 62-275,146 and 1-203,084 disclose a method of producing a water absorbent composite material by impregnating a fluff pulp sheet, paper sheet or nonwoven fabric with a water-soluble polymeric material together with a cross-linking agent and then subjecting the impregnated sheet to a cross-linking reaction of the water-soluble polymeric material with the cross-linking agent. Also, Japanese Unexamined Patent Publication Nos. 60-71,797  
40 and 61-89,364 disclose a method of imparting a water-absorbing property to a cellulose fiber sheet by converting a cellulose structure of the cellulosic fibers to a carboxymethyl cellulose salt structure while maintaining the sheet form of the cellulosic fibers.

45 Among the above-mentioned known methods, the method in which a high water-absorbent resin in the

form of fibers is produced and optionally the water-absorbent resin fibers are formed into a sheet; is disadvantageous in that since the production process is complicated and a specific material has to be used, the process cost is high.

Also, the method in which the water-absorbent resin powder is dispersed in a binder resin solution, and the resultant coating liquid is coated on a surface of a supporting material, is disadvantageous in that since a film made from the binder resin serves as a barrier to the water-absorbent resin powder, the water-absorbing rate of the resultant article is significantly reduced. To avoid this disadvantages, if the binder resin is employed in a reduced amount, or selected from water-soluble resins, the resultant water-absorbent article necessarily exhibits a disadvantage in that when water is absorbed, the resultant water-absorbed resin gel particles are disconnected from the supporting material.

Various types of the methods, in which a fluff pulp sheet, pulp paper sheet or nonwoven fabric is impregnated with a water-soluble monomeric material together with a cross-linking agent, and then the water-soluble monomeric material is converted to a crosslinked, water-absorbent polymeric material to provide a water-absorbent composite material, were researched. However, the methods are disadvantageous in that when the monomeric material is impregnated in a large amount in the supporting sheet and then polymerized and cross-linked, the softness of the supporting sheet is reduced and the resultant composite article exhibits an enhanced stiffness and fragility and a significantly poorer processability and hand feeling (touch).

Also, various methods for producing a water-absorbent composite material by impregnating a fluff pulp sheet, a paper sheet or nonwoven fabric with a water-soluble resin together with a cross-linking agent and cross-linking the water-soluble resin with the crosslinking agent to convert the water-soluble resin to a water-insoluble, water-absorbent resin, are known. In these methods, for the purpose of providing a water-absorbent resin having an excellent water-absorbing property, the water-soluble resin to be impregnated in the supporting sheet is required to have a high molecular weight. This high molecular weight causes an aqueous solution of the water-soluble resin to exhibit a high viscosity and thus the impregnation of the supporting sheet with the aqueous water-soluble resin solution becomes difficult. Also, resultant water-absorbent composite material exhibits an increased stiffness and fragility and a poor processability and hand feeling similar to those of the above-mentioned monomer-impregnating methods.

Also, the method by which an enhanced water-absorbing property is imparted to a cellulosic fiber sheet by forming a sheet from cellulosic fibers, and cellulosic structure of the cellulosic fibers are converted to cross-linked carboxymethyl cellulose structure, while maintaining the cellulosic fibers in the sheet form, is advantageous in that the softness, hand feeling and processability of the resultant water-absorbent sheet are satisfactory. Nevertheless, this method is disadvantageous in that after absorbing water, the cross-linked carboxymethyl cellulose fiber sheet exhibits a significantly poorer mechanical strength and thus is easily broken.

## SUMMARY OF THE INVENTION

An object of the present invention is to provide a water-absorbent nonwoven fabric which is free from the disadvantages of the conventional high water-absorbent materials, has a high water-absorption similar to the conventional high water-absorbent resins and exhibits a satisfactory softness, hand feeling and processability and a satisfactory mechanical strength even after absorbing water, and a process for producing the same.

The above-mentioned object can be attained by the water-absorbent nonwoven fabric of the present invention comprising synthetic fibers and water-absorbent cellulosic fibers intertwined with each other, the water-absorbent cellulosic fibers comprising a cross-linked carboxymethyl cellulose having a degree of substitution with carboxymethyl groups of 0.35 to 1.6.

The water-absorbent nonwoven fabric of the present invention preferably has a wet tensile strength of 0.1 to 10.0 kgf/25 mm determined in accordance with Japanese Industrial Standard P 8135.

Also, the water-absorbent nonwoven fabric of the present invention has a pure water absorption of 25 to 160 times the dry weight of the nonwoven fabric.

The process of the present invention for producing a water-absorbent nonwoven fabric as mentioned above, comprises the steps of forming a precursory nonwoven web in which synthetic fibers and cellulose fibers are intertwined with each other; subjecting the cellulose fibers in the precursory web to a carboxymethylating treatment with monochloroacetic acid salt in the presence of an alkali metal hydroxide in a reaction medium consisting of at least one member selected from the group consisting of water and lower aliphatic alcohol having 2 to 4 carbon atoms; and subjecting the resultant carboxymethyl cellulose fibers in the precursory web to a cross-linking treatment with a cross-linking agent, to convert the precursory web to a water-absorbent nonwoven fabric.

Another process of the present invention for producing a water-absorbent nonwoven fabric as mentioned above, comprises the steps of forming a precursory nonwoven web in which synthetic fibers and cellulose fib-

ers are intertwined with each other; subjecting the cellulose fibers in the precursory web to a cross-linking treatment with a cross-linking agent; and subjecting the cross-linked cellulose fibers in the precursory web to a carboxymethylating treatment with monochloroacetic acid salt in the presence of an alkali metal hydroxide in a reaction medium consisting of at least one member selected from the group consisting of water and lower aliphatic alcohol having 2 to 4 carbon atoms, to convert the precursory nonwoven web to a water-absorbent nonwoven fabric.

Still another process of the present invention for producing a water-absorbent nonwoven fabric as claimed in claim 1, comprising the steps of forming a precursory web in which synthetic fibers and cellulose fibers are intertwined with each other; subjecting the cellulose fibers in the precursory web to a carboxymethylating treatment with monochloroacetic acid salt in the presence of an alkali metal hydroxide in a reaction medium consisting of at least one member selected from the group consisting of water and lower aliphatic alcohol having 2 to 4 carbon atoms, and simultaneously to a cross-linking treatment with a cross-linking agent, to convert the precursory web to a water-absorbent nonwoven fabric.

In one embodiment of the above-mentioned processes of the present invention, the precursory nonwoven web prepared by blending the synthetic fibers with the cellulose fibers and forming a nonwoven web from the fiber blend in accordance with a dry web-forming method.

In another embodiment of the above-mentioned processes of the present invention, the precursory nonwoven web is prepared by blending the synthetic fibers with the cellulose fibers and forming a nonwoven web from the fiber blend in accordance with a paper-making method.

In still another embodiment of the above-mentioned processes of the present invention, the precursory nonwoven web is prepared by forming a nonwoven web from the synthetic fibers in accordance with a dry nonwoven fabric-forming method, wet nonwoven fabric-forming method, spun-bonding method or melt-blowing method; separately forming a cellulose fiber sheet from cellulose fibers in accordance with a wet or dry paper-making method; laminating the cellulose fiber sheet on the synthetic fiber nonwoven web; and intertwining the cellulose fibers and the synthetic fibers with each other in accordance with a water-jet intertwining method, as described, for example, in "Research Disclosure", 17060, June, 1978.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The materials usable for forming the water-absorbent nonwoven fabric of the present invention will be explained in detail as follows.

The synthetic fibers usable for the present invention can be selected from known synthetic fibers, for example, polyolefin fibers, polyester fibers, polyamide fibers, polyacrylic acid ester fibers and polyurethane fibers. The synthetic fibers may be utilized in the form of a fiber mass or a sheet, namely a nonwoven fabric.

The synthetic fiber nonwoven fabric usable for the present invention may be selected from conventional synthetic fiber nonwoven fabrics produced by known methods, for example, dry nonwoven fabric-forming method, wet nonwoven fabric-forming method, spun-bonding method and melt-blowing method.

The synthetic fibers are not restricted to those having a specific thickness. Preferably, the synthetic fibers have a d tex of 0.33 to 11.1 (a denier of 0.3 to 10). If the d tex of the synthetic fibers is more than 11.1 (a denier more than 10), the resultant precursory nonwoven fabric exhibits a reduced softness and the resultant water-absorbent nonwoven fabric exhibits an unsatisfactory softness, hand feeling and processability. Also, if the d tex of the synthetic fibers is less than 0.33 (a denier less than 0.3), the resultant water-absorbent nonwoven fabric sometimes has an excessively high density and exhibits a paper-like appearance and a stiff hand feeling, and thus it becomes difficult to control the appearance and physical and chemical properties of the resultant water-absorbent nonwoven fabric.

In the nonwoven fabric of the present invention, the synthetic fibers may be partially bonded to each other, to an extent such that the water absorption of the resultant nonwoven fabric is not restricted by the bonding. This bonding effectively enhances the resistance of the resultant nonwoven fabric to deformation or breakage thereof.

In the water-absorbent nonwoven fabric of the present invention, the synthetic fibers are uniformly mixed and intertwined with water-absorbent cellulosic fibers. The water-absorbent cellulosic fibers comprises a cross-linked carboxymethyl cellulose having a degree of substitution with carboxymethyl groups of 0.35 to 1.6.

The mixing ratio of the synthetic fibers to the water-absorbent cellulosic fibers is preferably in the range of from 1:1 to 1:19, more preferably from 1:2 to 1:10.

If the mixing ratio of the synthetic fibers to the cellulosic fibers is more than 1:1, the content of the cellulosic fibers in the resultant nonwoven fabric becomes too small and thus the resultant nonwoven fabric exhibits an unsatisfactory water absorption. Also, if the mixing ratio is less than 1:19, it becomes difficult to evenly intertwine the synthetic fibers and the water-absorbent cellulosic fibers, and thus when the resultant nonwoven

fabric is subjected to a water absorption, the cellulosic fibers are easily separated from the fabric and the resultant nonwoven fabric exhibits a reduced wet tensile strength.

The water-absorbent cellulosic fibers usable for the present invention are prepared by carboxymethylating and cross-linking cellulose fibers.

5 The cellulose fibers usable for the present invention can be selected from conventional cellulose fibers, for example, wood pulp fibers, non-wood pulp fibers made from herbaceous plants, and regenerated cellulose fibers.

10 The pulp fibers made from woods include chemical pulp fibers which are produced from soft wood chips or hard wood chips by a kraft pulping method, sulfite pulping method, soda pulping method, or polysulfide pulping method; mechanical pulp fibers which are made by mechanically pulping wood chips by using a refiner; semi-chemical pulp fibers made by pre-treating wood chips with a chemical reactant and then mechanically pulping the treated chips; and waste paper pulp fibers. The pulp fibers as mentioned above may be bleached or not bleached.

15 The non-wood pulp fibers made from herbaceous plants include those made by pulping cotton fibers, Manilla hemp fibers, flax fibers, straw fibers, bamboo fibers, bagasse fibers, kenaf fibers, Kozo (paper mulberry) fibers and Mitsumata fibers by the pulping method similar to that applied to the wood chips.

20 The regenerated cellulose fibers include viscose rayon fibers which are produced by converting cellulose material to a viscose solution, spinning the viscose solution into filamentary streams and regenerating the filamentary viscose solution streams in an acid solution; copper-ammonia rayon fibers which are produced by dissolving a cellulose material in a copper-ammonia solution, spinning the resultant cellulose solution, and regenerating the resultant filamentary cellulose solution streams in an acid solution; and other regenerated cellulose fibers produced, for example, by dissolving a cellulose material in a non-aqueous solvent, for example, N-methylmorpholine-N-oxide and converting the resultant solution to fibers.

25 It is known that cellulose derivative fibers having a high water absorption can be obtained by carboxymethylating and cross-linking cellulose fibers. Various methods are known for carboxymethylating the cellulose fibers. Basically, the cellulose fibers can be carboxymethylated by reacting the cellulose fibers with an alkaline hydroxide compound and a monochloroacetic acid salt in a reaction medium consisting of at least one member selected from the group consisting of water and aliphatic alcohols having 2 to 4 carbon atoms, for example, isopropyl alcohol. Japanese Unexamined Patent Publication (Kokai) Nos. 60-71,797 and 61-89,364 disclose a method of carboxymethylating a cellulose fibers without changing the form of the cellulose fibers. The alkaline hydroxide compound is preferably selected from alkali metal hydroxides, more preferably sodium hydroxide which is inexpensive.

30 The monochloroacetic acid salt is preferably selected from alkali metal salts and ammonium salts of monochloroacetic acid, more preferably sodium monochloroacetate and potassium monochloroacetate.

35 The method of introducing cross-linkages into the cellulose fibers is not restricted to a specific type of method. In an embodiment, a cross-linking agent is reacted with the cellulose fibers and then the crosslinked cellulose fibers are subjected to a carboxymethylating reaction. In another embodiment, the cross-linking reaction and the carboxymethylating reactions are simultaneously applied to the cellulose fibers. In still another embodiment, the cellulose fibers are carboxymethylated and then cross-linked.

40 The cross-linking agent usable for the present invention is preferably selected from aldehydes, for example, formaldehyde and glyoxal; N-methylol compounds, for example, dimethylolurea, dimethylolethyleneurea, and dimethylolimidazolidone; polycarboxylic acids, for example, oxalic acid, maleic acid, succinic acid and polyacrylic acid; polyepoxy compounds, for example, ethyleneglycoldiglycidylether, polyethyleneglycoldiglycidylether and diepoxybutane; divinyl compounds, for example, divinyl sulfone, and methylene bis-acrylamide; polyhalide compounds, for example, dichloroacetone, dichloropropanol and dichloroacetic acid; halohydrin compounds, for example, epichlorohydrin and epibromohydrin; and polyaziridine compounds.

45 The amount of the cross-linkages is variable depending on the type of the cross-linking agent and the reaction conditions. Preferably, the cross-linking agent is used in an amount of 0.1 to 10% by weight, more preferably 0.5 to 8% by weight, based on the weight of the cellulosic fibers.

50 The cross-linked, carboxymethylated cellulosic fibers has a pure water absorption which is variable depending on a degree of substitution with carboxymethyl groups and a density of the cross-linkages. Theoretically, the pure water absorption of the water-absorbent cellulosic fibers increases with an increase in the degree of substitution with the carboxymethyl groups. Nevertheless, the degree of substitution with the carboxymethyl groups is preferably in the range of from 0.35 to 1.6 from the view point of practice. Even if the degree of substitution with the carboxymethyl groups is increased to a level more than 1.6, the resultant water-absorbent cellulosic fibers exhibit a saturated pure water absorption and thus the resultant nonwoven fabric becomes costly.

The carboxymethylating reaction applied to the cellulosic fibers at a degree of substitution more than 1.6

sometimes causes a depolymerization of cellulose molecules and thus the resultant product exhibits a reduced water absorption.

Also, if the degree of substitution with carboxymethyl groups is less than 0.35, the resultant nonwoven fabric exhibits an unsatisfactory water absorption.

The water absorption of the cellulosic fibers increases with a decrease in the density of the cross-linkages. If the cross-linkage density is too low, the resultant water-absorbent cellulosic fibers exhibit a reduced mechanical strength when the fibers pickup water and are gelled. Also, a water-soluble carboxymethyl cellulose remains in the water-absorbent cellulosic fibers and thus the resultant nonwoven fabric exhibits an increased stickiness. Also, if the cross-linkage density is too high, the resultant cellulosic fibers exhibit a reduced water absorption.

Preferably, the degree of substitution with carboxymethyl groups and the cross-linkage density of the water absorbent cellulosic fibers are set forth so that the resultant woven fabric exhibits a pure water absorption of 25 to 160 times, more preferably 30 to 150 times, the dry weight of the nonwoven fabric.

The water-absorbent nonwoven fabric of the present invention comprises synthetic fibers and water-absorbent cellulosic fibers intertwined with each other. The water-absorbent cellulose fibers comprises cross-linked, carboxymethylated cellulose. The synthetic fibers effectively impart an appropriate softness, hand feeling and processability to the nonwoven fabric. Also, since the synthetic fibers have substantially no water absorption, the synthetic fibers effectively serve to maintain a tensile strength of the nonwoven fabric at a high level even when the nonwoven fabric is wetted with water.

The water-absorbent cellulosic fibers, which are merely intertwined with the synthetic fibers, do not affect on the softness, hand feeling and processability of the resultant nonwoven fabric. Also, the cellulosic fibers have carboxymethyl groups and cross-linking groups and thus are insoluble in water and exhibit a high water absorption. Further, the water-absorbent cellulosic fibers intertwined with the synthetic fibers exhibit a high resistance to separation from the nonwoven fabric even if the fabric is wetted with water.

In the nonwoven fabric of the present invention, the synthetic fibers and the water-absorbent cellulosic fibers may be evenly blended and intertwined with each other. In another embodiment, the synthetic fibers are in the form of a nonwoven web and the water-absorbent cellulosic fibers are intertwined with the synthetic fibers in the nonwoven web.

The water-absorbent nonwoven fabric of the present invention exhibits not only a high absorption of water but also a high absorption of an ion-containing aqueous solution, for example, an aqueous common salt solution or urine. Also, the water-absorbent nonwoven fabric of the present invention is advantageous in that after absorbing water, the resultant water-holding nonwoven fabric practically does not release water even when a pressure is applied thereto. Accordingly, the water-absorbent nonwoven fabric of the present invention are widely useful as a hygienic material, for example, a disposable diaper or sanitary napkin; an agricultural material, for example, soil water-retaining agent or a seedbed sheet; a food-related material, for example, a freshness-keeping material for food or dehydrating material; and a building material, for example, a water condensation-preventing material for building.

In an embodiment of the process of the present invention, the water-absorbent nonwoven fabric is produced by the steps of forming a precursory nonwoven web in which synthetic fibers and cellulose fibers are intertwined with each other; subjecting the cellulose fibers in the precursory web to a carboxymethylating treatment with monochloroacetic acid salt in the presence of an alkali metal hydroxide in a reaction medium consisting of at least one member selected from the group consisting of water and lower aliphatic alcohol having 2 to 4 carbon atoms; and subjecting the resultant carboxymethyl cellulose fibers in the precursory web to a cross-linking treatment with a cross-linking agent, to convert the cellulose fibers to water-absorbent cellulosic fibers and thereby to convert the precursory web to a water-absorbent nonwoven fabric.

In another embodiment of the process of the present invention, a water-absorbent nonwoven fabric is produced by the steps of forming a precursory nonwoven web in which synthetic fibers and cellulose fibers are intertwined each other; subjecting the cellulose fibers in the precursory web to a cross-linking treatment with a cross-linking agent; and subjecting the cross-linked cellulose fibers in the precursory web to a carboxymethylating treatment with monochloroacetic acid salt in the presence of an alkali metal hydroxide in a reaction medium consisting of at least one member selected from the group consisting of water and lower aliphatic alcohol having 2 to 4 carbon atoms, to convert the cellulose fibers to water-absorbent cellulosic fibers, and thereby to convert the precursory nonwoven web to a water-absorbent nonwoven fabric.

In still another embodiment of the process of the present invention, a water-absorbent nonwoven fabric is produced by the steps of forming a precursory web in which synthetic fibers and cellulose fibers are intertwined with each other; subjecting the cellulose fibers in the precursory web to a simultaneous carboxymethylating and cross-linking treatment with monochloroacetic acid salt and a cross-linking agent in the presence of an alkali metal hydroxide in a reaction medium consisting of at least one member selected from the group con-

sisting of water and lower aliphatic alcohol having 2 to 4 carbon atoms, to convert the cellulose fibers to water-absorbent cellulosic fibers, and thereby to convert the precursory web to a water-absorbent nonwoven fabric.

In the process of the present invention, the precursory nonwoven web can be prepared by blending the synthetic fibers with the cellulose fibers and forming a nonwoven web from the fiber blend in accordance with a dry web-forming method, for example, air laying or carding method.

Also, the precursory nonwoven web can be prepared by blending the synthetic fibers with the cellulose fibers and forming a nonwoven web from the fiber blend in accordance with a paper-making method.

Where the precursory nonwoven web is prepared from the blend of the synthetic fibers and the cellulose fibers, the synthetic fibers are preferably partially bonded to each other to enhance the wet mechanical strength of the precursory nonwoven web. The partial bonding of the synthetic fibers can be effected by any known bonding method, for example, a method in which a bonding agent-containing liquid is sprayed on a web of the blend and heated, a method in which a portion of the synthetic fibers are heat-fusible, and is used to partially bond the synthetic fibers to each other therethrough by heating, a needle-punching method or a stitch-bonding method.

Further, the precursory nonwoven web can be prepared by forming a nonwoven web from the synthetic fibers in accordance with a dry nonwoven fabric-forming method, wet nonwoven fabric-forming method, spun-bonding method or melt-blowing method; separately forming a sheet from cellulose fibers by a wet or dry paper-making method; laminating the cellulose fiber sheet on the synthetic fiber nonwoven web; and hydraulically intertwining the cellulose fibers and the synthetic fibers with each other in accordance with a water-jet fiber-intertwining method, as disclosed in Research Disclosure, 17060, June 1978. The nonwoven fabric produced by this process has excellent processability and hand feeling. In this process, the nonwoven synthetic fiber web must be strong enough against the water-jet streams applied thereto under a high pressure. Therefore, the nonwoven web is preferably formed from continuous synthetic filaments.

The present invention will be further explained by the following specific examples which are merely representative and do not restrict the scope of the present invention in any way.

In the examples and comparative examples, pure water absorption, wet tensile strength and degree of substitution with carboxymethyl groups are determined by the methods as mentioned below.

#### (1) Pure water absorption

Pure water was prepared by deionizing water by flowing through an ion-exchange resin and distilling the deionized water.

Four specimens of a nonwoven fabric having dimensions of 2.5 cm × 2.5 cm were placed in a 200 mesh nylon wire bag having dimensions of 10 cm × 10 cm. The specimen-containing nylon wire bag was immersed in the pure water at a temperature of 25°C for 10 minutes to allow the specimens to absorb the pure water, then taken up from the pure water and suspended for 10 minutes to allow a portion of the pure water to drip down. Then the weight of the water-absorbed specimens was measured.

The water absorption of the specimens was represented by the weight of pure water retained in the specimens per g of the dry weight of the specimens.

#### (2) Wet tensile strength

The wet tensile strength of a specimen of a nonwoven fabric having a width of 25 mm was measured in a longitudinal direction of the fabric in accordance with Japanese Industrial Standard (JIS) P 8135.

#### (3) Degree of substitution with carboxymethyl groups

Four specimens of a nonwoven fabric having dimensions of 2.5 cm × 2.5 cm were dried in a vacuum oven at a temperature of 60°C for 4 hours, and then the dry weight of the specimens was measured. A difference between the weight of the dried specimens and the total weight of the synthetic fibers in the specimens corresponded to the dry weight of the water-absorbent cellulosic fibers.

The dry specimens were placed in a laboratory disk (Schale), and immersed in 50 ml of an aqueous methyl alcohol-hydrochloric acid solution, which was prepared by dissolving hydrochloric acid in a concentration of 1 mole/liter in an aqueous solution of 70% by weight of methyl alcohol, for one hour. The treated specimens were fully washed with methyl alcohol to completely remove hydrochloric acid, and then dried in the ambient air atmosphere.

The dried specimens were placed in a triangle flask having an inside volume of 300 ml, 20 ml of 0.1N sodium hydroxide aqueous solution and 100 ml of pure water were placed in the flask, and the content in the

flask was slowly stirred for one hour. Thereafter, the degree of substitution of the cellulose with carboxymethyl groups was determined by a titration using a titrant consisting of 0.1N hydrochloric acid aqueous solution and an indicator consisting of phenolphthalein, in accordance with the equations (1) and (2)

$$Y = 0.1A - 0.1B \quad (1)$$

$$\text{Substitution degree} = 162Y / (1000W - 80Y) \quad (2)$$

wherein A represents an amount in ml of the 0.1N sodium hydroxide aqueous solution, B represents an amount in ml of the 0.1N hydrochloric acid aqueous solution, Y represents the amount in milli equivalent of carboxymethyl groups and W represents a weight in g of the water absorbent cellulosic fibers (carboxymethyl cellulose).

#### Example 1

A precursory nonwoven web was produced by preparing a nonwoven web consisting of spun-bonded polypropylene fibers having a thickness of 2.78 d tex (2.5 deniers) and having a basis weight of 12 g/m<sup>2</sup>; separately preparing a pulp fiber sheet having a basis weight of 38 g/m<sup>2</sup> from soft wood bleached kraft pulp (NBKP) fibers by a water-jet intertwining method; laminating the pulp fiber sheet on the polypropylene fiber nonwoven web; and intertwining the soft wood bleached kraft pulp (NBKP) fibers and the polypropylene fibers with each other by a water-jet intertwining method.

The resultant precursory nonwoven web was cut into pieces each having dimensions of 20 cm × 30 cm and a weight of 3g. The cut pieces were immersed in a mixed aqueous solution consisting of 10.4% by weight of sodium hydroxide, 34.6% by weight of potassium monochloroacetate, 1.0% by weight of epichlorohydrin and 54.0% by weight of water at room temperature for one minute. Then, the fabric pieces were removed from the mixed solution, interposed and pressed between filtering paper sheets to adjust the amount of the mixed solution retained in the fabric pieces to 2g per g of the fabric pieces. The mixed solution-containing fabric pieces were placed into a polyethylene film bag and heated in a dryer at a temperature of 60°C for 4 hours for simultaneously carboxymethylating and cross-linking the NBKP fibers in the precursory nonwoven web.

The resultant cross-linked and carboxymethylated fabric pieces were immersed in 70% by weight methyl alcohol aqueous solution at room temperature for 10 minutes and then pressed between filtering paper sheets. These operations were repeated four times to fully wash the fabric pieces. Finally, the washed fabric pieces were further immersed in pure methyl alcohol, pressed between filtering paper sheets and then dried in the ambient air atmosphere. Water-absorbent nonwoven fabric pieces were obtained. In the fabric pieces, the water-absorbent NBKP fibers had a degree of substitution with carboxymethyl groups of 0.47.

The water-absorbent nonwoven fabric had the pure water absorption and the wet tensile strength as shown in Table 1.

#### Example 2

A precursory nonwoven web having a basis weight of 80 g/m<sup>2</sup> was prepared from a nonwoven web consisting of spun-bonded polyethylene terephthalate fibers having a thickness of 2.56 d tex (2.3 denier) and having a basis weight of 12 g/m<sup>2</sup>, and a soft wood bleached kraft pulp (NBKP) fiber sheet having a basis weight of 68 g/m<sup>2</sup> and prepared by the same procedures as in Example 1.

The precursory web was wound in a length of 20 m around a polypropylene cylinder having a diameter of 3 cm and a length of 30 cm. The wound precursory web was immersed in a mixed aqueous solution consisting of 10.4% by weight of sodium hydroxide, 34.6% by weight of potassium monochloroacetate, 1.0% by weight of epichlorohydrin and 54.0% by weight of water so as to fully impregnate the precursory web with the mixed solution.

The mixed solution was contained in an amount of 6.4g per g of the wound precursory web. The mixed solution-containing web was placed in a polyethylene film bag and left to stand at room temperature for 24 hours to carboxymethylate and cross-link the NBKP fibers. Then, the resultant nonwoven fabric was centrifugalized. The fabric was immersed in a 70% by weight methyl alcohol aqueous solution at room temperature for 10 minutes and centrifugalized. These operations were repeated 10 times to fully wash the nonwoven fabric. Finally, the fabric was immersed in 100% methyl alcohol and centrifugalized. The finally washed nonwoven fabric was dried in a dryer at a temperature of 60°C, to thereby obtain a water-absorbent nonwoven fabric.

In this water-absorbent nonwoven fabric, the crosslinked and carboxymethylated NBKP fibers had a degree of substitution with carboxymethyl groups of 0.44.

The water-absorbent nonwoven fabric had the pure water absorption and the wet tensile strength as shown in Table 1.



Example 3

A precursory nonwoven web having a basis weight of 50 g/m<sup>2</sup> was produced from a blend of 70% by weight of hard wood bleached kraft pulp (LBKP) fibers and 30% by weight of polyethylene terephthalate staple fibers having a thickness of 1.67 d tex (1.5 denier) and a length of 5 mm by a paper-forming method and then applying a heat embossing treatment to the resultant web to partially bond the polyester fibers to each other.

The same treatment as in Example 1 was applied to the precursory nonwoven web to carboxymethylate and cross-link the LBKP fibers. A water-absorbent nonwoven fabric was obtained. This nonwoven fabric had a degree of substitution of the LBKP fibers with carboxymethyl groups of 0.48.

Also, the nonwoven fabric had the pure water absorption and the wet tensile strength as shown in Table 1.

Example 4

A precursory nonwoven web having a basis weight of 60 g/m<sup>2</sup> was produced from a blend of 80% by weight of viscose rayon staple fibers having a thickness of 3.33 d tex (3.0 denier) and a length of 51 mm and heat-fusible polyester staple fibers having a thickness of 1.67 d tex (1.5 denier) and a length of 40 mm, by feeding the blend into a carding engine, heat-pressing the resultant web between a pair of heating rollers so as to partially fuse-bond the polyester fibers.

The same treatment was applied to the precursory nonwoven web to carboxymethylate and cross-link the viscose rayon staple fibers. A water-absorbent nonwoven fabric was obtained. This nonwoven fabric had a degree of substitution of the viscose rayon staple fibers with a carboxymethyl group of 0.45.

Also, the nonwoven fabric had the pure water absorption and the wet tensile strength as shown in Table 1.

Example 5

A water-absorbent nonwoven fabric was produced by the same procedures as in Example 1, except that the carboxymethylating and cross-linking treatment was applied twice to the NBKP fibers in the precursory nonwoven web.

The resultant nonwoven fabric had a degree of substitution of NBKP fibers with carboxymethyl group of 0.81.

The nonwoven fabric also had the pure water absorption and the wet tensile strength as shown in Table 1.

Example 6

A water-absorbent nonwoven fabric was produced by the same procedures as in Example 1, except that the carboxymethylating and cross-linking treatment was applied to the NBKP fibers in the precursory nonwoven web at a temperature of 60°C for 15 minutes.

The resultant nonwoven fabric had a degree of substitution of the NBKP fibers with carboxymethyl groups of 0.35.

Also, the nonwoven fabric had the pure water absorption and the wet tensile strength as shown in Table 1.

Comparative Examples 1 to 4

In Comparative Examples 1 to 4, the precursory nonwoven webs of Examples 1 to 4 were subjected to measurements of pure water absorption and wet tensile strength. The results are shown in Table 1.

Comparative Example 5

A paper sheet made from the same NBKP fibers as in Example 1 and having a basis weight of 50 g/m<sup>2</sup> was subjected to the same carboxymethylating and crosslinking treatment as in Example 1. The resultant water-absorbent paper sheet had a degree of substitution with carboxymethyl groups of 0.44.

The paper sheet had the pure water absorption and the wet tensile strength as shown in Table 1.

### Comparative Example 6

A precursory nonwoven fabric having a basis weight of 80 g/m<sup>2</sup> and a density of 0.25 g/cm<sup>3</sup> was produced from copper-ammonia (cupra) rayon continuous filaments having a thickness of 2.22 d tex (2.0 denier) by intertwinning them with each other by a spun-bonding method.

The precursory nonwoven fabric was subjected to the same carboxymethylating and cross-linking treatment as in Example 1. The resultant water-absorbent nonwoven fabric had a degree of substitution of the cupra rayon filaments with carboxymethyl groups of 0.45.

The nonwoven fabric had the pure water absorption and the wet tensile strength as shown in Table 1.

### Comparative Example 7

A water-absorbent nonwoven fabric was produced by the same procedures as in Example 1, except that the carboxymethylating and cross-linking treatment was applied to the NBKP fibers in the precursory nonwoven web at a temperature of 60°C for 10 minutes.

The resultant water-absorbent nonwoven fabric had a degree of substitution of the NBKP fibers with carboxymethyl groups of 0.32.

This nonwoven fabric had the pure water absorption and the wet tensile strength as shown in Table 1.

Table 1

Example No.	Item	Water-absorbent nonwoven fabric		Degree of substitution with carboxymethyl groups
		Pure water absorption (g/g)	Wet tensile strength (kgf/25 mm)	
Example	1	84	3.9	0.47
	2	96	4.1	0.44
	3	65	6.5	0.48
	4	62	2.5	0.45
	5	147	3.9	0.81
	6	30	3.9	0.35
Comparative Example	1	20	4.2	0
	2	23	4.4	0
	3	13	6.7	0
	4	18	2.5	0
	5	121	(*) <sub>1</sub>	0.44
	6	95	(*) <sub>1</sub>	0.45
	7	21	3.9	0.32

Note: (\*)<sub>1</sub> ... When immersed in pure water, the specimen was swollen and gelled and thus could not be subjected to the tensile strength measurement.

Table 1 clearly shows that the water-absorbent nonwoven fabrics of Examples 1 to 6 in accordance with the present invention exhibited satisfactory pure water absorption and wet tensile strength, whereas the comparative nonwoven fabrics were unsatisfactory in at least one item of the pure water absorption or the wet tensile strength. Namely, the specific advantages were illustrated by the examples.

The water-absorbent nonwoven fabric of the present invention exhibits a high water absorption similar to the conventional water-absorbent resin powder and is free from the disadvantage that the water-absorbent resin in the form of fine particles or grains is difficult to handle when an article is formed from the resin.

The water-absorbent nonwoven fabric has a satisfactory softness, hand feeling and processability and an excellent mechanical strength even after absorbing water. Therefore, the water absorbent nonwoven fabric can be employed alone to form various articles without need of another supporting material, and is widely useful for various fields of industry.

**Claims**

1. A water-absorbent nonwoven fabric comprising synthetic fibers and water-absorbent cellulosic fibers intertwined with each other, the cellulosic fibers comprising a cross-linked carboxymethyl cellulose having a degree of substitution with carboxymethyl groups of 0.35 to 1.6.
2. The water-absorbent nonwoven fabric as claimed in claim 1, which has a wet tensile strength of 0.1 to 10.0 kgf/25 mm determined in accordance with Japanese Industrial Standard P 8135.
3. The water-pickup nonwoven fabric as claimed in claim 1, which has a pure water absorption of 25 to 160 times the dry weight of the nonwoven fabric.
4. The water-absorbent nonwoven fabric as claimed in claim 1, wherein the synthetic fibers are selected from the group consisting of polyolefin fibers, polyester fibers, polyamide fibers, polyacrylate fibers and polyurethane fibers.
5. The water-absorbent nonwoven fabric as claimed in claim 1, wherein the synthetic fibers have a thickness of from 0.33 to 11.11 d tex (0.3 to 10 deniers).
6. The water-absorbent nonwoven fabric as claimed in claim 1, wherein the mixing ratio in weight of the synthetic fibers to the water-absorbent cellulosic fibers is in the range of from 1:1 to 1:19.
7. The water-absorbent nonwoven fabric as claimed in claim 1, wherein the cross-linkage of the water-absorbent cellulosic fibers is derived from a crosslinking reaction of cellulose fibers with a cross-linking agent comprising at least one member selected from the group consisting of aldehyde compounds, N-methylol compounds, polycarboxylic acids, polyepoxy compounds, divinyl compounds, polyhalide compounds, haloalohydrin compounds and polyaziridine compounds.
8. The water-absorbent nonwoven fabric as claimed in claim 7, wherein the cross-linking agent is used in an amount of 0.1 to 10% by weight based on the weight of the cellulose fibers.
9. The water-absorbent nonwoven fabric as claimed in claim 1, wherein the synthetic fibers are partially bonded to each other.
10. The water-absorbent nonwoven fabric as claimed in claim 1, wherein the synthetic fibers are in the form of a nonwoven web, and the water-absorbent cellulosic fibers are intertwined with the synthetic fibers in the nonwoven web.
11. A process for producing a water-absorbent nonwoven fabric as claimed in claim 1, comprising the steps of forming a precursory nonwoven web in which synthetic fibers and cellulose fibers are intertwined with each other; subjecting the cellulose fibers in the precursory web to a carboxymethylating treatment with monochloroacetic acid salt in the presence of an alkali metal hydroxide in a reaction medium consisting of at least one member selected from the group consisting of water and lower aliphatic alcohol having 2 to 4 carbon atoms; and subjecting the resultant carboxymethyl cellulose fibers in the precursory web to a cross-linking treatment with a cross-linking agent, to convert the precursory web to a water-absorbent nonwoven fabric.
12. A process for producing a water-absorbent nonwoven fabric as claimed in claim 1, comprising the steps of forming a precursory nonwoven web in which synthetic fibers and cellulose fibers are intertwined with each other; subjecting the cellulose fibers in the precursory web to a cross-linking treatment with a cross-linking agent; and subjecting the cross-linked cellulose fibers in the precursory web to a carboxymethylating treatment with monochloroacetic acid salt in the presence of an alkali metal hydroxide in a reaction medium consisting of at least one member selected from the group consisting of water and lower aliphatic alcohol having 2 to 4 carbon atoms, to convert the precursory nonwoven web to a water-absorbent nonwoven fabric.
13. A process for producing a water-absorbent nonwoven fabric as claimed in claim 1, comprising the steps of forming a precursory web in which synthetic fibers and cellulose fibers are intertwined with each other; subjecting the cellulose fibers in the precursory web to a carboxymethylating treatment with monochloroacetic acid salt in the presence of an alkali metal hydroxide in a reaction medium consisting of at least

one member selected from the group consisting of water and lower aliphatic alcohol having 2 to 4 carbon atoms, and simultaneously to a cross-linking treatment with a cross-linking agent, to convert the precursory web to a water-absorbent nonwoven fabric.

- 5     **14.** The process as claimed in claim 11, 12 or 13, wherein the precursory nonwoven web is prepared by blending the synthetic fibers with the cellulose fibers and forming a nonwoven web from the fiber blend in accordance with a dry web-forming method.
- 10    **15.** The process as claimed in claim 11, 12 or 13, wherein the precursory nonwoven web is prepared by blending the synthetic fibers with the cellulose fibers and forming a nonwoven web from the fiber blend in accordance with a paper-making method.
- 15    **16.** The process as claimed in claim 11, 12 or 13, wherein the precursory nonwoven web is prepared by forming a nonwoven web from the synthetic fibers in accordance with a dry nonwoven fabric-forming method, wet nonwoven fabric-forming method, spun-bonding method or melt-blowing method; separately forming a sheet from cellulose fibers; and intertwining the cellulose fibers and the synthetic fibers with each other in accordance with a water-jet fiber-intertwining method.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 94 30 5926

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	DATABASE WPI Section Ch, Week 9203, Derwent Publications Ltd., London, GB; Class A94, AN 92-020362 & JP-A-3 269 144 (TOYOCO KK) 29 November 1991 * abstract * ---	1,4,6,7,10	D04H1/42
Y	US-A-3 556 919 (JOHNS ET AL.) * column 3, line 6 - column 7, line 52 * ---	1,4,6,7,10	
A	GB-A-1 397 154 (PERSONAL PRODUCTS COMPANY) * page 1, line 35 - page 4, line 14 * * page 7, line 11 - line 35 * ---	11-16	
Y	GB-A-1 397 154 (PERSONAL PRODUCTS COMPANY) * page 1, line 35 - page 4, line 14 * * page 7, line 11 - line 35 * ---	1,4,6,7	
A	DATABASE WPI Week 9204, Derwent Publications Ltd., London, GB; AN 92-030723 & JP-A-3 279 471 (TOYOCO KK) 10 December 1991 * abstract * -----	1,11	TECHNICAL FIELDS SEARCHED (Int.Cl.6) D04H
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 November 1994	Examiner V Beurden-Hopkins, S
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure F : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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