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(71) Applicant: **KIMBERLY-CLARK WORLDWIDE, INC.**
[US/US]; 2300 Winchester Road, Neenah, Wisconsin
54956 (US).

(72) Inventors: **BRANHAM, Kelly**; 2300 Winchester Road,
Neenah, Wisconsin 54956 (US). **HONARBAKHSH,
Sara**; 2300 Winchester Road, Neenah, Wisconsin 54956
(US).

(74) Agents: **JOHNSTON, Jason, W.** et al.; Dority & Man-
ning, P.a., P O Box 1449, Greenville, South Carolina
29602-1449 (US).

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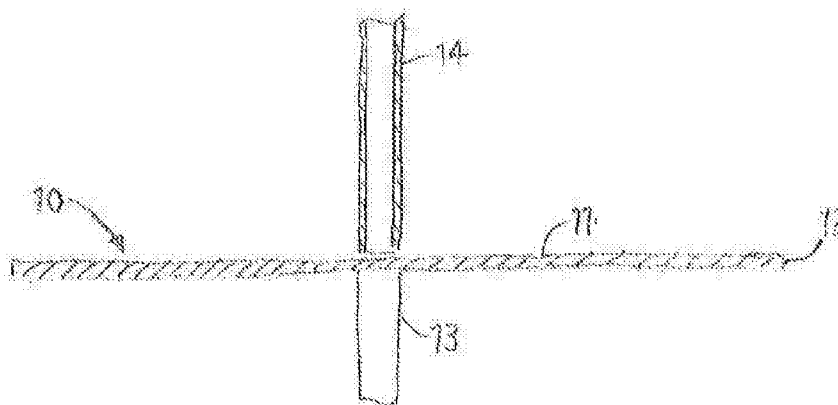


FIG. 1

(57) Abstract: A technique for forming fibers (e.g., nanofibers, microfibers, etc.) from an aqueous spinning solution is provided. Through careful control over the nature and relative concentration of the components in the solution, fibers can be formed that remain relatively water resistant. To help accomplish these unique features, a pH-sensitive polymer is employed in the spinning solution that is generally soluble in water at a certain pH value, yet generally insoluble in water at a different pH value. This property allows for selective adjustment of the pH both before and after spinning to control the water-solubility of the polymer as desired.



SOLUTION SPINNING OF FIBERS

Related Application

The present application claims priority to U.S. application serial no. 13/953,097, filed on July 29, 2013, which is incorporated herein in its entirety by
5 reference thereto.

Background of the Invention

Solution spinning has become an important process for forming fibers, such as nanofibers and microfibers. To ensure good homogeneity of the polymer in the spinning solution, which aids in fiber formation, many traditional fiber processes
10 employ the use of organic solvents, such as acetone, formic acid, methylene chloride, ethylene chloride, tetrahydrofuran, toluene, hexafluoroisopropanol, and trifluoroacetic acid. Due to the potential environmental concerns associated with such organic solvents, attempts have also been recently made to spin fibers from aqueous solutions. Unfortunately, aqueous solutions are often problematic in that
15 they typically require the use of fiber-forming polymers that are generally soluble in water. While fibers can be readily spun from such polymers, the resulting fibers are highly susceptible to property degradation upon exposure to water due to the presence of a high concentration of water-soluble materials. As such, a need
20 currently exists for a method of forming fibers from an aqueous spinning solution.

Summary of the Invention

In accordance with one embodiment of the present invention, a method for forming fibers from an aqueous spinning solution is disclosed. The spinning solution contains a pH-sensitive polymer and a solvent that includes water. The
25 pH-sensitive polymer is generally soluble in water at a first pH level and generally insoluble in water at a second pH level. The method comprises spinning the solution into fibers while at the first pH level and selectively adjusting the pH of the fibers during and/or after spinning so the pH is at the second pH level.

In accordance with another embodiment of the present invention, a fiber
30 that is formed from an aqueous spinning solution is disclosed. The fiber contains one or more pH-sensitive polymers that are generally soluble in water at a first pH level and generally insoluble in water at a second pH level and optionally one or more hydrophilic polymers that are generally soluble in water at the first pH level

and the second pH level. The pH-sensitive polymers constitute about 50 wt. % or more of the polymer content of the fiber and the hydrophilic polymers constitute less than about 50 wt. % of the polymer content of the fiber.

Other features and aspects of the present invention are discussed in greater detail below.

Brief Description of the Drawings

A full and enabling disclosure of the present invention, including the best mode thereof, directed to one of ordinary skill in the art, is set forth more particularly in the remainder of the specification, which makes reference to the appended figures in which:

Fig. 1 illustrates a device that may be employed in the present invention to centrifugally spin fibers;

Fig. 2 is an SEM microphotograph showing the fibers formed in Example 2 at a magnification of 510X; and

Fig. 3 is an SEM microphotograph showing the fibers formed in Example 2 at magnification of 1850X.

Detailed Description of Representative Embodiments

Definitions

As used herein, the term "fibers" refer to elongated structures having a definite length or that are substantially continuous in nature. The fibers may be, for example, "nanofibers" or "microfibers." The term "nanofibers" generally refers to fibers having an average diameter of less than about 1 micrometer, in some embodiments about 800 nanometers or less, in some embodiments from about 5 nanometers to about 500 nanometers, and in some embodiments, from about 10 nanometers to about 100 nanometers, while the term "microfibers" generally refers to fibers having an average diameter of from about 1 micrometer to about 100 micrometers, in some embodiments about 2 micrometers to about 50 micrometers, in some embodiments from about 3 micrometers to about 40 micrometers, and in some embodiments, from about 5 micrometers to about 25 micrometers.

As used herein, the term "meltblown" web generally refers to a nonwoven web that is formed by a process in which a molten thermoplastic material is extruded through a plurality of fine, usually circular, die capillaries as molten fibers into converging high velocity gas (e.g., air) streams that attenuate the fibers of

molten thermoplastic material to reduce their diameter. Thereafter, the meltblown fibers are carried by the high velocity gas stream and are deposited on a collecting surface to form a web of randomly dispersed meltblown fibers.

As used herein, the term "spunbond" web generally refers to a nonwoven web containing substantially continuous filaments. The filaments are formed by extruding a molten thermoplastic material from a plurality of fine, usually circular, capillaries of a spinnerette with the diameter of the extruded filaments then being rapidly reduced as by, for example, eductive drawing and/or other well-known spunbonding mechanisms.

Detailed Description

Reference now will be made in detail to various embodiments of the invention, one or more examples of which are set forth below. Each example is provided by way of explanation of the invention, not limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment, can be used on another embodiment to yield a still further embodiment. Thus, it is intended that the present invention covers such modifications and variations within the scope of the appended claims and their equivalents.

Generally speaking, the present invention is directed to a technique for forming fibers (e.g., nanofibers, microfibers, etc.) from an aqueous spinning solution. The present inventors have discovered that through careful control over the nature and relative concentration of the components in the solution, fibers can be formed that remain relatively water resistant. To help accomplish these unique features, a pH-sensitive polymer is employed in the spinning solution that is generally soluble in water at a first pH level, yet generally insoluble in water at a second pH level. This property allows for selective adjustment of the pH both before and after spinning to control the water-solubility of the polymer as desired. Namely, the pH can be controlled prior to spinning so that the pH-sensitive polymer is dissolved in the solution in a substantially homogeneous fashion. After spinning, however, the pH may be altered so that when contacted with water, the

resulting fibers do not readily dissolve. Among other things, this allows the fibers to substantially retain their mechanical strength and integrity even when wet.

Various embodiments of the present invention will now be described in more detail.

5 I. Solution

A. pH-Sensitive Polymer

As noted, the spinning solution of the present invention contains a pH-sensitive polymer. Typically, such polymers constitute from about 30 wt.% to about 90 wt.%, in some embodiments from about 40 wt.% to about 80 wt.%, and in
10 some embodiments, from about 50 wt.% to about 70 wt.% of the spinning solution. The particular nature of the polymer may vary so long as it is generally soluble in water (e.g., at 25°C) at a certain pH level, yet generally insoluble in water (e.g., at 25°C) at a different pH level. The polymer may contain a relatively acidic functional group (e.g., carboxylic, sulfonic, etc.) and/or relatively basic functional
15 group (e.g., tertiary amine) that imparts the desired pH sensitivity.

Acidic pH-sensitive polymers, for instance, often contain carboxylic groups. Examples of such carboxylic-containing acidic polymers may include, for instance, (meth)acrylic acid polymers, vinyl acetate polymers, vinyl ether polymers, etc. As used herein, the term "(meth)acrylic" includes acrylic and methacrylic monomers,
20 as well as salts or esters thereof, such as acrylate and methacrylate monomers. Particular examples of such (meth)acrylic monomers may include, for instance, acrylic acid, methacrylic acid, methyl acrylate, ethyl acrylate, n-propyl acrylate, i-propyl acrylate, n-butyl acrylate, s-butyl acrylate, i-butyl acrylate, t-butyl acrylate, n-amyl acrylate, i-amyl acrylate, isobornyl acrylate, n-hexyl acrylate, 2-ethylbutyl
25 acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, n-decyl acrylate, methylcyclohexyl acrylate, cyclopentyl acrylate, cyclohexyl acrylate, methyl methacrylate, ethyl methacrylate, 2-hydroxyethyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, i-propyl methacrylate, i-butyl methacrylate, n-amyl methacrylate, n-hexyl methacrylate, i-amyl methacrylate, s-butyl-methacrylate, t-butyl methacrylate,
30 2-ethylbutyl methacrylate, methylcyclohexyl methacrylate, cinnamyl methacrylate, crotyl methacrylate, cyclohexyl methacrylate, cyclopentyl methacrylate, 2-ethoxyethyl methacrylate, isobornyl methacrylate, etc., as well as combinations thereof. In one particular of the present invention, an acidic polymer may be

employed that is a terpolymer formed from an acrylate component (e.g., ethyl acrylate), methacrylate component (e.g., methyl methacrylate) and (meth)acrylic acid component (e.g., acrylic acid or methacrylic acid). Such polymers are commercially available under the name CARBOSET® from Lubrizol. Basic pH-sensitive polymers may also be employed in the present invention. For instance, basic pH-sensitive polymers often contain primary, secondary, and/or tertiary amine groups. Examples of such amine-containing basic polymers may include, for instance, polyamides (e.g., N-substituted polyamides), polyimides, polyimines (e.g., polyethyleneimine), polyureas, etc.

The pH at which the polymer is capable of being dissolved in water as a relatively homogenous solution will of course vary depending on the nature of the pH-sensitive polymer. When acidic polymers are employed, for instance, the pH at which a transition from solution to colloid occurs is typically from about 5 to about 15, in some embodiments from about 7 to about 14, and in some embodiments, from about 8 to about 12. The acidic polymer may, for instance, remain in solution at a first pH level of about 5 or more, in some embodiments about 7 or more, in some embodiments about 8 or more, and in some embodiments, about 9 or more. Of course, at a second pH level of less than about 5, the acidic polymer may instead form a colloidal system with water and thus remain generally water-insoluble. In stark contrast, when basic polymers are employed, the pH level at which a transition from solution to colloid occurs is typically from about 1 to about 5. The basic polymer may, for instance, remain in solution within a pH range of about 5 or less, in some embodiments about 4 or less, and in some embodiments, about 3 or less. Within a pH range of greater than about 5, however, the basic polymer may form a colloidal system with water and thus remain generally water-insoluble.

To aid in the desired pH transition, a pH modifier is also typically employed in the spinning solution. Such pH modifiers may be present in any effective amount needed to achieve the desired pH level. In some embodiments, for example, pH modifier(s) are present in an amount from about 0.001 wt.% to about 5 wt.%, in some embodiments from about 0.005 wt.% to about 2 wt.%, and in some embodiments, from about 0.01 wt.% to about 1 wt.% of the solution.

Various pH modifiers may be utilized to achieve the desired pH level. Basic pH modifiers, for instance, may be employed in combination with acidic pH-sensitive polymers, while acidic pH modifiers may be employed in combination with basic pH-sensitive polymers. Examples of suitable basic pH modifiers may include, for instance, ammonia; mono-, di-, and tri-alkyl amines (e.g., triethylamine); mono-, di-, and tri-alkanolamines (e.g., monoethanolamine, isopropanolamine, diethanolamine, and triethanolamine); etc., as well as mixtures of basic pH modifiers. Examples of suitable acidic pH modifiers may likewise include, for instance, inorganic acids, such as hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, and polyphosphoric acid; organic acids, as well as mixtures of acidic pH modifiers. Prior to spinning, the pH modifier helps ensure that the pH-sensitive polymer remains in solution. However, the present inventors have discovered that certain types of pH modifiers can be employed that readily evaporate from the fibers during and/or after their formation due to their relatively low boiling point. Of course, the boiling point is normally selected so that the modifier can be readily removed during and/or after spinning, but not to such an extent that a significant portion of the modifier is inadvertently released from the solution prior to spinning. In this regard, the pH modifier typically has a boiling point in water (atmospheric pressure) of from about 10°C to about 50°C, in some embodiments from about 15°C to about 45°C, and in some embodiments, from about 25°C to about 35°C. The boiling point of ammonia in water (ammonium hydroxide) is, for instance, about 37.7°C.

B. Solvent

In addition to a pH-sensitive polymer and optional pH modifier, a solvent may also be employed in the spinning solution. As indicated above, the spinning solution used to form the fibers of the present invention is generally aqueous in nature. In this regard, water (e.g., deionized water) typically constitutes about 50 wt.% or more, in some embodiments, about 70 wt.% or more, and in some embodiments, about 90 wt.% to 100 wt.% of the solvent(s) used in the solution. In some embodiments, a secondary solvent may also be employed in conjunction with water to form a solvent mixture. Suitable secondary solvents may include, for instance, glycols (e.g., ethylene glycol, propylene glycol, butylene glycol, triethylene glycol, hexylene glycol, polyethylene glycols, ethoxydiglycol,

dipropyleneglycol, etc.); glycol ethers (e.g., methyl glycol ether, ethyl glycol ether, isopropyl glycol ether, etc.); alcohols (e.g., methanol, ethanol, n-propanol, isopropanol, and butanol); ketones (e.g., acetone, methyl ethyl ketone, and methyl isobutyl ketone); esters (e.g., ethyl acetate, butyl acetate, diethylene glycol ether acetate, methoxypropyl acetate, ethylene carbonate, propylene carbonate, etc.); amides (e.g., dimethylformamide, dimethylacetamide, dimethylcaprylic/capric fatty acid amide and N-alkylpyrrolidones); sulfoxides or sulfones (e.g., dimethyl sulfoxide (DMSO) and sulfolane); and so forth. It should be understood, however, that such secondary solvents are by no means required in the present invention.

In fact, as indicated above, one benefit of the present invention is that conventional organic solvents, such as acetone, formic acid, methylene chloride, ethylene chloride, tetrahydrofuran, toluene, hexafluoroisopropanol, and trifluoroacetic acid, are not required in the present invention. Thus, in certain embodiments, the spinning solution may be generally free of organic solvents such that they constitute, for example, about 10 wt.% or less, in some embodiments, about 5 wt.% or less, and in some embodiments, 0 to about 1 wt.% of solvent(s) used in the solution.

The total amount of solvent(s) employed in the spinning solution may vary, but is generally such that the resulting solution has a relatively high viscosity, such as from about 50,000 to about 800,000 centipoise, in some embodiments from about 60,000 to about 500,000 centipoise, and in some embodiments, from about 100,000 to about 400,000 centipoise, as determined using a Brookfield programmable rheometer (Model DV-III). As is well known in the art, the speed and spindle size of the rheometer may be selected based on the general range of expected viscosities for the solution and to achieve a torque value between 10% and 100%. For example, in certain embodiments, the viscosity of the spinning solution may be determined with spindle number 7 and at a speed of 1 rpm. The total amount of solvent(s) employed in the spinning solution typically ranges from about 10 wt.% to about 60 wt.%, in some embodiments from about 15 wt.% to about 50 wt.%, and in some embodiments, from about 20 wt.% to about 40 wt.%, based on the total weight of the spinning solution.

C. Other Components

Although not required, a variety of other additives may also be employed in the spinning solution, such as catalysts, antioxidants, stabilizers, surfactants, spinning aids, waxes, nucleating agents, particulates, and other materials added to enhance processability or impart other properties to the fibers. In one embodiment, for example, a hydrophilic polymer is employed in the solution that is generally soluble in water (e.g., 25°C) at both the first and second pH ranges noted above. Among other things, such polymers can facilitate the ability of the pH-sensitive polymer to be spun. The hydrophilic polymer typically has a relatively high molecular weight to ensure that the resulting fibers can remain relatively water resistant. For instance, the hydrophilic polymer may have a weight average molecular weight of about 100,000 to about 5,000,000 grams per mole, in some embodiments from about 500,000 to about 3,000,000 grams per mole, and in some embodiments, from about 1,000,000 to about 2,000,000 grams per mole. When employed, such hydrophilic polymers typically constitute from about 0.5 wt.% to about 20 wt.%, in some embodiments from about 1 wt.% to about 15 wt.%, and in some embodiments, from about 2 wt.% to about 10 wt.% of the solution. Any suitable hydrophilic polymer may generally be employed, such as polyvinyl alcohol, polyacrylamide, collagen, pectin, chitin, chitosan, poly(α -amino acids), polyvinylpyrrolidone, polyethers, polysaccharides, polyurethanes, etc. Polyethers may be particularly suitable, such as polyalkylene oxides (e.g., polyethylene oxide ("PEO") and polypropylene oxide ("PPO")). Polyalkylene oxides may, for instance, have on average about 30 to about 15,000 oxide units (e.g., glycol units) per polymeric molecule.

II. Spinning

Generally speaking, any of a variety of known solution spinning techniques may generally be employed in the present invention, such as electrospinning, centrifugal spinning, etc. Centrifugal spinning, for instance, involves the application of the spinning solution to a rotary sprayer having a rotating nozzle. The nozzle may have a concave inner surface and a forward surface discharge edge. The spinning solution moves through the rotary sprayer along the concave inner surface so that it is distributed toward the forward surface of the discharge edge of the nozzle. Separate fibrous streams are formed from the spinning

solution while the solvent vaporizes to produce fibers. A shaping fluid can flow around the nozzle to direct the spinning solution away from the rotary sprayer. The fibers may be collected on the surface in the form of a coherent nonwoven web of fibers. Optionally, an electrical field can be added to the process, such as
5 between the spin disk and the collector, which creates a voltage potential between an electrode and the spin disk and/or the collector. While having a minimal impact on their formation, such an electric field may help the fibers separate and produce a more uniform web structure.

Referring to Fig. 1, one particular embodiment of a device that may be
10 employed to centrifugally spin fibers is shown. As shown, the device may include a rotating spin disk 10 having a flat surface 11 and a forward surface discharge edge 12 mounted on a drive shaft 13, which is connected to a high speed motor (not shown). The spinning solution may be pumped through a supply tube 14 running coaxially with the drive shaft 13 and in close proximity to the center of the
15 spin disk 10, opposite to the side of the disk attached to the drive shaft 13. As the spinning solution exits the supply tube 14, it is directed into contact with the rotating spin disk 10 and travels along the flat surface 11, which fully wets the flat surface and distributes the spinning solution as a film until it reaches the forward surface discharge edge 12. The rotational speed of the spin disk 10 is typically
20 from about 4,000 to about 100,000 rpm, in some embodiments from about 6,000 to about 100,000 rpm, and in some embodiments, from about 8,000 to about 100,000 rpm. The forward surface discharge edge 12 can be sharp or rounded and can include serrations or dividing ridges. The rotation speed of the spin disk 10 propels the spinning solution along the flat surface 11 and past the forward surface
25 discharge edge 12 to form separate fibrous streams, which are thrown off the discharge edge by centrifugal force. If desired, the fibrous streams may be collected on a surface to form a fibrous web.

Regardless of the particular technique employed, the solvent and pH modifier may be removed from the fibers during and/or after spinning. In certain
30 embodiments, for example, the solvent and pH modifier are vaporized during the spinning process. Alternatively, however, the fibers (or a web containing the fibers) may simply be dried or heated to remove these components. It should also be understood that the solvent and pH modifier may be removed in separate steps

if so desired. In any event, the pH-sensitive polymer generally constitutes a majority of the polymers present in the resulting fibers. That is, pH-sensitive polymers typically constitute about 50 wt.% or more, in some embodiments, about 70 wt.% or more, and in some embodiments, from about 90 wt.% to 100 wt.% of the polymer content of the fibers. Because the pH-sensitive polymer within the fibers is generally insoluble in water at a second pH level due to the removal of the pH modifier, the resulting fibers are able to better retain good mechanical and physical properties after exposure to water due to its presence at high concentrations. To the contrary, hydrophilic polymers (e.g., polyethylene oxide) that are generally soluble within the first and second pH ranges noted above typically constitute less than about 50 wt.%, in some embodiments, about 30 wt.% or less, and in some embodiments, from 0 wt.% to about 10 wt.% of the polymer content of the fibers.

The fibers of the present invention may be used alone or in the form of a coherent fibrous web structure. Typically, the fibrous web is a "nonwoven" web to the extent that individual fibers are randomly interlaid, not in an identifiable manner as in a knitted fabric. The basis weight of the fiber web may generally vary, but is typically from about 1 gram per square meter ("gsm") to 150 gsm, in some embodiments from about 2 gsm to about 100 gsm, and in some embodiments, from about 5 gsm to about 50 gsm.

If desired, the fibers may also be employed in a composite that contains a combination of the fibers with other types of fibers (e.g., staple fibers, filaments, etc.). For example, additional synthetic fibers may be utilized, such as those formed from polyolefins (e.g., polyethylene, polypropylene, polybutylene, etc.); polytetrafluoroethylene; polyesters (e.g., polyethylene terephthalate, polylactic acid, etc.); polyamides (e.g., nylon); polyvinyl chloride; polyvinylidene chloride; polystyrene; and so forth. The composite may also contain pulp fibers, such as high-average fiber length pulp, low-average fiber length pulp, or mixtures thereof. One example of suitable high-average length fluff pulp fibers includes softwood kraft pulp fibers. Low-average length fibers may also be used in the composite. An example of suitable low-average length pulp fibers is hardwood kraft pulp fibers. Such composites may be formed using a variety of known techniques. The relative percentages of the additional fibers may vary over a wide range depending

on the desired characteristics of the composite. For example, the composite may contain from about 1 wt.% to about 60 wt.%, in some embodiments from 5 wt.% to about 50 wt.%, and in some embodiments, from about 10 wt.% to about 40 wt.% fibers of the present invention, as well as from about 40 wt.% to about 99 wt.%, in some embodiments from 50 wt.% to about 95 wt.%, and in some embodiments, from about 60 wt.% to about 90 wt.% additional fibers.

If desired, the fiber web may also be employed in a multi-layered laminate structure. The other layers of the laminate may include a nonwoven web (e.g., a melt-spun web, such as a meltblown or spunbond web), film, strands, etc. In one embodiment, for example, the laminate may contain a fiber web positioned between two spunbond webs. Various techniques for forming laminates of this nature are described in U.S. Patent Nos. 4,041,203 to Brock et al.; 5,213,881 to Timmons, et al.; 5,464,688 to Timmons, et al.; 4,374,888 to Bornslaeger; 5,169,706 to Collier, et al.; and 4,766,029 to Brock et al. Of course, the laminate may have other configurations and possess any desired number of layers, such as a spunbond/fiber web/meltblown web/spunbond laminate, spunbond/fiber web laminate, etc. In yet another embodiment, the laminate may include a fiber web positioned adjacent to a film. Any known technique may be used to form a film, including blowing, casting, flat die extruding, etc. The film may be a mono- or multi-layered film. Any of a variety of polymers may generally be used to form a melt-spun nonwoven web or film used in the laminate structure, such as polyolefins (e.g., polyethylene, polypropylene, polybutylene, etc.); polytetrafluoroethylene; polyesters (e.g., polyethylene terephthalate, polylactic acid, etc.); polyamides (e.g., nylon); polyvinyl chloride; polyvinylidene chloride; polystyrene; and so forth.

III. Articles

The fibers and fiber webs of the present invention may be used in a wide variety of applications. For example, the fibers may be incorporated into filtration media, medical products, such as gowns, surgical drapes, facemasks, head coverings, surgical caps, shoe coverings, sterilization wraps, warming blankets, heating pads, etc., absorbent articles, and so forth. For example, the fibers may be incorporated into an "absorbent article" that is capable of absorbing water or other fluids. Examples of some absorbent articles include, but are not limited to,

personal care absorbent articles, such as diapers, training pants, absorbent underpants, incontinence articles, feminine hygiene products (e.g., sanitary napkins), swim wear, baby wipes, mitt wipe, and so forth; medical absorbent articles, such as garments, fenestration materials, underpads, bedpads, bandages, absorbent drapes, and medical wipes; food service wipers; clothing articles; pouches, and so forth.

Materials and processes suitable for forming such articles are well known to those skilled in the art. Absorbent articles, for instance, typically include a substantially liquid-impermeable layer (e.g., outer cover), a liquid-permeable layer (e.g., topsheet, surge management layer, ventilation layer, wrap, etc.), and an absorbent core. The topsheet, for instance, is generally employed to help isolate the wearer's skin from liquids held in the absorbent core. Due to its proximity to the skin, a fibrous web is generally employed in the topsheet to provide a cloth-like feeling. If desired, the fibrous web used in the topsheet may be formed from the fibers of the present invention. The outer cover is likewise designed to be liquid-impermeable, but yet typically permeable to gases and water vapor (i.e., "breathable"). This permits vapors to escape from the absorbent core, but still prevents liquid exudates from passing through the outer cover. While the outer cover generally contains a film to impart the desired impermeability to liquids, a fibrous web is often laminated to the film as a facing to impart a more cloth-like feeling. If desired, the fibrous web used in the outer cover may be formed from the fibers of the present invention.

In yet another embodiment, the fibers of the present invention may be incorporated into a wipe configured for use on skin, such as a baby wipe, adult wipe, hand wipe, face wipe, cosmetic wipe, household wipe, industrial wipe, personal cleansing wipe, cotton ball, cotton-tipped swab, and so forth. The wipe may assume a variety of shapes, including but not limited to, generally circular, oval, square, rectangular, or irregularly shaped. Each individual wipe may be arranged in a folded configuration and stacked one on top of the other to provide a stack of wet wipes. Such folded configurations are well known to those skilled in the art and include c-folded, z-folded, quarter-folded configurations and so forth. For example, the wipe may have an unfolded length of from about 2.0 to about 80.0 centimeters, and in some embodiments, from about 10.0 to about 25.0

centimeters. The wipes may likewise have an unfolded width of from about 2.0 to about 80.0 centimeters, and in some embodiments, from about 10.0 to about 25.0 centimeters. The stack of folded wipes may be placed in the interior of a container, such as a plastic tub, to provide a package of wipes for eventual sale to the consumer. Alternatively, the wipes may include a continuous strip of material which has perforations between each wipe and which may be arranged in a stack or wound into a roll for dispensing. The wipe may be a "wet wipe" in that it contains a solution for cleaning, disinfecting, sanitizing, etc. The particular wet wipe solutions are not critical to the present invention and are described in more detail in U.S. Patent Nos. 6,440,437 to Krzysik, et al.; 6,028,018 to Amundson, et al.; 5,888,524 to Cole; 5,667,635 to Win, et al.; 5,540,332 to Kopacz, et al.; and 4,741,944 to Jackson, et al. The amount of the wet wipe solution employed may depending upon the type of wipe material utilized, the type of container used to store the wipes, the nature of the cleaning formulation, and the desired end use of the wipes. Generally, each wipe contains from about 150 to about 600 wt.% and desirably from about 300 to about 500 wt.% of a wet wipe solution based on the dry weight of the wipe. When employed, the cleaning formulation is typically kept at the second pH level so as not to have a substantial adverse impact on the integrity of the fibers.

The present invention may be better understood with reference to the following examples.

EXAMPLE 1

The ability to form fibers in accordance with the present invention was demonstrated. Initially, 18.6 grams of polyethylene oxide (weight average molecular weight of 1.6×10^6 g/mol, Afla) was dissolved in 100.5 grams of deionized water. Thereafter, 201 grams of a pH-sensitive polymer was added to the solution and stirred for 15 minutes using a paddle-type mixer (Caframo, BDC Series) at a speed setting of 300 rpm. The pH-sensitive polymer was an acrylic polymer available from Lubrizol under the name CARBOSET® 514H. The mixture was left in a sealed bottle overnight to degas. The viscosity of the mixture was determined to be 83,000 centipoise, based on an average of three samples using a Brookfield programmable rheometer (Model DV-III), with spindle number 6 and speed of 1 rpm, and at ambient temperature and pressure.

EXAMPLE 2

The ability to form fibers in accordance with the present invention was demonstrated. Initially, 18.6 grams of polyethylene oxide (weight average molecular weight of 1.6×10^6 g/mol, Afla) was dissolved in 100.5 grams of deionized water. Thereafter, 201 grams of CARBOSET® 514H and 6.3 grams of ammonia (14% in an aqueous solution) was added to the solution and mixed for about 15 to 20 minutes until homogenous. The viscosity of the mixture was determined to be 292,000 centipoise, based on an average of three samples using a Brookfield programmable rheometer (Model DV-III), with spindle number 7 and speed of 1 rpm.

Prior to spinning, the solution was left overnight in a sealed container to degas (no vacuum or heat was employed). Two (2) milliliters of the degassed solution were then loaded into a Forcespinning® L-1000M system (FibeRio® Technology Corporation), which spun the solution into fibers for 1 minute at 5000 to 6000 rpm using a cotton-candy collector (no vacuum). Two needles (26G, 1.27 cm) were attached to each end of the spinneret, which was mounted on a spinning shaft. The distance from the tip of the needles to the collector was set to 8.9 centimeters. Once collected, the fibers were allowed to air dry. SEM microphotographs (510X and 1850X) of the resulting fibers are shown in Figs. 2-3.

The average fiber diameter was 1.5 micrometers (standard deviation of 0.6 micrometers). To test the resistance of the fibers to water, a dissolution test was also performed on three separate samples from Example 2. More particularly, a bundle of the fibers was cut and weighed, put in a glass vial, submerged in deionized water, and then left at room temperature for 7 days. Fibers were not oven dried before or after the test. After 7 days, the contents of the vials (water and fibers) were poured on a filter paper (Whatman filter paper, 90 mm diameter), which was disposed on a glass dish. The samples were left under a hood with a funnel on top and then allowed to dry for 7 days. Thereafter, the contents were weighed to determine the percent of fibers dissolved, which is equal to the $[\text{Fiber Weight} - \text{Weight of Dried Fibers}] / [\text{Fiber Weight}] \times 100$. The results are shown in Table 1 below.

Table 1: Sample Characteristics

Sample	Fiber Weight (g)	Vial/Cap Weight (g)	Water Volume (ml)	Weight of Glass Dish	Weight of Filter Paper (g)	Weight of Dried Fibers (g)	% Dissolved
1	0.114	14.778	10.000	48.313	0.582	0.1053	7.6
2	0.091	14.942	10.016	48.217	0.579	0.0760	16.5
3	0.078	15.062	10.024	48.325	0.576	0.0650	16.7

As indicated, the fibers are generally water resistant in that only a minimal amount dissolved in water.

- 5 While the invention has been described in detail with respect to the specific embodiments thereof, it will be appreciated that those skilled in the art, upon attaining an understanding of the foregoing, may readily conceive of alterations to, variations of, and equivalents to these embodiments. Accordingly, the scope of the present invention should be assessed as that of the appended claims and any
- 10 equivalents thereto.

WHAT IS CLAIMED IS:

1. A method for forming fibers from an aqueous spinning solution, wherein the spinning solution contains a pH-sensitive polymer and a solvent that includes water, wherein the pH-sensitive polymer is generally soluble in water at a first pH level and generally insoluble in water at a second pH level, the method comprising spinning the solution into fibers while at the first pH level and selectively adjusting the pH of the fibers during and/or after spinning so the pH is at the second pH level.
2. The method of claim 1, wherein pH-sensitive polymers constitute from about 30 wt.% to about 90 wt.% of the solution and solvents constitute from about 10 wt.% to about 60 wt.% of the solution.
3. The method of claim 1 or 2, wherein the pH-sensitive polymer is an acidic polymer, and preferably a polymer containing carboxylic functional groups, such as a (meth)acrylic acid polymer.
4. The method of claim 3, wherein the first pH level is about 5 or more and the second pH level is less than about 5.
5. The method of any of the foregoing claims, wherein the pH-sensitive polymer is a basic polymer, and preferably a polymer containing amine functional groups.
6. The method of claim 5, wherein first pH level is about 5 or less and the second pH level is greater than about 5.
7. The method of any of the foregoing claims, wherein the spinning solution further contains a pH modifier.
8. The method of claim 7, wherein the pH modifier is removed from the fibers during and/or after spinning.
9. The method of claim 7, wherein the pH modifier has a boiling point in water of from about 10°C to about 50°C at atmospheric pressure.
10. The method of any of the foregoing claims, wherein water constitutes about 50 wt.% or more of the solvents in the spinning solution.
11. The method of any of the foregoing claims, wherein the spinning solution is generally free of organic solvents.

12. The method of any of the foregoing claims, wherein the spinning solution further contains a hydrophilic polymer that is generally soluble in water at the first pH level and the second pH level.

13. The method of any of the foregoing claims, wherein the fibers are formed by centrifugal spinning.

14. A fiber formed according to the method of any of the foregoing claims, wherein the fiber is a nanofiber or microfiber.

15. A fiber that is formed from an aqueous spinning solution, the fiber containing one or more pH-sensitive polymers that are generally soluble in water at a first pH level and generally insoluble in water at a second pH level and optionally one or more hydrophilic polymers that are generally soluble in water at the first pH level and the second pH level, and wherein the pH-sensitive polymers constitute about 50 wt.% or more of the polymer content of the fiber and the hydrophilic polymers constitute less than about 50 wt.% of the polymer content of the fiber, wherein the fiber is a nanofiber or a microfiber.

16. A composite that comprises the fiber of claim 14 or 15 in combination with additional fibers.

17. A nonwoven web comprising the fiber of claim 14 or 15.

18. A laminate comprising the nonwoven web of claim 17 and layer of a melt-spun nonwoven web, film, strands, or combination thereof.

19. An absorbent article comprising an absorbent core positioned between a liquid-permeable layer and a substantially liquid-impermeable layer, wherein the absorbent core, liquid-permeable layer, the liquid-impermeable layer, or a combination thereof, comprise the nonwoven web of claim 17.

20. A wipe comprising the nonwoven web of claim 17.

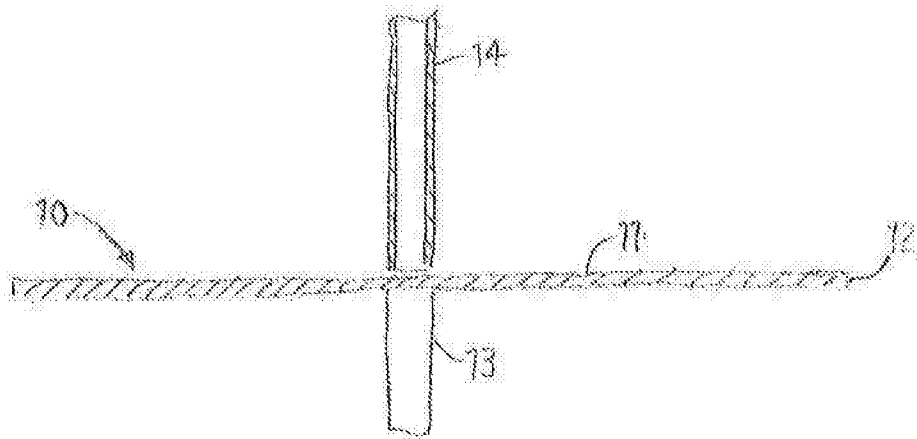


FIG. 1

2/3

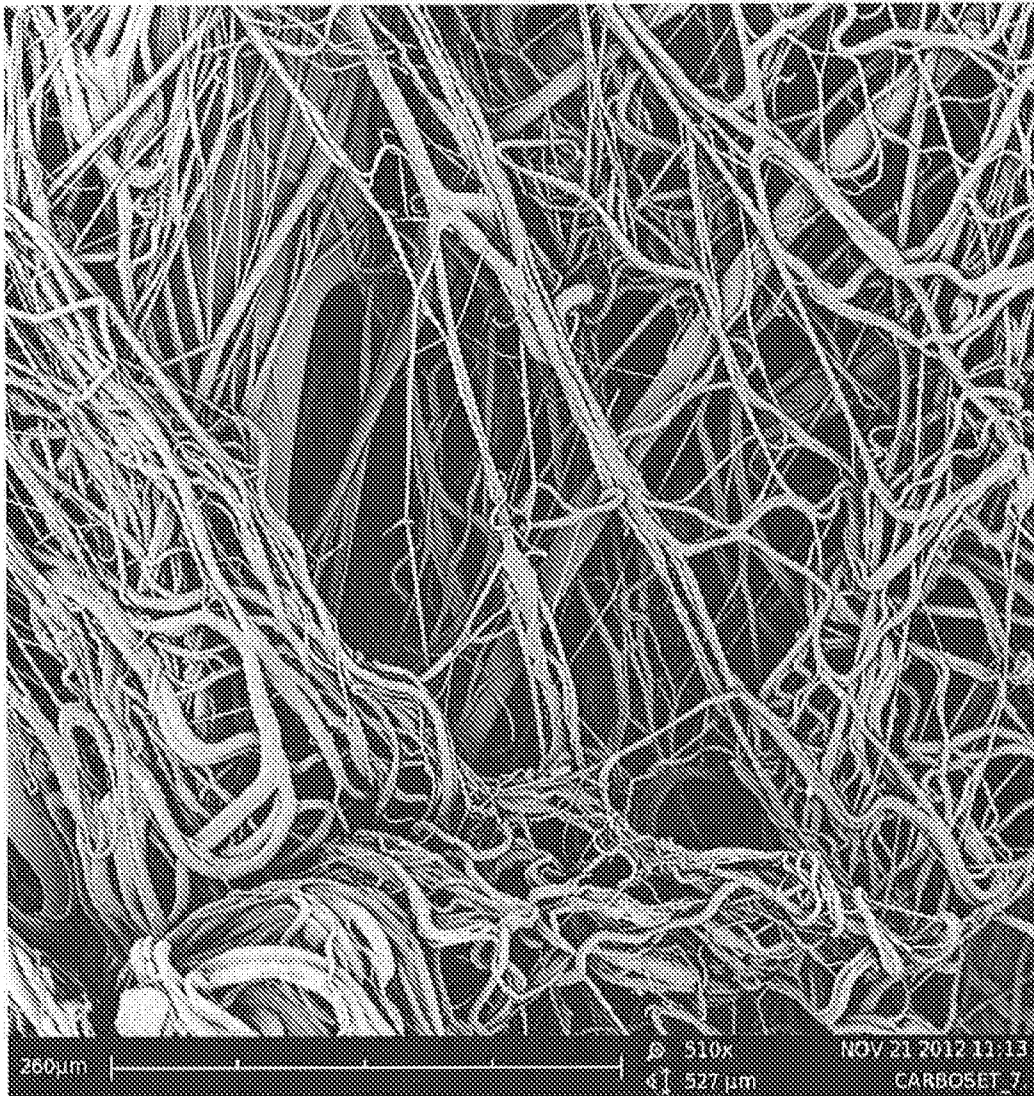


Fig. 2

3/3

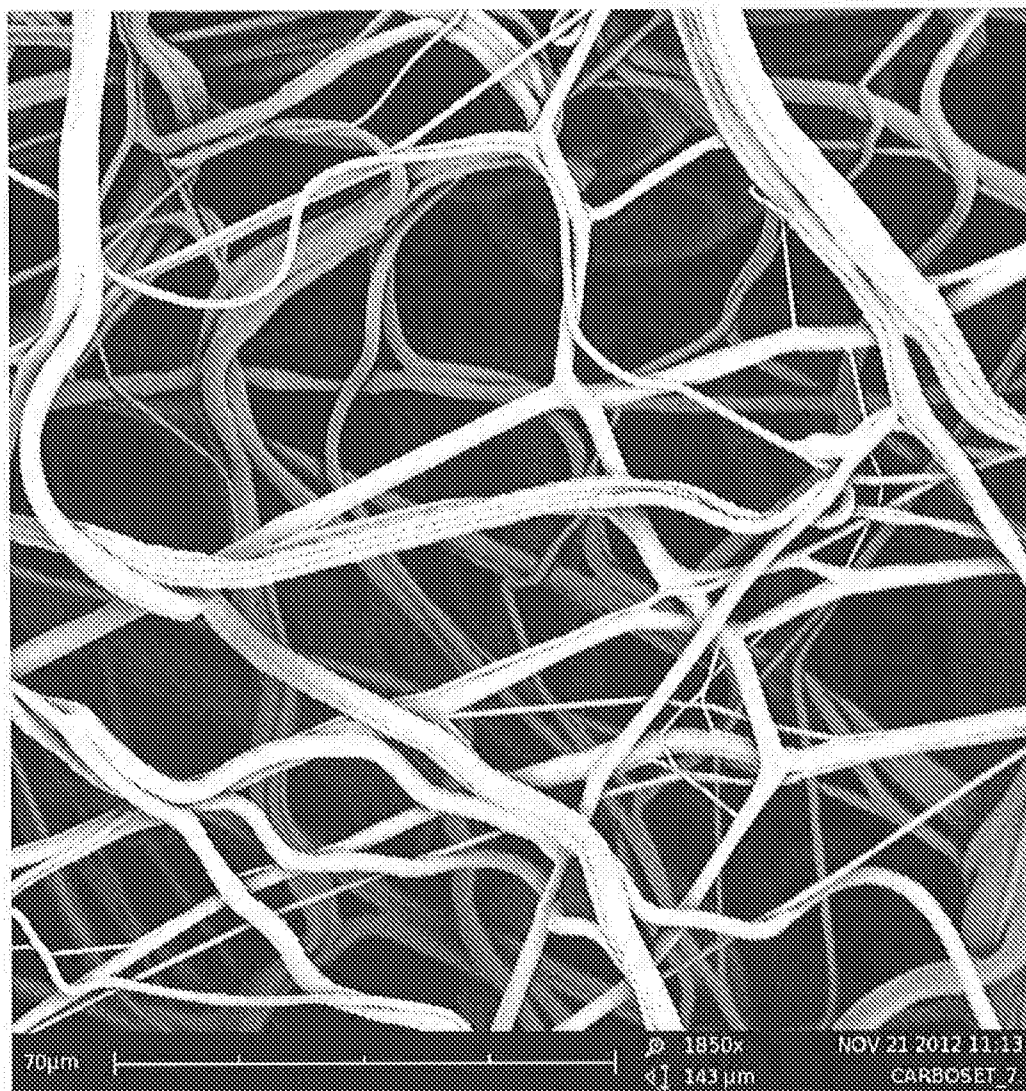


Fig. 3

A. CLASSIFICATION OF SUBJECT MATTER**D01D 5/00(2006.01)i**

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)

D01D 5/00; A61F 13/00; D21H 17/56; C07K 14/78; C08G 73/02; B32B 3/26; D01D 5/32

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: nanofiber, microfiber, pH-sensitive polymer, aqueous spinning solution

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2010-0055438 A1 (KAPLAN, D. L. et al.) 4 March 2010 See abstract, claims 1, 6, 10-14.	1-4, 15
A	US 6753454 B1 (SMITH, D. J. et al.) 22 June 2004 See abstract, claims 1-3, 7-8, 14-15, column 7, line 64 - column 8, line 20.	1-4, 15
A	US 2013-0175729 A1 (COLOPLAST A/S) 11 July 2013 See abstract, claim 13.	1-4, 15
A	US 2007-0077427 A1 (DUGAN, J. S.) 5 April 2007 See abstract, claims 1-12.	1-4, 15
A	US 2009-0218059 A1 (FARWAHA, R. et al.) 3 September 2009 See abstract, claims 11-16, paragraph [0054].	1-4, 15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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

"E" earlier application or patent but published on or after the international filing date

"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

08 October 2014 (08.10.2014)

Date of mailing of the international search report

10 October 2014 (10.10.2014)

Name and mailing address of the ISA/KR

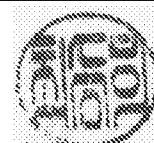
International Application Division
Korean Intellectual Property Office
189 Cheongsu-ro, Seo-gu, Daejeon Metropolitan City, 302-701,
Republic of Korea

Facsimile No. +82-42-472-7140

Authorized officer

CHOI, Sung Hee

Telephone No. +82-42-481-8740



INTERNATIONAL SEARCH REPORTInternational application No.
PCT/IB2014/062485**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 6, 8-9, 18-20
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claims 6, 8-9, 18-20 are regarded to be unclear since they refer to multiple dependent claims which are not drafted in accordance with PCT Rule 6.4(a).
3. ☒ Claims Nos.: 5, 7, 10-14, 16-17
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/IB2014/062485

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2010-0055438 A1	04/03/2010	CA 2562415 A1 EP 1613796 A2 EP 1613796 A4 JP 2007-515391 A JP 4698596 B2 US 2007-0187862 A1 US 2009-0234026 A1 US 2013-165004 A1 US 2013-190222 A1 US 7635755 B2 US 8614293 B2 US 8742069 B2 WO 2005-012606 A2 WO 2005-012606 A3	10/02/2005 11/01/2006 15/08/2007 14/06/2007 08/06/2011 16/08/2007 17/09/2009 27/06/2013 25/07/2013 22/12/2009 24/12/2013 03/06/2014 10/02/2005 17/11/2005
US 6753454 B1	22/06/2004	AT 261009 T AU 2001-10752 A1 CA 2386674 A1 DE 60008773 D1 DE 60008773 T2 DK 1220958 T3 EP 1220958 A1 EP 1220958 B1 WO 01-27365 A1	15/03/2004 23/04/2001 19/04/2001 08/04/2004 10/02/2005 12/07/2004 10/07/2002 03/03/2004 19/04/2001
US 2013-0175729 A1	11/07/2013	EP 2148704 A1 US 2010-0239560 A1 WO 2008-128546 A1	03/02/2010 23/09/2010 30/10/2008
US 2007-0077427 A1	05/04/2007	US 2006-0083917 A1	20/04/2006
US 2009-0218059 A1	03/09/2009	CN 101959904 A EP 2250203 A1 MX 2010009630 A US 8088252 B2 WO 2009-111000 A1	26/01/2011 17/11/2010 28/09/2010 03/01/2012 11/09/2009