NONWOVEN FABRIC AND PRODUCTS CONTAINING BACTERISTATIC AGENT

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The present invention relates to nonwoven fabrics, i.e., fabrics produced directly from fibers without the use of conventional spinning, weaving, or knitting operations and absorbent products covered therewith, more particularly to such fabrics wherein the fabric contains a bactericide intended to act as a deodorant, or as a rash preventative, or perform a similar function.

Certain quaternary ammonium compounds are known to be useful as bactericides and deodorants and at least one of these, di-isobutyl cresoxy ethoxy ethyl dimethyl benzyl ammonium chloride, is well known to be effective as a bactericide or bacteriostatic agent for combating diaper rash due to Bacillus ammounigenes. However, when used as a bactericide in garments which are to be worn next to the skin, there is danger they might have a toxic effect, particularly on infants. Therefore, they only should be included in diapers, for instance, in fairly small quantities. It also has been found that quaternary ammonium salts of the type contemplated are quite cationic and tend to react with anions to lose their effectiveness. Nonwoven fabrics produced by bonding together in the fibers of a loosely assembled web or webs of fibers with an adhesive have not been entirely satisfactory as covers for diapers or sanitary napkins when impregnated with these compounds. These fabrics must be quite soft as well as strong, wet and dry, and must possess a relatively high wet abrasion resistance. Fabrics developed in the past to meet these criteria generally have been anionic and therefore incompatible with small amounts of quaternary bactericides. This problem has been particularly critical in the case of disposable products to which the bactericide must be applied prior to purchase, such as disposable diapers, sanitary napkins, etc. In these products the small amount of bactericide permissible must have a satisfactory “shelf life” in situ in the fabric.

The present invention contemplates a nonwoven fabric containing a quaternary bacteriostatic agent of the type described and products employing this fabric close to the skin, wherein the “field” created by the adhesive and the fibers in the fabric is fully compatible with the bactericide and the fabric is sufficiently abrasion resistant and strong, wet and dry, for use as a cover for disposable diapers, sanitary napkins, etc., and for other products, such as diaper liners, which are abrasion resistant when wet. Among the quaternary compounds which may be employed in the fabric of this invention are the following:

1. Di-isobutyl cresoxy ethoxy ethyl dimethyl benzyl ammonium chloride.
2. Di-isobutyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride.
3. Alkyl dimethyl benzyl ammonium chloride.
4. Alkyl diethyl benzyl ammonium chloride.
5. Alkyl dimethyl benzyl ammonium bromide.
6. Di-isobutyl phenoxy ethoxy ethyl trimethyl ammonium chloride.
7. Di-isobutyl phenoxy ethoxy ethyl dimethyl allyl ammonium chloride.
8. Methyldecyl benzyl trimethyl ammonium chloride.
9. Cetyl trimethyl ammonium bromide.
10. Octadecyl dimethyl ethyl ammonium bromide.
11. Cetyl dimethyl ethyl ammonium bromide.
12. Octadecenyl-9-dimethyl ethyl ammonium bromide.
15. Cetyl pyridinium chloride.

Each of the above-listed bacteriostatic agents may be described generally as a quaternary ammonium salt having the following structural formulae:

\[
\left[ \begin{array}{c}
R_1 \\
R_2 \\
R_3 \\
An-
\end{array} \right]
\]

in which \( R_1 \) is an alkyl or a heterogeneous aliphatic radical having 8–18 carbon atoms or a radical of the formula

\[
\begin{array}{c}
\text{CH}_2- \\
\end{array}
\]

in which \( R_4 \) is an alkyl radical having 8–18 carbon atoms, each \( R_2 \) is a lower alkyl radical having not more than two carbon atoms, and \( R_3 \) is a methyl, ethyl, allyl, or benzyl radical; or as a quaternary salt having the following formula

\[
\left[ \begin{array}{c}
R_1 \\
R_2 \\
R_3 \\
R_4 \\
An-
\end{array} \right]
\]

in which \( R \) is an alkyl or heterogeneous aliphatic radical containing 8–18 carbon atoms; \( An- \) being an anion in both instances. The first five of the above-listed compounds, as well as the eighth listed, methyldecylbenzyl trimethyl ammonium chloride, are preferred because it is believed they are particularly adaptable for use in the fabric of this invention. The first five compounds may be defined by the following structural formula:

\[
\left[ \begin{array}{c}
R_1 \\
R_2 \\
R_3 \\
An-
\end{array} \right]
\]

in which \( R_1 \) is an alkyl or heterogeneous aliphatic group having 8–18 carbon atoms; \( R_2 \) is a short chain alkyl radical (a methyl or an ethyl group); and \( An- \) is an anion.

Fibrous webs may be bonded with internally plasticized polyvinyl acetates to form a substantially nonionic fabric which is quite soft and strong, wet and dry, and capable of resisting abrasion when wet. The term “internal plasticization” connotes modification by copolymerization or triplymerization with another resin. In other words, an internally plasticized polyvinyl acetate is a copolymer of vinyl acetate and a plasticizing constituent, or a triplymer of vinyl acetate and constituents including at least one having plasticizing properties. Suitable internally plasticized copolymers and triplymers may include copolymers of vinyl acetate and an alkyl acrylate, copolymers of vinyl acetate and an alkyl methacrylate, triplymers of vinyl acetate, alkyl acrylate, and alkyl methacrylate, copolymers of vinyl acetate and vinyl stearate, and others. Alkyl acrylates and methacrylates comprising lower alkyl radicals containing less than nine carbon atoms are preferred. The preferred acrylates may be defined by the following general formula:

\[
\text{R}-\text{C}=\text{O}-\text{OOR}
\]
where R is an alkyl radical containing less than nine carbon atoms. The preferred methacrylates likewise may be defined by the following general formula:

\[
\begin{array}{c}
\text{H} \\
\text{C-H} \\
\text{C-COO}\text{R}
\end{array}
\]

where R is as defined above. Generally speaking, the copolymer or triopolymer should comprise predominantly or more than 50 percent vinyl acetate, based upon the weight of the total monomers. It is preferred that the copolymer or triopolymer comprise at least about 70 percent vinyl acetate, on the same basis, and excellent results have been obtained with copolymers of vinyl acetate and alkyl acrylates containing less than 15 percent acrylate based upon the weight of the total monomers. These internally plasticized binders may be applied to the web in such a way that the resulting fabrics will be substantially or completely nonionic and extremely compatible with the above-listed quaternary compounds.

The fabric of this invention employed as the inner covering or facing sheet of a disposable diaper or a sanitary napkin preferably weigh between 150 and 300 grams per square yard and comprise approximately 15 to 25 percent binder solids. However, heavier fabrics may be used and certain other abrasion resistant fabrics of this invention, such as diaper liners, may weigh as much as 600 to 700 grams per square yard. Due to their extreme thinness, these fabrics in the disposable diaper and sanitary napkin cover range must be extremely well bonded by the adhesive they contain. In order to assure maximum strength with softness and extensibility, the binder may be applied to these lightweight webs in an intermittent or open pattern by printing or other techniques, such as disclosed in U. S. Patent No. 2,039,312 to J. H. Goldman. When the binder is applied in a pattern to particular areas of the web, it is even more important that the adhesive within these areas be as effective as possible in forming strong bonds with the fibers passing through these areas. It is particularly important that the napkin and diaper covers be resistant to abrasion and rubbing when wet and the fabric of this invention, whether pattern bonded or impregnated, may be designed to satisfy this demand.

An illustrative fabric of this invention may be formed by printing a laminate of five or six card webs with a substantially nonionic aqueous dispersion of an adhesive binder comprising a copolymer of vinyl acetate and approximately 15 percent ethyl acrylate based upon the weight of the total monomers. The web may weigh approximately 170 grams per square yard and comprise approximately 75 percent of substantially 1.5 denier viscose rayon staple fibers averaging about 2 inches in length and 25 percent of substantially 1.5 denier bleached absorbent cotton fibers averaging about 1.5 inches in length. The binder may be deposited in an intermittent pattern of spaced areas with the result that the amount deposited in the fabric weighs about 35 grams per square yard on a dry basis. The resulting fabric will be soft and strong, wet and dry. It also will be flexible and highly extensible. The copolymer of vinyl acetate and ethyl acrylate described, will form particularly good bonds with the rayon and cotton fibers in the web with the result that the fabric will be capable of resisting a good deal of abrasion and stretching when wet without serious loss of bond integrity.

The binder dispersion may be applied to the fabric by bringing the card web laminate in contact with an engraved roll carrying the binder, such as is generally described in U. S. Patent No. 2,545,952 to E. R. Goldman. In the above example, the binder dispersion may comprise approximately 50 percent resin solids, a small amount of a dispersing agent such as carboxymethyl cellulose, a small amount of an anti-foaming agent such as the product sold as Anti-Foam A by the Dow Corning Corporation, and other conventional agents to assist in processing. A suitable quaternary compound may be added to the web as by impregnation before or after the web is printed with the binder. For instance, the web may be wetted with a 0.025 percent solution of di-isobutyl phenoxo ethoxy ethyl dimethyl benzyl ammonium chloride, prior to printing with the binder, and the impregnation controlled in such a way that the concentration of the quaternary on the fabric after drying will be in the neighborhood of 0.05 percent by weight of the fabric. The fabric bonded with the copolymer of vinyl acetate and ethyl acrylate, described, will be substantially nonionic with the result that this small amount of quaternary compound, 0.05 percent, will remain effective over a reasonable fabric shelf life.

Another example of a fabric according to this invention may be formed by depositing, in the same way as a web, an aqueous dispersion of a triopolymer comprising approximately 90 percent vinyl acetate, approximately 5 percent methyl methacrylate, and approximately 5 percent butyl acrylate based upon the weight of the total monomers. The web may weigh about 270 grams per square yard and comprise substantially 100 percent viscose rayon staple fibers of substantially 1½ denier and averaging about 2 inches in length. The binder may be applied to the web in a pattern of intersecting lines or strips in such a way that the amount of binder deposited weighs substantially 50 grams per square yard on a dry basis. The binder may be printed on the web in a substantially nonionic aqueous dispersion containing about 40 percent resin solids in the manner generally described in connection with the preceding example. The resulting fabric will possess softness, flexibility, biastability, wet strength, wet abrasion resistance, etc., as in the preceding example. A 0.1 percent solution of di-isobutyl cresoxy ethoxy ethyl dimethyl benzyl ammonium chloride may be applied to the web after application of the binder by printing with a roll presenting a multiplicity of hard rubber projections. The projections may be dipped in a pan carrying the quaternary solution and then brought in contact with the web to transfer the quaternary from the ends of the projections to the fibers in the web. This process may be controlled to deposit approximately 0.2 percent of the quaternary compound in the web on a dry fabric basis. As in the previous example, this fabric will be substantially nonionic and the quaternary will remain active and effective during any reasonable shelf life.

The maximum amount of quaternary compound which may be carried in a fabric to be worn close to the skin may vary with the use intended and with the particular quaternary compound employed. For example, with di-isobutyl cresoxy ethoxy ethyl dimethyl benzyl ammonium chloride and di-isobutyl phenoxo ethoxy ethyl dimethyl benzyl ammonium chloride, it is preferred that no more than about 0.2 to 0.4 percent of the compound by weight of the dry fabric be deposited uniformly in the fabric for webs weighing between 150 and 300 grams per square yard.

Sanitary napkins, disposable diapers, and other absorbent pads to be used next to the skin may be formed merely by covering an absorbent inner body of conventional structure, such as several layers of creped cellulose, with the fabric of this invention and securing the fabric in place by gluing or other conventional means. Thus, the surface of the pad to be worn next to the skin will include a nontoxic deposition of a quaternary bactericide which will remain fully effective to act as a deodorant, rash preventative, etc., over the life of the pad.

Having now described the invention in specific detail and indicated the manner in which it may be carried into practice, it will be readily apparent to those skilled in the art that innumerable variations, applications, modifications and extensions of the basic principles involved
may be made without departing from its spirit or scope. We therefore intend to be limited only in accordance with the appended patent claims.

The invention claimed is:

1. A relatively soft nonwoven fabric comprising a loosely assembled web of overlapping intersecting fibers, a substantially nonionic binder material distributed throughout the web in adhesive contact with the fibers therein, the binder forming bonds between the fibers and said bonds having wet abrasion resistance, said binder comprising a material selected from the group consisting of copolymers of vinyl acetate and an alkyl acrylate, copolymers of vinyl acetate and an alkyl methacrylate and tripolymers of vinyl acetate, an alkyl acrylate, and an alkyl methacrylate, said binder comprising at least about 70 percent of vinyl acetate based upon the weight of the total monomers, said acrylates having the following structural formula:

\[
\text{[R']_n - N - R}_2
\]

and said methacrylates having the following structural formula:

\[
\text{[R']_n - N - CH}_2
\]

wherein \( R \) is an alkyl radical having less than nine carbon atoms, and no more than about 0.4 percent by weight of the dry fabric of a quaternary ammonium salt distributed uniformly throughout the fabric, said salt being selected from the group consisting of compounds having the following structural formula:

\[
\text{[R']_n - N - CH}_2
\]

in which \( R \) is selected from the group consisting of alkyl and heterogeneous aliphatic radicals each having 8-18 carbon atoms and radicals of the formula:

\[
\text{[R']_n - N - CH}_2
\]

in which \( R \) is an alkyl radical having 8-18 carbon atoms, each \( R' \) is a lower alkyl radical having not more than two carbon atoms, and \( R \) is selected from the group consisting of methyl, ethyl, allyl, and benzyl radicals; and

\[
\text{[R - N - CH}_2\text{]}_n^\text{An-}
\]

in which \( R \) is selected from the group comprising alkyl and aliphatic radicals each containing 8-18 carbon atoms; in both of which An— is an anion.

2. A relatively soft nonwoven fabric comprising a loosely assembled web of overlapping intersecting fibers, a substantially nonionic binder material distributed throughout the web in adhesive contact with the fibers therein, the binder forming bonds between the fibers and said bonds having wet abrasion resistance, said binder comprising a material selected from the group consisting of copolymers of vinyl acetate and an alkyl acrylate, copolymers of vinyl acetate and an alkyl methacrylate and tripolymers of vinyl acetate, an alkyl acrylate, and an alkyl methacrylate, said binder comprising at least about 70 percent of vinyl acetate based upon the weight of the total monomers, said acrylates having the following structural formula:

\[
\text{[R']_n - N - CH}_2
\]

and said methacrylates having the following structural formula:

\[
\text{[R - N - CH}_2\text{]}_n^\text{An-}
\]

in which \( R \) is an alkyl or heterogeneous aliphatic group having 8-18 carbon atoms; \( R' \) is a short chain alkyl radical (a methyl or an ethyl group); and An— is an anion.

3. A relatively soft nonwoven fabric comprising a loosely assembled web of overlapping intersecting fibers, a substantially nonionic binder material distributed throughout the web in adhesive contact with the fibers therein, the binder forming bonds between the fibers and said bonds having wet abrasion resistance, said binder comprising a material selected from the group consisting of copolymers of vinyl acetate and an alkyl acrylate, copolymers of vinyl acetate and an alkyl methacrylate and tripolymers of vinyl acetate, an alkyl acrylate, and an alkyl methacrylate, said binder comprising at least about 70 percent of vinyl acetate based upon the weight of the total monomers, said acrylates having the following structural formula:

\[
\text{[R - N - CH}_2\text{]}_n^\text{An-}
\]

and said methacrylates having the following structural formula:

\[
\text{[R - N - CH}_2\text{]}_n^\text{An-}
\]

wherein \( R \) is an alkyl radical having less than nine carbon atoms, and no more than about 0.4 percent by weight of the dry fabric of a quaternary ammonium salt distributed uniformly throughout the fabric, said salt having the following structural formula:

\[
\text{[R - N - CH}_2\text{]}_n^\text{An-}
\]

and said methacrylates having the following structural formula:

\[
\text{[R - N - CH}_2\text{]}_n^\text{An-}
\]

wherein \( R \) is an alkyl radical having less than nine carbon atoms, and no more than about 0.4 percent by weight of the dry fabric of a quaternary ammonium salt distributed uniformly throughout the fabric, said salt having the following structural formula:

\[
\text{[R - N - CH}_2\text{]}_n^\text{An-}
\]

and said methacrylates having the following structural formula:

\[
\text{[R - N - CH}_2\text{]}_n^\text{An-}
\]

wherein \( R \) is an alkyl radical having less than nine carbon atoms, and no more than about 0.4 percent by weight of the dry fabric of a quaternary ammonium salt distributed uniformly throughout the fabric, said salt having the following structural formula:

\[
\text{[R - N - CH}_2\text{]}_n^\text{An-}
\]

and said methacrylates having the following structural formula:
and wherein R is an alkyl radical having less than nine carbon atoms, and no more than about 0.4 percent by weight of the dry fabric of a quaternary ammonium salt distributed uniformly throughout the fabric, said salt being selected from the group consisting of compounds having the following structural formula:

\[
\begin{array}{c}
\text{R}_1 \\
\text{R}_2 \\
\text{R}_3 \\
\text{An}
\end{array}
\]

in which \( R_1 \) is selected from the group consisting of alkyl and heterogeneous aliphatic radicals each having 8–18 carbon atoms and radicals of the formula:

\[
\begin{array}{c}
\text{H} \\
\text{CH}_2
\end{array}
\]

in which \( R_4 \) is an alkyl radical having 8–18 carbon atoms, each \( R_4 \) is a lower alkyl radical having not more than two carbon atoms, and \( R_3 \) is selected from the group consisting of methyl, ethyl, allyl, and benzyl radicals; and

\[
\begin{array}{c}
\text{R} \\
\text{X}
\end{array}
\]

in which R is selected from the group comprising alkyl and aliphatic radicals each containing 8–18 carbon atoms; in both of which An is an anion.

5. An absorbent pad comprising an inner absorbent layer and a nonwoven fabric covering at least the inner face thereof; said fabric comprising a loosely assembled web of overlapping intersecting fibers, a substantially non-ionic binder material distributed throughout the web in adhesive contact with the fibers therein, the binder forming bonds between the fibers and said bonds having wet abrasion resistance, said binder comprising a material selected from the group consisting of copolymers of vinyl acetate and an alkyl acrylate, copolymers of vinyl acetate and an alkyl methacrylate and tripolymers of vinyl acetate, an alkyl acrylate, and an alkyl methacrylate, said binder comprising at least about 70 percent of vinyl acetate based upon the weight of the total monomers, said acrylates having the following structural formula:

\[
\begin{array}{c}
\text{H} \\
\text{H}
\end{array}
\]

and said methacrylates having the following structural formula:

\[
\begin{array}{c}
\text{CH}_3 \\
\text{H}
\end{array}
\]

wherein R is an alkyl radical having less than nine carbon atoms, and no more than about 0.4 percent by weight of the dry fabric of a quaternary ammonium salt distributed uniformly throughout the fabric, said salt having the following structural formula:

\[
\begin{array}{c}
\text{R}_1 \\
\text{R}_2 \\
\text{R}_3 \\
\text{An}
\end{array}
\]

in which \( R_1 \) is an alkyl or heterogeneous aliphatic group having 8–18 carbon atoms; \( R_3 \) is a short chain alkyl radical (a methyl or an ethyl group); and \( An \) is an anion.

6. An absorbent pad comprising an inner absorbent layer and a nonwoven fabric covering at least the inner face thereof; said fabric comprising a loosely assembled web of overlapping intersecting fibers, a substantially non-ionic binder material distributed throughout the web in adhesive contact with the fibers therein, the binder forming bonds between the fibers and said bonds having wet abrasion resistance, said binder comprising a material selected from the group consisting of copolymers of vinyl acetate and an alkyl acrylate, copolymers of vinyl acetate and an alkyl methacrylate and tripolymers of vinyl acetate, an alkyl acrylate, and an alkyl methacrylate, said binder comprising at least about 70 percent of vinyl acetate based upon the weight of the total monomers, said acrylates having the following structural formula:

\[
\begin{array}{c}
\text{H} \\
\text{H}
\end{array}
\]

and said methacrylates having the following structural formula:

\[
\begin{array}{c}
\text{CH}_3 \\
\text{H}
\end{array}
\]

wherein R is an alkyl radical having less than nine carbon atoms, and no more than about 0.4 percent by weight of the dry fabric of a quaternary ammonium salt distributed uniformly throughout the fabric.

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