PRODUCTION OF BONDED
NONWOVENS BY THE WET METHOD

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ABSTRACT
Textile nonwovens can be prepared with particular advantage by treatment of textile fibers suspended in an aqueous medium with dissolved quaternary organic ammonium salts and with water-soluble salts of polymers having carboxyl groups of vinylpyrrolidione polymers, precipitation of binder polymers dispersed in water onto the treated suspended fibers, separation of the aqueous medium from the fibers and drying the bonded fibers.

9 Claims, No Drawings
PRODUCTION OF BONDED NONWOVENSBY THE WET METHOD

This invention relates to a process for the production of bonded nonwoven fabrics, natural or synthetic textile fibers are suspended in an aqueous medium and a bonding agent is added. The aqueous medium is then separated on a machine substantially resembling known paper machines and the structure is generally dried at elevated temperature.

Fibers known as binder fibers, for example of polyvinyl acetate or of cellulose loaded with polycrylates, are often used as binders for bonding nonwovens. The webs of fibrous material thus acquire adequate wet tear resistance to enable them to be removed from the wire of the machine. When drying and heating is carried out, the polyvinyl acetate fibers of the polycrylates are softened so that the textile fibers are bonded together. The tear resistance of bonded nonwovens obtained by these known methods is however inadequate. For this reason, the bonded nonwovens are often additionally impregnated with a plastics dispersion or solution. However, the handling of nonwovens prepared in this way is usually hard and similar to that of paper.

It is furthermore known from British Pat. No. 1,071,136 that paper and nonwovens can be prepared from fibers which have been treated successively with melamine resins or urea resins and an aqueous dispersion of a plasticized thermoplastic. If bonded nonwovens are prepared from such pre-treated plastics by the wet method, products are obtained however from which the plasticizer can easily migrate. As a result, the handle becomes less good and in some cases the material becomes more prone to soiling.

We have now found that the production of bonded nonwovens by the wet method by suspending textile fibers in an aqueous medium, precipitating a binder polymer dispersed in the aqueous medium onto the fibers, separating the aqueous medium and drying the nonwoven at elevated temperature can be advantageously carried out by first treating the fibers suspended in the aqueous medium with a quaternary ammonium salt dissolved in the aqueous medium which has at least one alkyl or aralkyl group containing from seven to 20 carbon atoms, and adding to the suspension of the fibers a water-soluble salt of a homopolymer and/or copolymer containing carboxyl groups and/or a water-soluble homopolymer and/or copolymer of vinylpyrrolidone and then adding an aqueous dispersion of the binder polymer.

Those quaternary ammonium salts are particularly suitable which contain four identical or different alkyl, cycloalkyl and/or aralkyl radicals attached to a quaternary nitrogen atom, at least one of the radicals being an alkyl or aralkyl radical containing from seven to 20 carbon atoms. Linear or branched alkyl groups having one to 20 carbon atoms are of particular interest as the organic radicals of the quaternary ammonium salts. Specific examples of such radicals are methyl, ethyl, n-propyl, isopropyl, n-butyl, tertiary-butyl, n-amyl, n-hexyl, 2-ethylhexyl, n-decyl, lauryl, stearyl and palmityl. The cyclohexyl radical is a particularly suitable cycloalkyl radical, and the benzyl radical is a particularly suitable aralkyl radical. Water-soluble quaternary ammonium salts which have four linear or branched alkyl groups having one to 20 carbon atoms of which one or two have seven to 20 carbon atoms, quaternary ammonium salts which have three linear or branched alkyl groups having one to 20 carbon atoms and one benzyl group and quaternary pyridinium salts which bear on the nitrogen atom a linear or branched alkyl group having seven to 20 carbon atoms or a benzyl radical are particularly suitable. The quaternary ammonium salts may be derived from salts which are capable of forming quaternary ammonium salts provided the quaternary ammonium salts have adequate solubility in water. The salts of inorganic acids, especially chlorides and sulfates, are of particular interest. Specific examples of suitable quaternary ammonium salts are as follows:

- N,N,N-trimethyl-N-stearylammonium chloride,
- N,N-dimethyl-N-stearyl-N-benzalammonium chloride,
- N,N-dimethyl-N-lauryl-N-benzalammonium chloride,
- N,N-dimethyl-N-lauryl-N-benzalammonium sulfate,
- N,N-benzylpyridinium chloride, N-laurylpyridinium chloride,
- N-lauryl-N-ethyl-N-dili(triethylenglycol)-ammonium methosulfate,
- N-stearyl-N-methyl-N,N-di-(I-hydroxypropyl)-ammonium methosulfate,
- N-lauryl,N,N,N-trimethylammonium methosulfate,
- N-lauryl,N,N,N-dimethyloleandomonium chloride,
- N-lauryl-2-ethylhexadecyloleandomonium methosulfate,
- N-stearyl,N,N-dimethyl-N-phenylammonium methosulfate,
- N,N-dimethyl-N-lauryl-N-benzalammonium chloride and N-benzylpyridinium chloride are of special interest as quaternary ammonium salts.

The quaternary ammonium salts may be added to the aqueous suspensions of the textile fibers in pure form, as suspensions in water, or, preferably, in the form of their concentrated aqueous solutions. Treatment of the fibers with the quaternary ammonium salts is generally carried out at room temperature and preferably while stirring. In special cases it may be advantageous to use temperatures which are above or below room temperature, for example at +5° C or +5° C. The temperature of the aqueous liquor is usually from 10° to 30° C. Treatment of the fibers with the quaternary ammonium salts usually requires from 15 to 30 minutes. In special cases, for example when elevated temperature is used, further processing may be commenced only a few minutes after addition of the quaternary ammonium salt to the suspension of fibers.

Polymers of α,β-olefinically unsaturated monocarboxylic acids containing three or four carbon atoms, such as acrylic and/or methacrylic acid, are preferred as water-soluble salts of homopolymers and copolymers containing carboxyl groups. They are preferably derived from caustic alkali solutions, such as caustic soda and caustic potash solutions, or ammonia. Other examples are copolymers of maleic acid, fumaric acid, itaconic acid and/or crotonic acid. The polymers may contain any addition to the α,β-olefinically unsaturated monocarboxylate or dicarboxylic acids of the said type which preferably contain from three to 20 carbon atoms) copolymerized units of other olefinically unsaturated monomers, particularly esters of acrylic and/or methacrylic acid with lower alcohols, particularly alkanols containing one to four carbon atoms, such as methyl acrylate, methyl methacrylate, ethyl acrylate and n-butyl acrylate, vinyl esters, particularly vinyl acetate, α,β-olefinically unsaturated nitriles, particularly acrylonitrile, amides of α, β-olefinically unsaturated carboxylic acids and their derivatives, particularly acrylamide, methacrylamide, N-methylolmethacrylamide, N-methylolacrylamide, maleimide, maleamide, N-methoxymethylacrylamide and N-methoxymethylmethacrylamide, vinyl esters of lower fatty acids, particularly vinyl acetate, vinyl and vinylidene halides, particularly vinyl chloride, and vinylaromatic compounds, particularly styrene. The proportion of such copolymers may be varied within wide limits, practically the only limitation being the requirement that the salts of the copolymers should have adequate solubility in water.

It is possible in the new process to use water-soluble homopolymers and/or copolymers of vinylpyrrolidone instead of or together with the salts of homopolymers and/or copolymers containing carboxyl groups. In addition to the copolymers specified in the preceding paragraph, α,β-olefinically unsaturated monocarboxylic and/or dicarboxylic acids, particularly acrylic acid, methacrylic acid and maleic acid.
acid, may be used as comonomers for vinylpyrrolidone. The carboxyl groups may also be introduced into the polymers by partial hydrolysis of comonomers such as acrylonitrile or acrylamide. Suitable polymers containing carboxyl groups and the polymers of vinylpyrrolidone generally have K values of 20 to 80, preferably 30 to 60 (measured according to H. Fikentscher, Celluloschemie, volume 13 (1932), page 58).

The ratio of quaternary organic ammonium salt (solid) to water-soluble salt of polymer containing carboxyl groups (solid) or the vinylpyrrolidone polymer (solid) is generally from 10:1 to 20:1, preferably from 13:1 to 17:1.

Polymers suitable for the preparation of bonded nonwovens, which are generally in the form of their aqueous dispersions, are suitable as binder polymers. Aqueous dispersions which contain from 40 to 60 percent by weight of acrylic ester and/or methacrylic ester polymers having carboxylic acid groups are particularly suitable. These polycarboxylates are usually derived from esters of acrylic or methacrylic acid with alkanols containing from one to 12, particularly from one to eight, carbon atoms, which often form the major component of the copolymers. Such polycarboxylates generally contain (as monomers having carboxyl groups) from 1 to 10 percent by weight of α,ω-olefinically unsaturated monomeric carboxylic acid, and/or dicarboxylic acids which preferably contain from three to five carbon atoms. The proportion of such olefinically unsaturated carboxylic acids in the copolymers is preferably from 2 to 5 percent by weight with reference to the copolymer. Acrylic and methacrylic acids are particularly suitable; crotonic acid, maleic acid, fumaric acid and itaconic acid are also suitable. The polycarboxylates may additionally contain polymerized units of further olefinically unsaturated monomers, for example vinylaromatic compounds such as styrene, vinyl halides or vinylidene halides, such vinyl chloride and vinylidene chloride, acrylonitrile, methacrylonitrile and/or vinyl esters of saturated aliphatic monocarboxylic acids usually containing from two to 12 carbon atoms, such as vinyl acetate, vinyl propionate, vinyl laurate and vinyl pivalate and also (usually in amounts of from 1 to 10 percent, particularly from 2 to 7 percent, by weight with reference to the copolymer) of amides of α,ω-olefinically unsaturated monocarboxylic acid and/or dicarboxylic acids usually containing from three to five carbon atoms or their derivatives, particularly acrylamide, methacrylamide, N,N-methacrylamide, N,N-diisopropylacrylamide, N,N-dimethylacrylamide, N,N-dihydroxymethylacrylamide, N,N-butoxyethylmethacrylamide, and vinylsulfonic acids and their salts. The aqueous dispersion of such polycarboxylates may contain the usual amounts of conventional anionic or nonionic emulsifiers with or without small amounts of protective colloids.

Other suitable binder polymers are aqueous dispersions based on polymers of vinyl chloride and/or vinylidene chloride, based on butadiene-styrene copolymers or butadiene-acrylonitrile copolymers and/or based on vinyl ester polymers, for example polymers of vinyl acetate or vinyl propionate, which may contain conventional anionic or nonionic emulsifiers with or without protective colloids.

Generally from 5 to 50 percent, preferably from 15 to 35 percent, by weight of binder polymer (in each case calculated as solids and with reference to the amount of textile fibers) are used in the new process.

The amount of textile fibers (with reference to the amount of water) is usually from 0.5 to 3 percent, preferably from 0.7 to 1.5 percent, by weight, the fibers preferably being from 5 to 25 mm in length. The textile fibers may consist for example of cellulose or cellulose derivatives, synthetic polyamides having recurrent CONH—groups in the molecular chain, such as polycaprolactam or polyhexamethylene adipamide, saturated polyesters, such as polyethylene glycol terephthalate, or polyacrylonitrile.

Additives conventionally used for finishing textiles and/or paper, provided they are compatible with the other additives, may be used in the conventional way and if desired may be added to the aqueous medium.

The invention is illustrated by the following Examples, in which parts and percentages are by weight.

**EXAMPLE 1**

25 parts of rayon staple fibers having a denier of 1.7 and a length of from 1 to 10 mm is suspended in 2,500 parts of water and then 6 parts of a 54 percent aqueous solution of N-lauryl-N,N-dimethyl-N-benzylammonium chloride is added. The whole is stirred for 15 minutes and 2 parts of a 10 percent aqueous solution of a commercial copolymer (partly hydrolyzed with ammonia) of equal parts of methyl acrylate and acrylonitrile is gradually added. Then 60 parts of a 40 percent aqueous dispersion of a copolymer of 90 parts of n-butyl acrylate, 6 parts of acrylic acid and 4 parts of N-methylmethacrylamide (which contains as an emulsifier 1.7 parts of a sulfonated oxethylated product of n-nonylephenol which contains 18 to 20 ethylene oxide radicals and 0.3 part of Tur- key red oil) is added. The binder polymer is deposited during stirring on the fibers within about 15 minutes. The aqueous fiber suspension is then introduced into an inclined wire web forming machine, the water is suction filtered, and the web is lifted off from the wire and dried at from 90° to 130°C.

A nonwoven fabric is obtained which in the dry condition has a tensile strength of from 50 to 80 kg/cm², measured according to DIN 53,112. The nonwoven has a soft textile handle. It is strongly fungicidal and bactericidal and is particularly suitable for hygienic disposable articles.

**EXAMPLE 2**

20 parts of rayon staple fibers having a denier of 1.7 and a length of 10 mm is suspended in 2,000 parts of water and then 6 parts of a 50 percent aqueous solution of N-benzylpyridinium chloride is added to the suspension. The whole is stirred for about 15 minutes and then 1 part of a 20 percent aqueous solution of sodium polycrylate (K value of the polycrylate acid = 30) is added. 40 parts of a 40 percent aqueous dispersion of a copolymer of 85 parts of n-butyl acrylate, 5 parts of N-methylolacrylamide, 3 parts of 1,4-butanediol dimethacrylate and 7 parts of acrylic acid is then added. The binder polymer is deposited on the fibers during stirring. The aqueous suspension of the fibers is then fed to the wire section of a web forming machine, the water is sucked off as usual and the web is dried at from 120° to 140°C. A nonwoven is obtained which in the dry condition has a tensile strength of 54 kg/cm² according to DIN 53,112.

**EXAMPLE 3**

10 parts of polycaprolactam fibers having a denier of 3 and a length of 10 mm and 10 parts of rayon staple fibers having a denier of 1.5 and a length of 10 mm are suspended in 2,000 parts of water. 4 parts of a 90 percent paste suspension of N-stryaryl-N,N-di-(o-hydroxysopropyl)-N-methylammonium methosulfate is added to the suspension while stirring. Stirring is continued for about another half hour and then 2 parts of a 10 percent aqueous solution of a copolymer (neutralized with ammonia) of 70 parts of acrylic acid, 20 parts of methacrylamide, 5 parts of acrylonitrile and 3 parts of ethyl acrylate, and 30 parts of a 50 percent aqueous dispersion of a copolymer of 55 parts of N-butyl acrylate, 45 parts of vinyl acetate and 2 parts of acrylic acid are then added in the sequence given. After the last-mentioned binder polymer has been deposited on the fibers, the web is formed as described in Example 1 and dried at from 110° to 130°C. The nonwoven obtained has a soft textile handle and is suitable for hygienic disposable articles.

**EXAMPLE 4**

20 parts of polycaprolactam fibers having a denier of 1.5 and a length of from 8 to 10 mm and 5 parts of polyhex-
3,657,031

amethylene adipamide fibers having a denier of 6 and a length of 32 mm are suspended in 2,500 parts of water. 5 parts of N,N-diolearyl-N,N-dimethylammonium chloride is then added as a concentrated aqueous solution and this quaternary ammonium salt is allowed to go on to the fibers for about 20 minutes while stirring. A concentrated aqueous solution of 2 parts of the ammonium salt of a copolymer of equal parts of acrylic acid and methacrylic acid prepared in the usual way is then added followed by 50 parts of a 50 percent aqueous dispersion, prepared in the usual way, of a copolymer of 93 parts of ethyl acrylate, 3 parts of acrylonitrile, 3 parts of N-methylolacrylamide and 1 part of acrylic acid. After the binder polymer has gone onto the fiber, the web is formed and dried as described in Example 1. A nonwoven is obtained which is suitable for example for the production of hygienic disposable articles.

We claim:

1. In a process for the production of bonded nonwoven by the wet method by suspending textile fibers in an aqueous medium, impregnating the suspended fibers by precipitation thereon of a binder polymer dispersed in the aqueous medium, separating the aqueous medium from the impregnated fibers and forming a web of said impregnated fibers, and drying the impregnated fiber web at elevated temperature, the improvement which comprises adding to the suspension of the fibers in the aqueous medium, prior to said impregnating with the binder polymer, (A) a quaternary ammonium salt, dissolved in the aqueous medium, which has at least one alkyl or aralkyl group containing from seven to 20 carbon atoms and (B) at least one of a water-soluble salt of a homopolymer or copolymer containing carboxyl groups or a water-soluble homopolymer or copolymer of vinyl-pyrrolidone.

2. In a process as claimed in claim 1 the improvement wherein compound (A) is a quaternary ammonium salt, dissolved in the aqueous medium, which has four linear or branched alkyl radicals each having from one to 20 carbon atoms of which one or two have seven to 20 carbon atoms and polymer (B) is a water-soluble salt of a polymer of an α,β-olefinically unsaturated monocarboxylic or dicarboxylic acid containing from three to five carbon atoms.

3. In a process as claimed in claim 1, the improvement wherein compound (A) is a quaternary ammonium salt, dissolved in the aqueous medium, which bears three linear or branched alkyl groups having from one to 20 carbon atoms and one benzyl group and polymer (B) is a water-soluble salt of a polymer of an α,β-olefinically unsaturated monocarboxylic or dicarboxylic acid containing from three to five carbon atoms.

4. In a process as claimed in claim 1, the improvement wherein compound (A) is a quaternary pyridinium salt, dissolved in the aqueous medium, which bears on the nitrogen atom a linear or branched alkyl group having from seven to 20 carbon atoms or a benzyl radical and polymer (B) is a water-soluble salt of a polymer of an α,β-olefinically unsaturated monocarboxylic or dicarboxylic acid containing from three to five carbon atoms.

5. In a process as claimed in claim 1, the improvement wherein polymer (B) is a potassium, sodium or ammonium salt of a polymer of an α,β-olefinically unsaturated carboxylic acid containing from three to four carbon atoms.

6. In a process as claimed in claim 1, the improvement wherein compound (A) is a quaternary ammonium salt, dissolved in the aqueous medium, which bears three linear or branched alkyl groups having from one to 20 carbon atoms and one benzyl group and polymer (B) is a potassium, sodium or ammonium salt of a polymer of acrylic acid or methacrylic acid.

7. In a process as claimed in claim 1, the improvement wherein compound (A) is a quaternary ammonium salt which bears three linear or branched alkyl groups having from one to 20 carbon atoms and one benzyl group and polymer (B) is a potassium, sodium or ammonium salt of a polymer of acrylic acid or methacrylic acid.

8. In a process as claimed in claim 1, the amount of said binder being 5-50 percent by weight, calculated as solids, with reference to the textile fibers, and the amount of said textile fibers being 0.5 to 3 percent by weight, based on the water of said aqueous medium.

9. In a process as claimed in claim 1, the weight ratio of said quaternary ammonium salt to said polymer (B) being in the range of 10:1 to 20:1.

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