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(71) Applicant *(for all designated States except US)*: **THE PROCTER & GAMBLE COMPANY** [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **BOND, Eric, Bryan** [US/US]; 253 Terwilligers Run, Maineville, OH 45039 (US). **CHHABRA, Rajeev** [IN/US]; 8526 Charleston Valley Drive, Mason, OH 45040 (US). **ISELE, Olaf, Erik, Alexander** [DE/US]; 8772 Rupp Farm Drive, West Chester, OH 45069 (US). **XU, Han** [CN/US]; 8495H Jonathan Lane, Maineville, OH 45039 (US).

(74) Common Representative: **THE PROCTER & GAMBLE COMPANY**; c/o Eileen L. Hughett, 6110 Center Hill Road, Cincinnati, OH 45224 (US).

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(54) Title: FIBERS, NONWOVENS AND ARTICLES CONTAINING NANOFIBERS PRODUCED FROM BROAD MOLECULAR WEIGHT DISTRIBUTION POLYMERS

(57) Abstract: The present invention is directed to articles comprising nanofibers. The nanofibers, having a diameter of less than 1 micron, may comprise a significant number of the fibers in one layer of the web contained by the article. Preferably, the nanofibers are produced in a melt film fibrillation process. The articles include diapers, training pants, adult incontinence pads, catamenials products such as feminine care pads and pantiliners, tampons, personal cleansing articles, personal care articles, and personal care wipes including baby wipes, facial wipes, and feminine wipes.

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FIBERS, NONWOVENS AND ARTICLES CONTAINING NANOFIBERS PRODUCED FROM BROAD MOLECULAR WEIGHT DISTRIBUTION POLYMERS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application No. 60/563,330, filed April 19, 2004.

FIELD OF THE INVENTION

The present invention relates to fibers, nonwovens and articles made from nanofibers and method of producing the nanofibers. The nanofibers can be made from a polymer having a broad molecular weight distribution.

BACKGROUND OF THE INVENTION

The need for articles produced from nonwoven containing nanofibers has continued to increase. The diameters of nanofibers are generally understood to be less than about 1000 nanometer or one micron. The nanofibers webs are desired due to their high surface area, low pore size, and other characteristics. The nanofibers, also commonly called microfibers or very fine fibers, can be produced by a variety of methods and from a variety of materials. Although several methods have been used, there are drawbacks to each of the methods and producing cost effective nanofibers has been difficult.

Methods of producing nanofibers include a class of methods described by melt fibrillation. Non limiting examples of melt fibrillation methods include melt blowing, melt fiber bursting, and melt film fibrillation. Methods of producing nanofibers, not from melts, are film fibrillation, electro-spinning, and solution spinning. Other methods of producing nanofibers include spinning a larger diameter bi-component fiber in an islands-in-the-sea, segmented pie, or other configuration where the fiber is then further processed so that nanofibers result.

Melt fibrillation is a general class of making fibers defined in that one or more polymers are molten and extruded into many possible configurations (e.g. co-extrusion, homogeneous or bicomponent films or filaments) and then fibrillated or fiberized into filaments.

Melt blowing is a commonly used method of producing fibers. Typical fiber diameters range from 2 to 8 micron. Melt blowing can be used to make fibers with smaller diameters but with considerable changes needed to the process. Commonly, redesigned nozzles and dies are needed. Examples of these include U.S. Patent Nos. 5,679,379 and 6,114,017 by Fabbricante et

al. and U.S. Patent Nos. 5,260,003 and 5,114,631 by Nyssen et al. These methods utilize relatively high pressures, temperatures, and velocities to achieve the small fiber diameter.

Melt fiber bursting is a derivative of mineral fiber making process that has been applied to polymer fiber making. Examples of mineral melt fiber bursting process include US Patent No. 4,001,357 by Walz et al. and US Patent Nos. 4,337,074 and 4,533,376 by Muschelknautz et al. The key to this process is the use of sonic and supersonic air (gas) velocities to burst the melt filament into a multiplicity of fine fibers. Typical fiber diameters range from less than 1 micron to about 6 micron. Examples of processes with bursting polymer melt into fine fibers include US Patent No. 5,075,161 by Nyssen et al.; European Patent Nos. 1 192 301 B1 and 0 724 029 B1 and European Patent Application 1 358 369 A2 by Gerking; and WO 04/020722 by Sodemann et al. These methods utilize Laval nozzles to speed up the gas velocities to sonic and/or supersonic range. When polymer melt is exposed to such high gas velocities, it bursts into multiplicity of fine fibers. The processes are configured by use of desired process conditions and die and nozzle geometries to produce desired fiber sizes.

Melt film fibrillation is another method to produce fibers. A melt film is produced from the melt and then a fluid is used to form nanofibers from the melt film. Two examples of this method include Torobin's U.S. Patent Nos. 6,315,806; 5,183,670; and 4,536,361; and Reneker's U.S. Patent Nos. 6,382,526, 6,520,425 and 6,695,992, assigned to the University of Akron.

Film fibrillation is another method of producing nanofibers although not designed for the production of polymeric nanofibers to be used in nonwoven webs. U.S. Patent No. 6,110,588 by Perez et al., assigned to 3M, describes of method of imparting fluid energy to a surface of a highly oriented, highly crystalline, melt-processed, solidified polymer film to form nanofibers. The films and fibers are useful for high strength applications such as reinforcement fibers for polymers or cast building materials such as concrete.

Electrospinning is a commonly used method of producing nanofibers. In this method, a polymer is dissolved in a solvent and placed in a chamber sealed at one end with a small opening in a necked down portion at the other end. A high voltage potential is then applied between the polymer solution and a collector near the open end of the chamber. The production rates of this process are very slow and fibers are typically produced in small quantities. Another spinning technique for producing nanofibers is solution or flash spinning which utilizes a solvent.

Two-step methods of producing nanofibers are also known. The first step is to spin a larger diameter multicomponent fiber in an islands-in-the-sea, segmented pie, or other configuration. The larger diameter multicomponent fiber is then split or the sea is dissolved so that nanofibers result in the second step. For example, U.S. Patent Nos. 5,290,626 by Nishio et al., assigned to Chisso, and 5,935,883, by Pike et al., assigned to Kimberly-Clark, describe the

islands-in-the-sea and segmented pie methods respectively. These processes involve two sequential steps, making the fibers and dividing the fibers.

To produce disposable articles containing nanofibers that are commercially advantageous, the cost of the nanofibers must be controlled. Equipment, process, process aids, and polymer costs can all be controlled. Therefore, it is an object of the invention to produce nanofibers which are low in cost. It is also desired to form products containing nanofibers for a variety of uses and benefits. The uses include executions such as a diaper, wipe, and absorbent material, among other uses.

SUMMARY OF THE INVENTION

To achieve lower fiber diameters, polymers with narrow molecular weight distribution polymers are commonly used. This is because the narrow molecular weight distribution polymer is able to flow faster, attenuate more easily, and form smaller diameter fibers. Narrow molecular weight distribution polymers and high attenuation energies, such as high gas velocities, flow rates, and take up speeds, are commonly used to create the nanofibers. Generally, all of these parameters must be optimized to form the nanofibers. Therefore, one having ordinary skill in the art would not utilize broad molecular weight distribution polymers in a single step melt fibrillation process to form nanofibers. One way of reducing the cost of the nanofiber is by using polymers with broad molecular weight distributions. Broad molecular weight distribution polymers have a broad range of molecular weights and are more easily produced and therefore, more widely available. Typically, broad molecular weight distribution polymers are stronger, less abrasive or linting, and more stable. Therefore, an object of the present invention is to produce articles containing nanofibers produced from broad molecular weight distribution polymers.

The present invention is directed to fibers, nonwovens and articles comprising nanofibers. The nanofibers can be made from a single step melt fibrillation process with a polymer having a molecular weight distribution greater than about three. The nanofibers, having a diameter of less than 1 micron, must comprise a significant number of the fibers in one layer of the web. Preferably, the nanofibers are produced in a melt film fibrillation process. Suitable hygiene articles include diapers, training pants, adult incontinence pads, catamenials products such as feminine care pads and pantiliners, tampons, personal cleansing articles, personal care articles, and personal care wipes including baby wipes, facial wipes, and feminine wipes.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to articles made from nanofibers. The nanofibers are produced from one or more thermoplastic polymers. The polymers of the present invention will

have a molecular weight distribution greater than three. The molecular weight distribution (MWD) is defined as the weight average molecular weight divided by the number average molecular weight. This can be determined by using ASTM D6474-99 Standard Test Method for Determining Molecular Weight Distribution and Molecular weight Averages of Polyolefins by High Temperature Gel Permeation Chromatography. Preferably, the MWD is greater than about 3.5, more preferably greater than about 4.0, even more preferably greater than about 4.5 and most preferably greater than about 5.

Typically, polymers have relatively low flow rates but are combined with other materials, such as peroxide, to increase the melt flow rate and narrow the MWD. This is because many processes which make fibers, particularly nanofibers, cannot use low melt flow rate polymers. Preferably, the process of the present invention will produce a film or larger structure which is thicker and/or has a higher polymer content. This film or larger structure is then formed into nanofibers.

Suitable thermoplastic polymers include any polymer suitable for melt spinning and having a broad MWD. The rheological properties of the polymer as it is present in the die must be such that the polymer is able to form a film. The melting temperature of the polymer is generally from about 25°C to 400°C.

Nonlimiting examples of thermoplastic polymers which may have a broad MWD include polypropylene and copolymers, polyethylene and copolymers, polyesters, polyamides, polystyrenes, biodegradable polymers including thermoplastic starch, PHA, PLA, polyurethanes, and combinations thereof. The homopolymer, copolymers, and blends thereof are included within this description. Preferred polymers are polypropylene, polyethylene, nylons, and polyethylene terphalate.

Optionally, the polymer may contain additional materials to provide additional properties for the fiber. These may modify the physical properties of the resulting fiber such as elasticity, strength, thermal or chemical stability, appearance, absorbency, odor absorbency, surface properties, and printability, among others. A suitable hydrophilic melt additive may be added. Optional materials may be present up to 50% of the total polymer composition as long as the MWD is still within the identified range.

The production of broad MWD polymers can be an *in situ* process or artificially created. One example of producing a broad MWD for polypropylene is to terminate the polymerization process earlier. This enables a higher melt flow rate and broader MWD. An example of an *in situ* process is where during the production of polypropylene, the peroxide level is changed for making resin so that the MWD can be broader. An example of artificially created broad MWD would be blending various types of polyesters together. Most polyester resins have MWD ratio

less than three. However, careful blending of various MW polyester resins can produce a broader MWD. The blending can also be done with other polymeric materials, most preferably polypropylene.

It may be desired to use a mixture of narrow and broad MWD in a web. The broader MWD polymer will fibrillate easier which may result in fibers having different diameters. If the polymers will not blend, separate nozzles may be utilized for the different MWD polymers. Other uses of narrow and broad MWD polymers are for bonding, particularly for thermal bonding. Distinct areas of a web having different MWD polymers will have different thermal bonding properties and therefore different performance. This may enable the different areas to be suitable for barrier, air permeability, absorbency, controlled delivery, opacity, mechanical properties, post-processing, thermal properties, and other characteristics.

The average fiber diameter of a significant number of fibers in the nanofiber layer of the web can be less than one micron and preferably from about 0.1 microns to 1 micron, more preferably from about 0.3 microns to about 0.9 microns. The basis weight of the nanofiber layer can be less than about 25 gsm, commonly from about 0.1 to about 15 gsm, preferably less than 10 gsm or 5 gsm. The nanofiber layer may have a basis weight in the range of from about 0.5 to about 3 gsm or from about 0.5 to about 1.5 gsm, depending upon use of the nonwoven web. It may be desired to form a web of several layers. The nanofiber layer may be combined with one, two, or more layers. A spunbond-nanofiber-spunbond web is one example. Basis weights for the total composite webs range from about 5 gsm to about 100 and are commonly from about 10 to about 50 gsm.

A uniform nanofiber web is typically desired and can be challenging to produce, particularly at low basis weights. Web uniformity can be measured through several methods. Examples of uniformity metrics include low coefficient of variation of pore diameter, basis weight, air permeability, and/or opacity. Uniformity can also mean lack of fiber bundles or roping, or visible holes, or other such defects. Uniformity may also be evaluated by the hydrohead or other liquid barrier measurement of the web. A higher barrier score generally indicates a more uniform web.

Pore diameter can be determined by methods known to those skilled in the art. The mean pore diameter of the nanofiber layer is preferably less than about 15 microns, more preferably less than about 10 microns, and most preferably less than about 5 microns. The desired coefficient of variation for a uniform web can be less than 20%, preferably less than about 15%, and more preferably about 10% or less. The lack of roping can be measured by counting the number of ropes or bundles of fibers in a measured area of the web. The lack of holes can also be measured by counting the number of holes having a diameter above a certain threshold in a measured area

of the web. A scanning electron microscope or other enlargement means can be used. For example, the holes may be counted if they are visible to the naked eye using a light box, or are more than 100 microns in diameter.

The fibers may be single- or multi-component fibers such as bicomponent fibers. The fibers may have a sheath–core or side-by-side or other suitable geometric configuration. After the fibers are made, the fibers may be treated or coated before formed into a web. Additionally, after a web is made, the web may be treated. Optionally, additives may be compounded into the polymer resin and these additives migrate out to the surface after the fibers are formed. The additives that move to the surface may need to be cured utilizing external energy, such as heat, or additives on surface may need to be chemically reacted with another component or curing may need to be catalyzed in the presence of another component, such that additional components may be added to the process while the fibers are being made or after the fibers are made using the resin with additives. Suitable treatments include hydrophilic or hydrophobic treatments. An example of hydrophobic treatment is poly-di-methyl-siloxanes. The specific treatment depends on the use of the web, type of polymer, and other factors. Desirable treatments are familiar to those skilled in the art.

The method of making the nanofibers of the present invention is any method that can utilize a thermoplastic polymer having a MWD greater than about three. Preferably, the method is a one step melt fibrillation process that can utilize a thermoplastic polymer having a MWD greater than three. Melt fibrillation processes are defined as a process utilizing a single phase polymer melt wherein fibers are formed. Single phases can include a dispersion but does not included solvent based melts such as those used in solution or electrospinning. Typical single step melt fibrillation processes include melt blowing, melt film fibrillation, spun bonding, melt spinning in a typical spin/draw process, and combination thereof. Single step processes do not include two-step processes where a larger fiber is first made and then split by removing part of the fiber or separating it. The process must be suitable for utilizing a thermoplastic polymer having a MWD greater than three and producing fibers having an average diameter of less than about 1 micron.

The method of making the nanofibers of the present invention is preferably a melt fibrillation process, or more preferably a melt film fibrillation process. Generally, this process involves providing a polymeric melt, utilizing a central fluid stream to form a polymeric film, and then using a fluid to form multiple nanofibers from the film. Suitable methods are detailed, for example, in U.S. Patent No. 4,536,361 to Torobin and U.S. Patent Nos. 6,382,526, 5,520,425 and 6,695,992 to Reneker. The film may be a hollow tube, relatively flat, or other suitable structure.

As further described in 4,536,361, the polymer is heated until it forms a liquid and flows easily. The melted polymer may be at a temperature of from about 0°C to about 400°C, preferably from about 10°C to about 300°C, and more preferably from about 20°C to about 220°C. The temperature of the polymer depends on the melting point of the polymer or polymer composition. The temperature of the polymer can be less than about 50°C above its melting point, preferably less than 25°C above its melting point, more preferably less than 15°C above its melting point, and just at or above its melting point or melting range. The melting point or range is measured using ISO 3146 method. The melted polymer will typically have a viscosity of from about 1 Pa-s to about 1000 Pa-s, typically from about 2 to about 200 Pa-s and more commonly from about 4 to about 100 Pa-s. These viscosities are given over a shear rate ranging from about 100 to about 100,000 per second. The melted polymer is at a pressure of about atmospheric pressure or slightly elevated.

In one method, the fiberizing fluid may push through the polymer liquid film to form a hollow polymer tube by blowing and applying pressure on the film and then inner surface of the tube. In another method detailed in 6,695,992, the fiberizing fluid will form a sheet of thin film from a slit or slot type die design. The fiberizing fluid may be at a temperature close to the temperature of the melted polymer. Non-limiting examples of the fiberizing fluid are gases such as nitrogen or more preferably air. The fiberizing fluid temperature may be a higher temperature than the melted polymer to help in the flow of the polymer and the formation of the hollow tube or flat film. Alternatively, the fiberizing fluid temperature can be below the melted polymer temperature to assist in the formation and solidification of the nanofibers. The fiberizing fluid temperature is less than about 50°C above the polymer melting point, preferably less than 25°C above the polymer melting point, more preferably less than 15°C above the polymer melting point, or just at or above the polymer melting point. The fiberizing fluid temperature may also be below the process temperature, down to 15°C. The pressure of the fiberizing fluid is sufficient to blow the nanofibers and can be slightly above the pressure of the melted polymer as it is extruded out of the orifice.

The fiberizing fluid will generally have a pressure below 5000 psi. Preferably, the fiberizing fluid pressure will be less than 1000 psi, more preferably less than about 100 psi, and most preferably from about 15 to about 80 psi.

The polymer throughput will primarily depend upon the specific polymer used, the nozzle design, and the temperature and pressure of the polymer. The polymer throughput will be more than about 1 gram per minute per orifice. Preferably, the polymer throughput can be more than about 5 gram per minute per orifice and more preferably greater than about 10 gram per minute per orifice. There will likely be several orifices operating at one time which increases the total

production throughput. The throughput, along with pressure, temperature, and velocity, are measured at the die orifice exit. Another way to describe the throughput is to use the term of extruded wet length. The polymer throughput will be more than about 0.3 gram per centimeter of extruded wet length. The extruded wet length is defined is the linear distance of the molten film before nanofibers are produced. For example, if the present invention is manifested using discrete nozzles and the nozzle orifice diameter is 1 centimeter, the mass throughput rate for that nozzle is 1 gram/minute, the overall rate is 0.318 gram per cm per minute. Preferably, the polymer throughput will be more than about 3 gram per cm per minute, more preferably greater than about 6 gram per cm per minute, and most preferably greater than 10 gram per cm per minute.

An entraining or other fluid may be used to induce a pulsating or fluctuating pressure field to help in forming a multiplicity of nanofibers. The entraining fluid can be provided by a transverse jet which is located to direct the flow of entraining fluid over and around the film and nanofiber forming region. The entraining fluid can have a velocity of from about 1 to about 100 meter per second and preferably from about 3 to about 50 meter per second. The temperature of the entraining fluid can be the same as the above fiberizing fluid, but it is typically about the same temperature as the melted polymer just as the film is formed. An air curtain or other ancillary air stream can also be used to affect the spray pattern of nanofibers from two or more nozzles. This air stream or curtain may aid in shielding the spray formations between adjacent nozzles or may aid in compressing the spray pattern. The air curtain or stream may improve the uniformity of the web.

Another fluid stream, a quench or heating fluid, can optionally be used. This third fluid stream can be located to direct fluid into the nanofibers to cool or heat the fibers. If the fluid is used as a quenching fluid, it is at a temperature of from about –20°C to about 100°C and preferably from about 10°C to 40°C. If the fluid is used as a heating fluid, it is at a temperature of from about 40°C to 400°C and typically from about 100°C to about 250°C. Any fluid stream may contribute to the fiberization of the polymer melt and can thus generally be called fiberizing fluids. Any of the fluid streams may contain the treatments or additives for changing the surface, chemical, physical, or mechanical properties of fibers made.

The distance from the orifice or nozzle to collector distance, commonly called die-to-collector distance (DCD), can be optimized. The optimization may aid in producing a more uniform web. A reduction in the DCD may help to reduce the amount of fiber bundling or roping. This lower distance does not enable the fibers to have time to entangle, wrap around one another, or bundle. It may be desired to utilize more than one DCD for a web, to change the DCD during production, or to have different beams with different DCDs. It may be desirable to form a web with different uniformities by changing the DCD.

Nonlimiting examples of other nanofiber making processes from polymeric melts include melt fiber bursting, advanced melt blowing, and fibers splitting from multicomponent fibers and solid films. Examples of melt fiber bursting processes utilizing bursting polymer melt into fine fibers include US Patent No. 5,075,161 by Nyssen et al.; European Patent Nos. 1 192 301 B1 and 0 724 029 B1 and European Patent Application 1 358 369 A2 by Gerking; and WO 04/020722 by Sodemann et al. These methods utilize Laval nozzles to speed up the gas velocities to sonic and/or supersonic range. When polymer melt is exposed to such high gas velocities, it bursts into multiplicity of fine fibers.

Nyssen et al. disclose in US Patent No. 5,075,161 a method of bursting polyphenylene sulfide melt into fine filaments. In this method, the Laval nozzle is positioned just after the spinning nozzle. Polymer fibers having an average fiber diameter of less than about 6 microns, preferable from about 0.2 microns to 6 microns, are produced by subjecting the polymer melt streams to drawing out and cooling to below the melt temperature by extruding them into a gaseous medium which flows essentially parallel to the polymer melt streams and attains sonic or supersonic speed. This simultaneous deformation and cooling gives rise to amorphous fine or extremely fine fibers of finite length. High speed fiber bursting minimizes the surface oxidation of the fibers. WO 04/020722 by Sodemann et al. disclose a similar method of producing fine filament spunbonded nonwoven from fiber bursting of thermoplastic polymers by using sonic and supersonic fluid velocities. In said process, the Laval nozzle is placed underneath the spinning nozzle. The spinning speed, melt temperature, and the position of the Laval nozzle are appropriately set to achieve only partial thermal oxidation of fine filaments at their surface. The fibers produced by this method have been disclosed to have diameter of less than 1 micron, and are connected to one another at discrete points. Methods and apparatus disclosed by Gerking in European Patent Applications 1 192 301 B1 and 1 358 369 A2 also utilize Laval nozzle to speed up gas to sonic and supersonic velocity that is used to burst the polymer melt into multiplicity of fine filaments.

Melt film fibrillation process differs from melt fiber bursting process in how the fibers are made and the starting melt geometry from which fine filaments are produced. Melt film fibrillation starts with a film, in some instances a hollow melt film tube, that is thinned by central air jet and then fibrillates into multiplicity of nanofibers. In contrast, the starting melt geometry of melt bursting is a filament melt that when exposed to sonic and supersonic gas velocity in Laval nozzle bursts into multiplicity of nanofibers. Fibrous webs made from the processes may differ in uniformity because of differences in fiber-to-fiber separation and fiber bundle formations.

Various processes and combination of processes can be used to make the webs of the present invention. Preferred methods are methods which produce uniform nanofiber layers. Melt fiber bursting can be combined with melt film fibrillation with two separate beams on a single line. Various aspects of melt fiber bursting could be incorporated into melt film fibrillation. For example, fibers of different strengths and diameters could be produced to provide a desired combination of properties. Alternatively, aspects of melt film fibrillation can be included in other melt fibrillation processes to increase the throughput rate by utilizing a hollow elongated tube to form fibers. For example, a melt film fibrillation process could be modified to include a Laval nozzle to aid in drawing down the fibers. Drawing down can aid in further attenuation and increase the strength of the fibers. This may be particularly preferred for high Tg polymers such as polyesters where crystallization is stress induced.

Without being bound by theory, it is believed that the benefit of broad MWD polymers will enable the process to run with lower energies and therefore more efficiently. Broad MWD polymers shear thin easier than narrow MWD polymers due to the presence of high molecular weight chains. These chains during shear flow orient themselves parallel to the flow direction, and combined with the profiled melt extrusion or thinned regions, result in production of fibers and nanofibers under more economical process conditions. The process temperature may be lower and the mass throughput increased. In addition, higher number average molecular weight resins are also preferred as they also increase orientation in the flow direction and promote fibrillation. The improved fibrillation may be desired as lower MWD polymers may be sticky or make fibrillation difficult resulting in lower uniformity of the web.

In addition to better fibrillation, broad MWD polymers can produce fibers that are better for thermal bonding. For example, the article Relationships Between the Properties of Fibers and Thermally Bonded Nonwoven Fabrics Made of Polypropylene by Erik Andreassen et al. in the Journal of Applied Polymer Science, Vol. 58, 1633-1645 (1995) describes thermal bonding of fibers.

The nanofibers of the present invention are used to make nonwoven webs suitable for articles. The web is defined as the total nonwoven composite. A web may have one or several layers which are consolidated by thermal point-bonding or other techniques to attain strength, integrity and certain aesthetic characteristics. A layer is the web or part of a web that is produced in a separate fiber lay down or forming step. The webs of the present invention will comprise one or more layers having a significant number of nanofibers having diameters of less than one micron. A significant number is defined as at least about 25%. The significant number of fibers can be at least about 35%, at least about 50%, or more than about 75% of the total number of fibers in the layer. The web could have more than about 90% or about 100% of the fibers having

a diameter of less than about one micron. The fiber diameters of the web are measured using a scanning electron microscope at a magnification of greater than about 500 times and up to about 10,000 times as needed for visual analysis. To determine if a significant number of fibers have diameters less than one micron, at least about 100 fibers and preferably more fibers must be measured. The measurements must occur at various regions throughout the layer. Sufficient sampling that is statistically significant must occur.

The fiber diameter of the remaining larger fibers in the nanofiber layer, up to 75%, may have fiber diameters in any range. Typically, the larger fiber diameters will be just above one micron to about 10 microns.

Preferably, a significant number of fibers in a nanofiber layer will have a fiber diameter of less than about 900 nanometers and more preferably from about 100 nanometers to about 900 nanometers. Other preferably ranges of fiber diameter are less than about 700 nanometers and from about 300 to about 900 nanometers. The preferred diameters depend upon the use of the web. It may be desirable to have a significant number of fibers having a diameter of less than about one micron and a significant number of fibers having a diameter of great than about one micron. The larger fibers may trap and immobilize the nanofibers. This may help to reduce the amount of clumping or roping of the nanofibers and prevent the nanofibers from being carried off by stray air currents.

The layer of nanofibers in a web of the present invention may contain more than one polymer. Different polymers or polymer blends may be used for different orifices to produce layers in a web having different fiber diameters and different polymer compositions.

It may be desirable to produce a single layer nonwoven with varying fiber diameters. Alternatively, it can be desired to produce a nonwoven web with multiple layers with each layer having different fiber diameters. The melt film fibrillation process can be modified to produce both small and large diameter fibers to make various webs. The smaller fiber diameters are referred to as having a significant number of fibers having a diameter of less than one micron. The larger diameter fibers include fibers from the melt blowing range (typically 3 to 5 microns) to the spunbond (typically around 10 microns) or any range of fiber diameters above 1 micron. For example, one layer can be produced with an average fiber diameter of less than one micron and another layer with an average fiber diameter of around 5 microns. This type of structure could be used where traditionally spunbond-meltblown-spunbond (SMS) webs are used. The webs with various fiber diameters can be produced on the same line with the same equipment. This is an inexpensive way as the same equipment and components can be used. The operating costs and equipment costs are both controlled. Also, if desired, the same polymer can be used to produce different fiber diameters.

The articles of the present invention will contain the described nonwoven webs. The web may comprise the entire articles, such as a wipe, or the web may comprise one component of the article, such as a diaper. Hygiene articles are preferred articles. The hygiene articles include diapers, training pants, adult incontinence pads, catamenials products such as feminine care pads and pantiliners, tampons, personal cleansing articles, personal care articles, and personal care wipes including baby wipes, facial wipes, body wipes, and feminine wipes. Personal care articles include articles such as wound dressings, active delivery wraps or patches, and other substrates that are applied to the body, particularly the skin. Disposable underwear or clothing and protective wear for personal or industrial uses may also be desired. Other uses of wipes can be clean room wipes or decontamination wipes for use to absorb or control spills and other industrial wipes.

In a diaper, the web may be used as a barrier layer such as a barrier-on-core or an outercover. The webs may also be used as a high barrier cuff with a high hydrostatic head to enable low leakage incident rates of thin, narrow crotch diapers desired for comfort and fit. A typical web utilizing nanofibers is a web wherein the nanofiber layer is combined with at least one spunbond layer and consolidated using thermal point-bonding, hydro-entangling or other techniques suitable and appropriate for the end-use. There may be one or two spunbond layers encompassing the nanofiber layer.

In a diaper or other disposable absorbent product, the nonwoven web containing nanofibers may be utilized as a barrier layer. The barrier layer may be disposed between an absorbent core and an outer layer containing a garment. The absorbent core is the component of the article that is primarily responsible for fluid handling properties such as acquiring, transporting, distributing, and storing body fluids. The absorbent core is typically located between a liquid pervious body-side inner layer and a vapor permeable, liquid impermeable outer cover. The outer layer, also known as the back sheet or outer covering, is located on the outside of the disposable product. In the case of a diaper, the outer layer contacts the user's garment or clothing. The barrier layer may alternatively or also be disposed between the absorbent core and an inner layer. The inner layer, also known as a top sheet, is located on the side closest to the user's skin. The inner layer may contact the user's skin or may contact a separate top sheet with contacts the user's skin. The barrier layer may be absorbent. The barrier layer most preferably has a balance between convective air flow and absorptive barrier property. The convective air flow property is effective to reduce the relative humidity within the space between the absorbent article and the wearer's skin. The combination of liquid absorption and liquid barrier property provides protection against the wet through problem and is especially beneficial when the

absorbent article is under impact and/or sustained pressure. Further description and benefits of the barrier layers may be found in WO 01/97731.

The webs may be used in wipes to enable improved lotion handling and reduced gradient of liquids. The webs may also provide controlled delivery of a substance. The delivered substance can be of liquids, lotions, actives, or other materials. Due to the high surface area of the nanofibers, the webs may be used as absorbent materials for wipes or cores of feminine care product pads, diapers, training pants, or adult incontinence. The webs may provide enhanced distribution of fluids and/or retention. Additionally, the webs for absorbent uses may be made with added particulates or absorbent or natural fibers for increased absorbance or certain layers of the webs may have different properties.

The nanofiber webs may also be used in articles wherein opaqueness is desired. Added opaqueness may result due to the small fiber diameter and uniformity or pigments may be added to the polymer melt or webs. The webs have also been found to have low linting. This may be due to longer length fibers or entangling of fibers in the web.

Other products that will benefit from a nanofiber web include filters. Filters can be for industrial, personal, or home use and can be used to filter air, liquids, or small particles. Industrial uses can include automotive, furnace, water, and other types of filters. A type of personal filter includes a filter mask such as a surgical mask. Other medical uses of webs containing nanofiber layers include surgical gowns, wound dressings, and medical barriers. The webs can also be used as noise and thermal insulators, for outdoor gear, clothing, and as conducting fibers.

EXAMPLES

Comparative Example 1: Basell Profax PH-835, nominally a 35 melt flow rate polypropylene has a molecular weight distribution less than 3, as determined from gel permeation chromatography in trichlorobenzene at 150°C calibrated with polystyrene standards, is introduced into a melt film fibrillation process. The actual molecular weight distribution of this particular batch was 2.63. The process temperature is 280°C with the fiberizing fluid temperature of 25°C. In order to make the desired fibers and nanofibers, the fluidizing pressure must be greater than 55psi. The mass throughput was also limited to 10 grams per cm per minute.

Comparative Example 2: FINA EOD-02-04, nominally a 100 melt flow rate polypropylene has a molecular weight distribution less than 3, as determined from gel permeation chromatography in trichlorobenzene at 150°C calibrated with polystyrene standards, is introduced into a melt film fibrillation process. The actual molecular weight distribution of this particular batch was 2.98. The process temperature is 240°C with the fiberizing fluid temperature of 25°C. In order to make

the desired fibers and nanofibers, the fluidizing pressure must be greater than 55psi. The mass throughput was limited to 8 grams per cm per minute.

Example 1: ExxonMobil Escorene 3155, nominally a 35 melt flow rate polypropylene has a molecular weight distribution more than 3, as determined from gel permeation chromatography in trichlorobenzene at 150°C calibrated with polystyrene standards, is introduced into a melt film fibrillation process. The actual molecular weight distribution of this particular batch was 3.15. The process temperature is 280°C with the fiberizing fluid temperature of 25°C. In order to make the desired fibers and nanofibers, the fluidizing pressure must be greater than 30psi. The mass throughput was up to 15 grams per cm per minute.

Example 2: FINA 3860X, nominally a 100 melt flow rate polypropylene has a molecular weight distribution more than 3, as determined from gel permeation chromatography in trichlorobenzene at 150°C calibrated with polystyrene standards, is introduced into a melt film fibrillation process. The actual molecular weight distribution of this particular batch was 4.6. The process temperature is 240°C with the fiberizing fluid temperature of 25°C. In order to make the desired fibers and nanofibers, the fluidizing pressure must be greater than 55psi. The mass throughput was up to 11 grams per cm per minute.

Example 3: Dow Chemical Company 05862N, a high density polyethylene has a molecular weight distribution more than 3, as determined from gel permeation chromatography in trichlorobenzene at 150°C calibrated with polystyrene standards, is introduced into a melt film fibrillation process. The actual molecular weight distribution of this particular batch was 3.27. The process temperature is 240°C with the fiberizing fluid temperature of 25°C. In order to make the desired fibers and nanofibers, the fluidizing pressure must be greater than 30psi. The mass throughput is up to 15 grams per cm per minute.

Example 4: Basell PDC 1274, nominally a 12 melt flow rate polypropylene has a molecular weight distribution more than 3, as determined from gel permeation chromatography in trichlorobenzene at 150°C calibrated with polystyrene standards, is introduced into a melt film fibrillation process. The actual molecular weight distribution of this particular batch was 4.61. The process temperature is 290°C with the fiberizing fluid temperature of 25°C. In order to make the desired fibers and nanofibers, the fluidizing pressure must be greater than 35psi. The mass throughput is up to 15 grams per cm per minute.

Example 5: Basell PDC 1267, nominally a 18 melt flow rate polypropylene has a molecular weight distribution more than 3, as determined from gel permeation chromatography in trichlorobenzene at 150°C calibrated with polystyrene standards, is introduced into a melt film fibrillation process. The actual molecular weight distribution of this particular batch was 3.86. The process temperature is 290°C with the fiberizing fluid temperature of 25°C. In order to make the desired fibers and nanofibers, the fluidizing pressure must be greater than 35psi. The mass throughput is up to 15 grams per cm per minute.

All documents cited are, in relevant part, incorporated herein by reference; the citation of any document is not to be construed as an admission that it is prior art with respect to the present invention.

While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

What is claimed is:

1. A nonwoven web comprising at least one layer having a significant number of nanofibers with diameters less than one micron, wherein said nanofibers are made from a polymer having a molecular weight distribution of greater than three.

2. The nonwoven web according to Claim 1 wherein the polymer has a molecular weight distribution of greater than 3.5.

3. The nonwoven web of Claim 1 wherein the nanofiber layer has at least 50% of nanofibers with a diameter of less than one micron.

4. The nonwoven web of Claim 1 wherein the nanofiber layer has a basis weight of from 0.5 gsm to 15 gsm.

5. The nonwoven web of Claim 1 wherein the polymer has a molecular weight distribution of greater than 4.

6. An article comprising a nonwoven web of Claim 1.

7. The article of Claim 6 wherein the article is selected from the group consisting of diapers, training pants, adult incontinence pads, catamenials products such as feminine care pads and pantiliners, tampons, personal cleansing articles, personal care articles, and personal care wipes such as baby wipes, facial wipes, body wipes and feminine wipes, and combinations thereof.

8. The article of Claim 7 wherein the nonwoven web is a barrier layer.

9. A process of making a nonwoven web comprising a nanofiber layer having a significant number of nanofibers with diameters less than one micron, wherein said nanofibers are made from a melt film fibrillation process comprising the steps of:

a. providing a polymeric melt having a molecular weight distribution of greater than 3,
b. utilizing a fluid stream to form a polymeric film, and
c. forming multiple nanofibers from the polymeric film.

INTERNATIONAL SEARCH REPORT

Interi Application No
PCT/US2005/013341

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D04H3/00 D01D5/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D04H D01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Lanniel, G

INTERNATIONAL SEARCH REPORT

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