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METHOD FOR MANUFACTURING NONWOVEN FIBROUS PRODUCTS FROM GEL FIBERS

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The portion of the term of the patent subsequent to Apr. 1, 1986, has been disclaimed and dedicated to the Public

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ABSTRACT OF THE DISCLOSURE

A process for preparing a dry, nonwoven fibrous sheet comprising:

(a) forming a web of self-bonding gel fibers of thermoplastic, fiber-forming polymer of acrylonitrile, said gel fibers having a gel network structure that has never been completely collapsed by drying and that consists essentially of interconnecting capillary spaces intimately intertwined with a fibrillar structure of polymeric material, and subjecting said web to a combination of superatmospheric pressure, a temperature of at least 25° C., and time, which combination is not sufficient to cause dry fibers of said polymer to fuse but which is sufficient to produce a web having a rewet tensile strength of at least about 0.05 lb./in./oz./sq. yd.;

(b) subjecting said web to drying conditions which cause said gel fibers to collapse while maintaining said web substantially free of forces tending to restrain shrinkage of said web; and

(c) recovering a dry, nonwoven fibrous sheet.

The product is useful as a textile fabric in the preparation of a variety of materials ranging from hard, boardy sheets to soft, fluffy fabrics to stretchable, tough fabrics.

This is a division of copending application Ser. No. 567,846 filed July 26, 1966 now U.S. Pat. 3,436,304 which issued Apr. 1, 1969, which, in turn, is a continuation-in-part of applications Ser. Nos. 457,139 and 457,178 both filed May 19, 1965, by Thomas C. Spence, and now both abandoned.

THE DISCLOSURE

The invention relates to nonwoven fibrous products made from gel fibers, and to improved methods for manufacturing such products.

PRIOR ART

Since the advent of synthetic fibers with their characteristic durability, it has been the goal of many textile scientists to provide a method of making fabrics and sheet-like products from those synthetic fibers without undertaking an expensive weaving operation. The papermaking technique of preparing a slurry of fibers, depositing a web of such fibers on a moving screen, and drying them to a product has not been entirely satisfactory because of the difficulty of fibrillating synthetic fibers into the long, curling fibrils characteristic of cellulosic fibers. Without these fibrils which intermingle to form a self-supporting sheet, it has been almost impossible to make a self-supporting web of synthetic fibers which can be processed to a useful product.

In standard papermaking processes, a wet leaf is deposited on a screen or cylinder and must be stripped from the substrate, passed between dewatering squeeze rolls, and dried to produce the final paper. In order to strip the wet leaf from the substrate, it must have enough self-supporting strength to withstand the jump between the moving substrate and the squeeze rolls employed in the next processing step. Cellulosic fibers produce a self-supporting wet leaf in the manufacture of paper because the fibers, while in the original dispersion and before being deposited on the moving porous substrate, are subjected to a violent beating action which provides the fibers with a greater surface area, partly by reason of breaking and splitting the fibers into smaller pieces and branched structures. The beating action also softens the fiber and permits hydrogen bonding to occur between fibers. The beaten fibers produce a self-supporting wet leaf by the combination of various forces, such as surface tension between fibers, interlocking of fibrilous branches, and interfiber hydrogen bonding. Synthetic fibers are not as responsive to a beating action as cellulosic fibers and normally must be beaten much more strenuously in order to produce even a small portion of the breaking and splitting which is found in cellulosic fibers. These results, in addition to the general absence of hydrogen bonding between synthetic fibers, make it very difficult to produce a self-supporting wet leaf of beaten synthetic fibers.

When any of the compacted and dried synthetic fibers (not having a gel network structure) such as nylon, polyesters, acrylics, etc., are dispersed in water and formed into a wet leaf or otherwise formed into a web, without previously being fibrillated by beating or other means, the wet leaf is so fragile that it cannot be stripped from the screen without causing it to fall apart. The prior art workers who fabricated non-woven materials from acrylonitrile fibers recognized the necessity of beating the fibers to cause fibrillation or of providing some other means of making a self-supporting wet leaf (see U.S. Pats. 3,047,455 and 3,047,456).

One means resorted to in order to achieve suitable fiber-to-fiber bond strength is treatment of the webs with thermosetting resins as binders, but these resins, after being thermoset, generally leave the fabric stiff and boardy. Various of the thermoplastic resins or polymers have been suggested for binders, for example, in the form of a latex but, again these resins often leave the fabric stiffer than desirable, and the bonding between the fibers is frequently observed to be short-lived, subject to discoloring with time, and not durable when subjected to many uses. A method is proposed in U.S. 2,920,992 for impregnating a web of acrylonitrile polymer fibers with an aqueous inorganic salt solution that is a solvent or plasticizer for the acrylonitrile polymer and then by evaporating the aqueous solvent for the salt, a more concentrated solvent solution is retained on the web which causes a general fusion of the overlapping fibers through the solvating action of the concentrated salt solution. In U.S. 2,810,646, it is reported that wet spun acrylonitrile polymer fibers are much more readily fibrillated than the corresponding dry spun fibers, and accordingly, that by subjecting these wet spun fibers to sufficient beating and fibrillation treatments, a web of acceptable bond strength can be obtained. In U.S. 3,047,455, it is reported that the paper products prepared by a method of U.S. 2,810,646 can be made to have improved web strength and like properties if the wet spun acrylonitrile polymer fibers or filaments are in a gel and an uncollapsed condition while being subjected to the beating or fibrillation treatment.

It would be of advantage, and it is the chief object and primary concern of the present invention, to provide an efficient means for preparing non-woven fibrous webs of certain thermoplastic polymer fibers having highly acceptable wet strength and excellent web properties with-

out having to resort to a fibrillation or beating treatment and without having to apply binding agents to the web.

OBJECTS

It has now been found that gel fiber in an uncollapsed, never dried condition has sufficient amount of self-bonding properties to cause interfiber bonding between adjacent fibers in the routine preparation of the wet leaf to the extent that it can be stripped from a moving substrate and conducted without support to squeeze rolls or other processing equipment. In some instances the self-bonding property of the gel fiber is less pronounced and it may be desirable or necessary to subject the wet leaf to a combination of pressure and temperature to make the wet leaf self-supporting. In any event, it has never been found necessary to beat the fibers or otherwise to produce fibrillation in order to prepare a self-supporting wet leaf. It is an object of this invention, therefore, to provide an improved method for manufacturing non-woven fibrous products from gel fibers. It is another object of this invention to produce a web of high tensile strength from acrylonitrile polymer gel fibers. It is still another object of this invention to produce from nonfibrillated gel fibers wet laid, non-woven sheets which have higher tensile strengths than heretofore known. It is another object of this invention to provide an improved method for producing special textured effects in non-woven fibrous products made from gel fibers. It is still another object of this invention to provide an improved method for drying a web of gel fibers. It is still another object of this invention to provide an improved process for making resin impregnated, non-woven fibrous products from acrylonitrile polymer gel fibers.

It is a further object of the invention to provide a means for manufacturing a non-woven web of generally parallel continuous filaments of a synthetic thermoplastic polymer capable of forming gel fibers.

Still other objects will appear from the more detailed description of the invention which follows.

STATEMENT OF THE INVENTION

This invention provides a process for preparing a non-woven fibrous product by forming a web of self-bonding, nonfibrillated, gel fibers of a thermoplastic fiber-forming polymer and subjecting said web to a combination of pressure, temperature and time which is insufficient to cause dry fibers of said polymer to fuse but is sufficient to produce a web having a rewet tensile strength of at least about 0.034 lb./in./oz./sq. yd. This web of gel fibers may, if desired, be then subjected to a heated aqueous medium to relax the fibers in the fabric. The web may be treated further in accordance with this invention by employing any of several drying methods, or by impregnating the web with resinous solids before or after drying. The dried web may then be annealed by a final heat treatment.

The products provided by this invention include a non-woven fibrous sheet materials consisting essentially of gel fibers, whether in the form of continuous filaments or staple fiber, bonded to each other at points of interfiber contact. Preferably the gel fibers are composed of a polymer of acrylonitrile. The sheet may contain other types of fibers blended with the self-bonding gel fibers, and the sheet may be impregnated with resinous solids, e.g., from a latex. The appearance of the product may vary from a hard, boardy sheet to a soft fluffy fabric to a stretchable, tough fabric.

The present invention thus provides an efficient, expedient, and economical means for preparing non-woven fibrous sheets from gel fibers. It makes unnecessary the normal practice of first fibrillating the fibers prior to formation of the web. Thus, the considerable energy requirements of the fibrillation treatment are obviated. Furthermore, elimination of the fibrillation step minimizes the loss of material which occurs due to fibers breaking into smaller particles or "fines" that may be lost in the operation or might have to be removed as undesirables from the final product. No binders are required to achieve suitable and highly acceptable web strengths, however, these can be added to the product by subsequent treatments if desired. Inducement of fusion by employing solvents for the polymer is unnecessary. The present invention provides for the manufacture of non-woven fibrous sheets and other products from gel fibers having highly desirable properties which heretofore were believed unobtainable except by the employment of fibrillation or by the use of bond-forming or bond-inducing agents.

DEFINITIONS

The critically important component of the products and processes of this invention is the "gel fiber," which is the fiber form of a thermoplastic polymeric material which is capable of forming a gel network structure. The fiber may be in the form of continuous filament or cut staple.

The gel network structure is a combination of fibrillar polymeric material and liquid from the bath employed to form the fiber. This bath may be a coagulating bath which coagulates streams of polymer solution into fibers in the spinning process, or, alternatively, it may be a wash bath employed to replace an organic solvent with an aqueous liquid. In any event, the gel network structure is formed consisting of interconnecting capillary spaces filled with the liquid intimately intertwined with a fibrillar structure of polymeric material. Such structures are described from various technical viewpoints in an article by J. P. Craig, J. P. Knudsen, and V. F. Holland, entitled, "Characterization of Acrylic Fiber Structure," Textile Research Journal, vol. 32, No. 6, pages 435–448 (June 1962). These authors state that in the case of acrylonitrile polymers the structure is of a fibril-void type with fibrils and voids of the order of 200 angstroms in diameter.

If the gel fiber is subjected to drying conditions, it collapses from its original swollen condition to form a dry fiber having the same characteristics and properties as fibers spun by other techniques which never involve passing through a gel network structure. So long as the gel fiber is not completely collapsed, it retains its gel network structure and can be reswollen to its original condition. Once the gel fiber has been dried to a completely collapsed condition, however, it cannot be reswollen. Only the gel fiber which has never been dried to a completely collapsed condition has the self-bonding properties which are necessary to this invention.

Gel fibers, as prepared, do not have fibrils branching out from the main portion of the fiber, but such fibrils can be produced by a beating action such as is used on wood pulp in the production of paper. The characteristic self-bonding property is present in both the fibrillated and nonfibrillated form of the gel fiber permitting either to be used in the process of this invention although it is preferred to use the nonfibrillated form and thereby eliminate the expense of beating the fiber.

One of the most revealing tests for showing the improvement achieved by making non-woven fabrics by the process of this invention is the measurement of the tensile strength of the fabric at various stages of its preparation. For example, if the gel fibers are formed into a web by papermaking techniques, i.e., formed from a water suspension of fibers, and pressed lightly to provide an initial dewatering, the product is a "wet leaf." When this product is subjected to a combination of elevated pressure and temperature to remove more water and to produce interfiber bonding, the product is a "pressed wet leaf." If the "pressed wet leaf" is then submerged in water or otherwise saturated with water it is a "rewet wet leaf." When webs made from various types of fibers are tested at these stages of fabrication, the results vary greatly. For example, wood pulp made into ordinary paper through these stages might typically have an initial wet leaf tensile strength of 0.10–0.12 lb./in./oz./sq. yd. (at a solids con-

tent of 20–30%), and a rewet wet leaf tensile strength which is unmeasurable because the paper is too weak to test. In the case of synthetic polymer fiber (not having the gel network structure), the initial wet leaf is too weak to test, the pressed wet leaf tensile strength is about 0.02–0.04, and the rewet wet leaf disintegrates into individual fibers when placed in water again. In the case of the gel fiber of this invention, the initial wet leaf tensile strength is about 0.2–0.4, the pressed wet leaf tensile strength about 1.2–1.8, and the rewet wet leaf tensile strength about 0.8–1.2. These results make it clear that the gel fiber has self-bonding properties which other types of fibers do not have.

WEB FORMATION

A web is prepared from the gel fibers as the first step in the process of this invention. Any convenient method of distributing the gel fibers in the form of a web or sheet is permissible, e.g., random deposition by a scattering mechanism, distribution by a stream of air or water, deposition by filtering from a liquid, and the like. A preferred method for use with staple fiber is the papermaking technique of forming a wet leaf from a suspension of staple fibers in water, followed by couching and pressing. In the preparation of a wet leaf of gel fibers, a dispersion is prepared of the gel fibers in a large quantity of water, e.g., 1 part by weight of gel fiber per 1,000–5,000 parts water, in the presence or absence of an added dispersing agent. The dispersion is then drained through a screen or other porous substrate to produce a sheet-like mass of fibers. This sheet-like mass is the "wet leaf," which, after further treatment, is the product of this invention.

In the case of continuous filament, the preferred method of forming a web is also from a suspension in water whereby the filaments may be laid substantially parallel, or alternatively, may be laid down in random direction in a tangled fashion. It is not critical to employ any single procedure since many are equally satisfactory. For example, a stream of water into which continuous filaments are introduced is an excellent carrier for the filaments. When this stream of water is directed onto a porous substrate, the water drains away leaving the filaments on the substrate. Depending on the relative movements and directions of the water stream and the substrate, the filaments may be laid down substantially parallel or in a random, tangled fashion. Other methods may also be employed. For example a tow of filaments may be deposited on a moving substrate in the form of a web of parallel filaments. A tow of filaments may be dropped into a pool of water causing the filaments to separate more or less randomly depending on the angle of incidence at which the tow contacts the surface of the pool. Still other procedures will be apparent to those skilled in this art.

Generally the preparation of a web from substantially parallel continuous filament is employed when it is desired to prepare a web with a maximum of tensile strength in the machine direction, i.e., the length of the web, and tensile strength in the transverse direction is relatively unimportant. Binding tapes for packaging are typical of this type of use. The web prepared from continuous filament laid down in a random fashion results in one having an initial strength essentially the same as that of a web prepared from staple fiber. However, once the interfiber bonding is destroyed the web of continuous filament has a secondary strength which is the strength of the individual filaments which have been straightened out into parallel strands without any substantial interfiber bonding.

It is advantageous when preparing the products in accordance with the invention, that the aqueous medium in the gel structure of the filament, (i.e., that portion other than the polymer), have a surface tension greater than about 30 dynes per centimeter. Lower surface tensions tend to interfere with lateral fiber bonding and an integral web may not result. It is, therefore, desirable in order to obtain excellently laterally bonded filaments that the aquagel be free of solutions containing surfactants, lubricants, wetting agents and the like textile finishes. Preferably, the aqueous medium of the gel structure (including any extrinsic liquid associated therewith) consists essentially completely of water, which has a surface tension of about 74 dynes per centimeter at 25° C.

GEL FIBERS AND BLENDS WITH OTHER FIBERS

The synthetic polymeric materials which are intended to be employed in the process of this invention are the thermoplastic fiber-forming materials such as polyacrylonitrile, polyamides, and polyesters. The preferred material is that which contains at least 80 weight percent of polymerized acrylonitrile. This includes, therefore, the homopolymer of acrylonitrile as well as copolymers, terpolymers, and interpolymers of acrylonitrile. Suitable comonomers which may be employed in amounts up to 20% by weight of the final product include allyl alcohol, vinyl acetate, acrylamide, methacrylamide, methylacrylate, vinyl pyridine, ethylene sulfonic acid, and its alkali metal salt; vinyl benzene sulfonic acid, and its salts; 2-sulfoethylmethacrylate, and its salts; vinyl lactams, such as vinyl caprolactam; and vinyl pyrrolidone, and mixtures thereof.

The preferred gel fibers employed in this invention are acrylonitrile polymer gel fibers which are preferably produced by wet spinning a solution of the polymer into an aqueous coagulating bath, washing the solvent therefrom, and recovering the fiber in the form of a swollen gel containing from about 50 to about 500 weight percent water based upon the dry weight of the polymeric fiber. There are many specific systems which follow the general principle of spinning a solution of the polymer in solvents such as ethylene carbonate, dimethylformamide, dimethylsulfoxide, butyrolactone, and various salt solutions, such as aqueous solutions of calcium thiocyanate, sodium thiocyanate, lithium bromide, zinc chloride, and others well-known in the art. Many of such systems are disclosed in United States Letters Patent Nos. 2,140,921; 2,425,192; 2,648,593; 2,648,646; 2,648,648; 2,648,649; 2,790,700; and 2,949,435.

After the polymeric fibers have been wet spun into an aqueous coagulating bath they are usually washed with water or with an inert, aqueous solution to remove any residual polymer solvent from the freshly formed filaments. The product thus formed is a gel fiber (sometimes called an "aquagel fiber"). Acrylonitrile polymer gel fibers prepared in this way may contain up to about 6 parts by weight of water for each part by weight of dry polymer therein, although more frequently, the proportion is about 1 to 3 parts by weight of water per part of polymer. The fiber in this condition, or after it has been oriented by stretching, may be employed in the process of this invention.

Another technique which may be employed for preparing acrylonitrile polymer gel fibers for use in the process of this invention is to dry spin the fiber, evaporate a portion of the solvent, and wash out the remainder of the solvent with water so as to form the aqueous gel network structure.

The gel fibers which are employed in the process of this invention may be staple fiber of short or long lengths or continuous filaments to produce end products of different qualities and characteristics. Generally, the staple length is not more than about two inches, although this is not intended to be a limitation on the process and product of this invention.

It is entirely feasible, and sometimes deisrable, to employ blends of fibers in which at least 10% are wet gel fibers of the self-bonding type described above. The remaining portion may or may not be fibrillated and may be any type of fiber or any substance, such as synthetic polymer fibers or cellulosic fibers used in the manufacture of paper.

SELF-BONDING OF GEL FIBERS IN WEB

The degree of self-bonding for any given type of gel fiber is proportional to the combination of pressure, temperature, and time applied to the area of such fiber. These factors cooperate in the sense that the same tensile strength for a web of bonded fibers can be obtained by employing a combination of low pressure and high temperature or by employing a different combination of high pressure and low temperature. Time is a factor within certain limitations since longer times under a given set of conditions of pressure and temperature normally produce higher tensile strengths in the webs being treated. Experimental data indicate that a larger effect is produced by varying the temperature and a smaller effect by varying the pressure. Time enters into the process in the sense that it is necessary to maintain the web at conditions of pressure and temperature for a sufficient length of time to produce self-bonding and this time vary from a few seconds to a few minutes. Minimum temperature and pressure conditions are about 25° C. and 5 p.s.i.

By employing the gel fibers described in connection with this invention, it is routine to produce a wet leaf having a wet tensile strength of about 0.3 lb./in./oz./sq. yd., while it has been expected by the prior art to achieve wet tensile strengths of only about 0.034 lb./in./oz./sq. yd. (see U.S. 2,999,788). When the wet gel fiber of this invention is an acrylonitrile polymer as described above, the ordinary pressure of producing the "wet leaf" and dewatering by squeezing the excess liquid from the initial mat is usually sufficient to produce some of the bonding effect.

In addition to the initial bonding of the web under the conditions of the wet leaf formation as described above, there is a further effect if one employs a combination of pressure, temperature, and time to the web before it is further processed. This combination is sufficient to produce good interfiber bonding as judged by the fact that the bonded wet leaf can then be saturated with water, e.g., by immersion in water, and the rewet wet leaf has a tensile strength of at least 0.034 lb./in./oz./sq. yd., which has been described in the prior art above as the minimum for self-supporting strength. The combination of pressure, temperature, and time is never that which would cause dry polymer to melt or fuse. For example, acrylonitrile polymers have been reported to have a softening or stick temperature of about 230°–280° C., while the bonding temperatures used in the process of this invention rarely exceed about 100° C.

Different effects can be produced by employing different means for producing pressure and temperature combination. A common means is to press the entire web uniformly with heated platens or rolls. This procedure produces interfiber bonding more or less uniformly over the entire web. Another means is to subject the web to a pattern of heated pressure points to produce interfiber bonding only at the points in the pattern, leaving the remaining fibers substantially unbonded. When the bonded web is subsequently subjected to drying conditions which collapse and dry the gel fibers, the fibers tend to shrink and various useful and ornamental effects can be produced by using different types of bonding means and different types of drying means. The final dried fabric product may be fluffy, boardy, textured, paper-like, leather- like, or film-like. The individual fibers in the fabric may be straight, folded, kinked, or bulked.

The patterned pressure means may be a pair of rolls, a pair of flat plates or a combination of rolls or plates with screens. The pattern is made by cooperating pressure points which are relatively small in diameter and are spaced from each other a distance which is not greater than about the length of the staple fiber in the wet leaf. The size and shape of the points is not critical, although a preferred size is in the order of 1/32 to 1/16-inch in maximum dimension. These points may be arranged in a square pattern or a diamond pattern or any other design which covers the desired area of the wet leaf. One suitable pressure means is a coarse, woven screen which, when used in combination with a continuous surface, produces intermittent pressure points at the location where the screen wires overlap each other. Alternatively, a pair of plates or rolls may be etched or machined to produce a knurled effect or other patterns of pressure points which can be applied to both sides of the fabric being treated. A preferred combination is to employ cooperating rolls which are machined to produce parallel ridges on each roll. If the ridges on one roll are at an angle to the ridges on the other roll, the effect produced on a fabric passing between the two rolls is a regular design of spaced points corresponding to the intersections of ridges.

RELAXATION OF WET LEAF

It is desirable, although not necessary, in some embodiments of this invention to apply a hot wet treatment to the wet leaf to remove some of the stresses in the fibers and to provide some preshrinkage. This treatment increases the elongation of the fabric and increases its toughness. Temperatures of about 60°–120° C. at atmospheric pressure for a few seconds to a few minutes are sufficient for this purpose. If this treatment is employed it is usually desirable to relax the sheet at least 50% of the total relaxation available in the sheet. This amount can be obtained by 1–10 seconds of treatment at 85°–100° C. In order to obtain substantially all of the relation approximately 10 minutes of treatment may be required. Boiling water is the most convenient medium for treatment. It is only necessary that the fabric be heated without drying the gel fibers in order for the relaxation to occur in a desired manner.

IMPREGNATION OF WEBS WITH RESIN SOLIDS

It has been known in the past that fabrics of various types can be impregnated by dipping them into a latex or an emulsion of resin solids. The resulting product acquires some of the properties of the resin solids. It has been unexpectedly discovered that particularly desirable effects can be obtained by impregnating web of gel fibers prepared as described above.

When a wet leaf of gel fibers is made in its highest tensile strength, is often somewhat stiff and does not have an acceptable drape nor a high tear strength. If milder conditions are employed in pressing of the wet leaf so as to make weaker interfiber bonds, the web has a softer feel and a better drape, but it also has a lower tensile strength and lower tear strength, e.g., about 1–2 lb./in./oz./sq. yd. in tensile strength and about .1–.15 lb./oz./sq. yd. in tear strength. If this web, after drying, is then impregnated with a latex binder, the tensile strength increases, but the tear strength does not increase proportionately, e.g., tensile strengths of about 5–6.5 lb./in./oz./sq. yd. are obtained while tear strengths of only about 0.15–0.25 lb./oz./sq. yd. are obtained. These values can be increased only slightly by employing the technique of treating the dry sheet with a latex and coagulating it in situ. It was not until the discovery of treating the wet leaf rather than the dried final product that the surprising combination of a high tensile strength and a high tear strength was achieved.

The wet leaf in the pressed, partially bonded condition is the preferred form of the web to be treated by impregnation with resin solids. The impregnation is preferably accomplished by dipping the web in a solution or dispersion off the resin solids, squeezing the material to remove excess liquid, and thereby producing a sheet having resin solids, desirably 5–50% by weight, incorporated therein. The resin may require fixation by evaporation of the liquid carrier, curing by the application of heat or a change in pH, or it may require coagulation, cross-linking,

or other reaction to fix the resin solids in the web. When sheets prepared by either of these general procedures have been dried, it will be found that they have a combination of a high tensile strength, a high tear strength, along with the general characteristics of a good handle and drape.

There are innumerable varieties of binders which may be employed to impregnate the non-woven fibrous product of this invention. These binders may be organic or inorganic, thermoplastic or thermosetting, or elastomeric or brittle. The binder is, however, preferably embodied in an aqueous carrier such as being dissolved in an aqueous solvent, being dispersed in an aqueous medium, or suspended in an aqueous emulsion or latex. Any chemical compound having the characteristics of a binder may be used if it is compatible with the acrylonitrile fibers employed in this invention.

Among the binder compositions which may be mentioned specifically are:

(A) The resinous latices such as:
- (1) butadiene/styrene
- (2) butadiene/acrylonitrile
- (3) carboxylated butadiene/acrylonitrile
- (4) blends of phenolic resins or other thermosetting resins with latices of butadiene/styrene or butadiene/acrylonitrile
- (5) polyvinyl esters
- (6) polyvinyl halides
- (7) copolymers of vinylidene chloride
- (8) chlorinated rubber
- (9) polyacrylates and polyalkylacrylates
- (10) polymers of acrylic acid, methacrylic acid, or the like

(B) The water-dispersible resins such as:
- (1) propylene/acrylic acid copolymer
- (2) ethylene/acrylic acid copolymer
- (3) polyvinyl chloride powder
- (4) urea-formaldehyde resins
- (5) phenol-formaldehyde resins
- (6) asphalt emulsions
- (7) polyurethanes
- (8) polyesters
- (9) epoxy resins

(C) The water soluble resins such as:
- (1) carboxymethyl cellulose
- (2) polyvinyl alcohol
- (3) polyvinyl pyrrolidone
- (4) methyl cellulose
- (5) corn starch
- (6) phenolic resins
- (7) urea-formaldehyde

(D) Inorganic binders such as:
- (1) metal hydroxides (e.g., aluminum, zinc, copper, etc.) which are adhesive in the hydrated form and may be formed in situ by raising the pH of aqueous solutions of soluble salts of the metals.

The amount of such solids employed to impregnate the gel fiber webs of this invention is normally from about 5–50% by weight of the final dry sheet depending on what type of properties are desired. For most embodiments of this invention it is preferred to employ as the impregnating composition one of the resinous latices listed under A above, particularly desirable ones because of the excellent results achived by employing them are the butadiene/acrylonitrile latices and the latices of polyacrylates, polymethacrylates, acrylic acid polymers, and others of the family of acrylic polymers.

It is not critical how the resin is applied to the web. The aqueous composition containing the resin normally is one having 10–30% or higher by weight of resin solids and it is usually convenient to apply these resin solids to the non-woven fabric by dipping the fabric in the aqueous, resin-containing composition, whether this is a latex, dispersion, solution, or the like. Other methods of application which are operable although not preferable, include spraying, brushing, painting, dusting, depositing, and any other procedure which distributes minute particles of binder evenly over the surface of the fibrous sheet material being treated.

In certain embodiments of this invention, it has been found desirable to impregnate the web of gel fibers with particles from a resin latex and then to coagulate the latex particles in situ before drying the impregnated sheet. This treatment frequently produces improved properties as compared to a product made without the coagulation step. The coagulation may be accomplished by any of many known methods, usually relating to a change in the pH of the system, a change in the ionic environment of the particles, or by applying heat. If, for example, acrylonitrile polymer gel fibers are incompletely washed when produced from a polymer solution in which the solvent is an aqueous solution of zinc chloride, there will be enough zinc ions and chloride ions associated with the gel structure of the fibers to cause coagulation of the latex applied to the web. Another coagulation procedure is to alter the pH with hydrochloric acid or some other fugitive material which would disappear upon later drying of the impregnated fabric.

The important feature of the newly discovered process for treating the non-woven fibrous material with a binder composition is that the fibrous material must be in the form of a web of gel fibers, e.g., a wet loaf, which have never been completely irreversibly dried and collapsed. In this never-dried condition, the gel fiber is remarkably receptive to the treatment with an aqueous impregnating composition. It is not known why this is so, but completely different results are obtained when one treats a fabric made from these gel fibers, which are irreversibly dried and then rewet before being impregnated with an aqueous binder composition.

Even though the foregoing describes a process for treating a web of a never-dried gel fibers, it is not intended that the impregnation of novel dried fabrics of this invention be disclaimed. It is acknowledged that the fabric is known generally in the prior art, but the impregnation of the fabrics of this invention produces a highly desirable product which has never bene known before this invention.

DRYING OF THE BONDED WEB

The drying of the web is accomplished by driving off the free water and solvent in the fabric, and all water and other volatile materials which may be in the gel structure of the individual fibers making up the fabric. The drying must cause the gel to collapse irreversibly to a dry fiber which cannot thereafter be reformed into a gel by the addition of water. The actual drying may be accomplished by any suitable means, e.g., hot air ovens, infra red lamps, heated metal surfaces, etc., which will volatilize the water and other materials in a reasonably short period of time. In general, temperatures of 120° C. to 200° C. are sufficient to dry a sheet of a few mils in thickness in about one minute of time. If subatmospheric pressure is employed, the temperature may be correspondingly lower and yet accomplish the same result.

When the web is finally dried to a finished product and the gel fiber is irreversibly collapsed to a dry fiber, a certain amount of shrinkage takes place, reducing the overall dimensions of the web. If the web has merely been pressed lightly at room temperature to produce a tensile strength of not more than about 0.3 lb./in./oz./sq. yd., the final drying step may cause the fabric to shrink 20–40% in area and the shrunken fabric may have a tensile strength of less than 0.1 lb./in./oz./sq. yd. This reduction in tensile strength is principally due to the breaking of interfiber bonds by the shrinkage forces of the fibers. However, when the web has originally been bonded in a pressing operation involving a combination of higher temperatures and pressures, e.g., 40°–100° C. and 5–250 p.s.i., its tensile strength is much greater, the subsequent

drying operation will not materially change the percent shrinkage but the tensile strength will be considerably greater. In this latter instance, the interfiber bonding has not been destroyed and more bonding has been produced during drying. A typical example of this effect is shown by an experiment where a wet leaf was pressed at 50° C. and 250 p.s.i. for 5 minutes to give a pressed wet leaf tensile strength of about 1.6 lb./in./oz./sq. yd. When this pressed wet leaf was dried at 40° C. in an air oven, the final product had a tensile strength of about 3.5, and when it was dried at 150° C. in an air oven, the final product had a tensile strength of about 7.6. Thus, it is important in certain embodiments of this invention to press the web at elevated temperatures and pressures in order to obtain the highest tensile strengths in the final product.

One of the simplest methods of drying the fabric is to subject the fabric to drying conditions while the fabric is in a completely relaxed condition. This means that the fabric is not restrained from movement in any direction nor are the fibers restrained except insofar as the interfiber self-bonding has restrained them. In other words, there is no external stress applied to the fabric nor to the fibers to prevent their movement during the drying operation. This drying is conveniently accomplished in a hot air oven which may be a continuous oven in the sense of having a moving screen upon which the fabric travels without restraint. It is to be understood that the weight of the fabric itself causes some minute stresses in the fabric but this is not regarded as an external force.

Because the shrinkage forces tend to produce warping and unevenness in fabric which has been bonded by overall pressing, this type of drying is usually employed with fabric which has been subjected to a pattern pressing. The shrinkage forces exert their effects on the unbonded areas between pressure points and do not cause undue warping. The fabric produced in this way is a highly bulked fiber product having a fluffy appearance due to the expansion and shrinkage of the fibers in the spaces between pressure points. The fluffed fabric also has the appearance of being stitched together, which is the result of the pressure points being applied at a patterned location on the sheet.

Another method of drying is accomplished by passing the web of gel fibers, whether it has been prepressed to provide some interfiber bonding or not prepressed and therefore has substantially no interfiber self-bonding, between two parallel barriers which restrict the movement of the web in its thickness direction but not substantially in either of the other two directions. The barrier may be a tangible solid material such as a screen or a platen, or the equivalent. Alternatively, the barrier may be an energy barrier such as heat or heat-producing energy. The requirement of the barrier is that the normal curling, kinking movement of individual fibers or networks of fibers be so restrained that the fibers and the sheet do not expand or curl beyond the thickness barrier. A heat barrier produces this effect by causing the fiber or sheet to be heated much more rapidly near the barrier than at some greater distance from the barrier, causing the fibers and the sheet to move away from the heat to the zone midway between the two barriers. The tangible, solid barrier accomplishes the same effect by physical contact. In one embodiment of this invention, the tangible solid is the heat source for the drying operation, thus providing both a heat barrier and a solid barrier. A preferred procedure which is convenient because of the ease of handling the material which is to be dried and because it accomplishes a certain smoothing effect, is to perform the drying between two heated surfaces which are parallel and spaced apart sufficiently for the web to pass therebetween without being placed under any substantial stresses. As the web dries, the individual fibers tend to shrink and to crimp, thus causing wrinkles to form in the fabric. The presence of the two spaced, heated surfaces prevents the wrinkle from growing into waves any larger than the distance between the heated surfaces. Thus a certain smoothing is produced, which causes the finished sheet to be essentially flat and capable of being conveniently stored in a roll. If a more pronounced smoothing effect is desired, the space between the heated surfaces is made smaller, even to the extent of being less than the thickness of the web before drying. While these spaced heating plates may produce small localized stresses in the wet leaf as it is being dried, these stresses are essentially negligible with respect to the overall fabric.

In general, the spacing between the barriers may be from about 0.8 to 30 times the thickness of the web entering the drying zone. Preferably this range will be from about 0.9 to about 15 times the predried thickness of the web.

It is not necessary to keep the web between two spaced barriers for the entire drying period; although it is important to employ the barriers during that portion of the drying when the rapid shrinking occurs. As may be expected, the heating of the wet leaf first raises the temperature sufficiently to cause the free water to evaporate, and then drives off the water in the gel fiber. During the first portion of the heating, rapid shrinking of the fabric takes place and it is important to keep the fabric between the barriers during that time. This situation permits various combinations of equipment and process conditions. In a batch process the fabric might be taken from its form as a wet leaf to complete irreversible dryness of the fiber in a fixed barrier. In a continuous process, however, the web might pass through continuous or semicontinuous barriers for the rapid shrinkage period, and finally into a heated zone without barriers for the final bit of shrinkage. In most instances, the web will experience its most rapid shrinkage within a few seconds of being subjected to the drying temperature.

When the fabric dries, it causes the individual fibers to shrink, and, depending upon the degree to which the fibers are in a random, or oriented position, the shrinkage of all of the fibers produces varied results in the appearance and handle of the fabric. In some instances, the fabric will be fluffy with the appearance and feel of a lamb fleece. In other instances, the fabric will have a laminar structure with the outside relatively stiff and the center relatively fluffy. Other effects can be produced by varying the process steps. In any event the individual fibers normally acquire a crimp by reason of the shrinkage forces. If compressive forces or tension forces were applied to the fabric during the drying step, the shrinkage would be substantially lessened. When such forces are employed in the process of this invention they are preferably in an amount necessary to restrain at least about 50% of the area shrinkage.

Various textured effects can be produced in the fabric by a combination of pressing the web with certain combinations of pressure and temperature, followed by subjecting that web to the drying step of this invention. If the combination of pressure and temperature which is applied to the web leaf is very mild so as to produce very little increase in the wet tensile strength of the web, the interfiber bonding will be sparse, and the subsequent drying and the accompanying shrinkage will produce a material which is fluffy and has a low tensile strength. The texture of such a material will be quite similar to that of a light wool felt. If the web is subjected to relatively higher conditions of temperature and pressure before the web is dried, the shrinkage forces will not be able to overcome as much of the interfiber bonding and the result will be a randomly mottled, leathery appearance and a relatively high tensile strength. The closer the spacing between the heated surfaces is to the thickness of the wet leaf, the smaller and more uniform is the mottled effect on the surface of the sheet. If the heated surfaces are farther apart, the surface takes on the appearance of a much coarser grained leather, or that of a coarse, textured hide such as an alligator hide or an elephant

hide. If the web is dried between two parallel, solid, heated surfaces, the spacing between the surfaces being from about 2–5 times the thickness of the web before drying, the product has a laminar appearance with kinked, wavy fibers forming a fluffiness in the center and somewhat flat, smoothed appearance on the outside. The drying temperature and the procedure for accomplishing the drying of the web are important in producing products of any desired tensile strength. In general, if the drying temperature is high, the tensile strength will be higher, and if the drying temperature is low, the tensile strength will be lower. Furthermore, if a material is dried at a low temperature, e.g., 40° C., it may later be heated to a high temperature, e.g., 150° C., to increase the tensile strength of the dried sheet. This occurs, presumably, because more interfiber bonding occurs during this period of heating the sheet to a high temperature.

Still another method of drying is one in which the web is dried while under sufficient restraint to prevent a substantial portion of the normal shrinkage from taking place. The web may be restrained by a compressive force applied to the face of the web or by a tensile force applied along two or more edges or the web. Although the restraining force may be applied so as to prevent any amount up to 100% of the shrinkage, it is usually desirable to apply sufficient force to resist at least one-half of the gel fiber axial shrinkage forces. For purposes of the present specification and claims, and to facilitate ready determination by the artisan, the term "restraining half the axial shrinkage force" shall mean "restraining half the area shrinkage of a web of the gel fibers" that would occur if the web were allowed to dry in a relaxed, free-to-shrink condition.

These shrinkage forces will depend in large measure on the history of the filament, for instance, to an extent on the polymer composition of the gel, the amount of swelling or water in the gel structure, the degree of orientation given the fibers, and somewhat on the fiber denier. The drying temperature will also have an influence on these forces. Since the axial shrinkage forces depend on many variables, it will be appreciated that the exact range of restraining forces required to overcome the axial shrinkage forces under all conditions, cannot adequately be set forth. However, these forces can readily be determined for any given set of conditions so that an appropriate restraining force for resisting the desired portion of the shrinkage can be applied. Generally, the amount of restraining force applied to the drying web in the practice of the invention will be in the range of from about 5 to 75 or 100 p.s.i., although very useful products can be obtained at pressures in the range of 0.5–5 p.s.i. under regulated drying conditions. Restraining or resisting forces greater than the minimum amount to overcome the axial shrinkage forces of the fiber can, of course, be utilized in the drying cycle. Care should be exercised that the applied restraining force is not so great that the gel fibers become substantially crushed to an extent such that the porous network of the web is destroyed. Undue crushing and general lateral fiber to fiber fusion frequently reduce the tensile strength and porosity or permeability of the web.

The restraining force is preferably applied throughout the drying cycle, i.e., maintained constantly once the drying of the gel fiber web is begun and imposed until the gel fibers are essentially completely irreversibly dried to a characteristically hydrophobic nature and the gel structure is collapsed or destroyed.

If the applied restraining force is compressive force it can be made great enough to prevent any shrinkage. If this type of force is not applied the axial shrinkage forces cannot be completely counteracted or restrained since the web is formed of the fibers lying in random directions. For instance, if the necessary restraining forces are applied as tension forces to the web in the direction of web travel only, i.e., as might be accomplished by tensioning the web between tension rolls or tensioning over a large roll, shrinkage will occur at right angles to the web travel. When the web is held by edge-holding devices in combination with machine direction tensioning, more shrinkage is prevented but all of the axial shrinkage forces cannot be contained employing this method.

The most convenient and effective means to achieve a compressive restraining force over the entire web surface in an omnidirectional, planar manner is to confine the web between two solid sheets of a suitable material, such as by confining it between two belts that are at least coextensive with, and can be adapted to move with the web during the irreversible drying thereof. Preferably, at least one of these belts, or similar restraining surface, is foraminous in nature to allow for the escape of water vapor or other volatile material during the drying of the web and collapse of the gel fibers. Other suitable means can, of course, be utilized to apply this coextensive compressive force to the drying web, such as, for erample, by passing the web confined on one side with a screen or similar foraminous structure, while the bottom side is a stationary solid surface, or when the bottom side is a rotating roll, which can also be heated. Preferably, the web is dried while being confined by one of the above indicated means or equivalents thereof while passing through a forced hot air oven.

In the special case of preparing webs from parallel continuous filaments the gel fibers are first collected in a generally parallel and side-by-side manner, such as a tow of fibers might be handled. Ordinarily a ribbon or tow several filaments thick is utilized to prepare a flat ribbon-like overall structure so as to facilitate uniform temperature and restraint throughout the plurality of filaments during the irreversible drying cycle. It is important that the gel filaments be combined before drying in a way to assure predominate lateral fiber-to-fiber contact with a certain amount of random array so that adequate fusion points develop between the filaments effecting an integral web.

After the web of gel filaments is collected as indicated, it may be dried using any conventional means suited to the purpose, such as by passing the web through a forced hot air oven or by passing it under infrared lamps or over heated metal drums, as long as the drying means utilized is adapted to impose on the drying web a resultant compressive force that acts upon the planar surfaces of the web and adequately restrains or resists the axial shrinking forces of the gel fibers released during the irreversible drying thereof. As indicated, the web during its drying cycle must be restrained to the extent of resisting at least up to one-half and preferably to the extent of essentially completely counteracting or resisting the fiber axial shrinkage forces released during the irreversible drying cycle. The application of a sufficient restraining force is apparently necessary in order to prevent differential motion between filaments and particularly at cross-over areas between filaments. Such differential motion apparently leads to debonding of the drying filaments or at least prevention of forming a bonded juncture.

Generally, it is observed that the minimum amount of restraining force applied to the drying ribbon in the practice of the invention in order to obtain an adequately bonded ribbon will be in the range of from about 2 to 6 p.s.i. when a direct exterior compressive restraining force is applied without accompanying axial restraint (tension) on the drying ribbon. When an accompanying axial (tension) force is applied, then the exterior compressive force minimum is generally in the range of about 0.1 to 0.6 p.s.i.

The restraining force should be controlled throughout the drying cycle so as to govern the differential shrinkage during the critical bonding period. That is, the restraining force should be controlled constantly once the drying of the web of gel fiber is begun and until the gel fibers are essentially completely irreversibly dried to a characteristically hydrophobic nature and the gel network structures

of essentially all fibers in the ribbon are collapsed. The control of the restraining force can be maintained by constantly applying the external compressive force or tension force throughout the drying; or, control can be accomplished, particularly when the web is dried around heated rolls, by intermittent application of the restraining force suitable to control the shrinkage or differential motion of the individual filaments. Thus, intermittent application of the restraining force may be present when the ribbon or web is dried by being passed continuously over a series of dryer cans or rolls and wrapped alternately clockwise and counterclockwise, while being restrained to about constant length.

The most convenient and effective means to achieve a restraining force over the entire ribbon surface when an external compressive force is desired, is to confine the ribbon between two solid sheets of a suitable material as has been previously described. When tensioning restraining forces are employed, the ribbon can, for example, be held between tensioning rolls while being passed through a hot air or radiant heated oven, or, as has been indicated, and preferably, the ribbon can be held under the requisite tension forces while being passed over and/or around a rotating or stationary heated drum so that a resultant compressive force is effected.

When webs are made of continuous filament laid down in a random fashion the methods of bonding and drying applicable to webs of staple fiber are employed, the choice of any one depending on the type of final product desired.

ANNEALING OF DRIED WEB

In the drying of gel fibers two events take place as has been mentioned above. The fiber is dried, in the sense that all water is removed, and the gel network structure is irreversibly collapsed, and these events can produce undesirable strains in the web. Different web strengths are observed depending on the temperature level of the drying step. Accordingly it has been found to be advantageous, in many instances, to subject a dried web to a higher temperature for a short period of time to relieve fabric stresses. The effect is similar to an annealing treatment of other materials. If the drying temperature has never caused the fiber to reach the annealing temperature, it is advisible to subject the dried web to such a temperature. The minimum temperature level desired for annealing is approximately 30° C. above the glass transition temperature (T_g) for the polymer involved. In the case of polyacrylonitrile T_g is approximately 80° C. according to Keavney and Eberlin, J. Appl. Polymer Sci. 3, 47 (1960). Glass transition temperatures for other polymers are available in the literature. The time for holding the fiber at the annealing temperature may be from a few seconds to a few minutes. Thus, it may require only a few seconds if the annealing temperature is 50°–100° C. above T_g while the time may be a few minutes for a lower annealing temperature. Since the sole purpose of this treatment is to relieve stresses, it is emphasized that annealing is not a necessary step in the process of this invention.

EXAMPLES

This invention may be more fully understood by references to the following examples which are intended to be illustrative of certain embodiments of the invention without restricting the broad scope of the invention in any manner whatsoever. Parts and percentages are by weight and temperatures in degrees centigrade unless otherwise specified. Tensile strengths and elongations are measured on an Instron tensile testing machine using one-inch strips of fabric and averaging the values 5–7 tests. Tear strengths are measured in accordance with the TAPPI Standard Elmendorf Tear Test. Tensile Energy Absorbed is the integrated area under the stress-strain curve determined in measuring tensile strength and elongation. Porosity is measured on a Gurley air permeometer.

EXAMPLE 1

Tensile strengths of wet leafs

Polyacrylonitrile fibers were spun from an aqueous $ZnCl_2$ solution (60%) into an aqueous $ZnCl_2$ bath (43%) at 12.5° C., were washed substantially free of $ZnCl_2$ and oriented by stretching the aquagel filaments about twelve times their original length in an aqueous bath at 95°–100° C. The intermediate wet gel fibers were so sized that on relaxed hot air drying they produced a 3-denier fiber. This stretched wet gel intermediate fiber was cut into ¼-inch staple, dispersed in water, formed into a wet leaf, couched and pressed between damp felts. (A standard Noble-Wood handsheet machine was used for this formation and couching.) The wet leaf was pressed for 3 minutes in a steam heated hydraulic flat press at the pressures and temperatures indicated in Table I below. The lay-up for handling the sample was: bottom platen, chrome plate, two sheets of blotter paper, 200-mesh screen, sample, sheet of Teflon, chrome plate, top platen.

The wet gel fiber was found to contain 2.13 parts water per part polymer in the wet gel structure. Axial shrinkage on relaxed drying at 140° C. was 28%, which represents 48% area shrink in a wet leaf. The dried fiber had a tenacity of 3.8 grams per denier.

Tensile strengths were measured on the wet leaf after pressing as described above, and also on each wet leaf which, after the pressing operation, was rewet by saturating it with water and then testing the tensile strength of the rewet sample. Test conditions and results are shown in Table I and are averages of many individual tests.

TABLE I

Pressure, p.s.i.	Temperature, ° C.	Tensile strength, lbs./in./oz./sq. yd. (dry basis) Pressed wet leaf	Rewet wet leaf
5	25	0.28	(*)
50	25	0.26	0.05
100	25	0.33	0.05
500	25	0.77	0.38
5	40	0.14	0.05
50	40	0.56	0.10
100	40	0.56	0.22
500	40	1.9	1.15
5	60	0.32	0.05
50	60	1.5	0.85
100	60	1.5	1.05
500	60	3.65	2.35
5	85	1.25	0.55
50	85	3.10	2.90
100	85	5.15	3.60
500	85	9.10	6.80

*Too weak to be tested.

EXAMPLE 2

Properties of dry webs prepared from gel fibers

Webs were prepared from acrylonitrile homopolymer gel fibers as described in Example 1. In each instance the web was formed as a wet leaf which was then subjected to certain conditions of pressure, temperature, and time, followed by drying to cause the gel fibers to irreversibly collapse. The dried sheet was subjected to various tests to determine its properties, with the following results:

(1) A series of wet leaf samples was subjected to pressures of 250 p.s.i. for times of 1 minute, 5 minutes, and 10 minutes, and temperatures of 40°, 60° and 85° C., following which the wet leaf was placed in one of two air ovens at 40° C. or at 150° C. and completely dried at that temperature and the dried sample was then tested to determine its tensile strength. The values varied from as low as about 0.7 to as high as about 8.8, with the higher values occurring at the higher temperatures and pressures and the lower values occurring at the lower temperatures and pressures.

A typical set of values showing how the tensile strengths developed from the wet leaf through different drying conditions is shown in the following table.

TABLE II

Initial pressing conditions applied to wet leaf	Tensile strength, lb./in./oz./sq. yd. (dry basis) In wet leaf	After drying at 40° C.	After drying at 150° C.
40° C./250 p.s.i./5 min	0.6	1.0	4.0
60° C./250 p.s.i./5 min	1.6	3.5	6.8
85° C./250 p.s.i./5 min	6.0	8.8	8.2

(2) A series of wet leaf samples were pressed at 250 p.s.i. and various combinations of temperatures (40°, 60°, and 85° C.) and times (1, 5, and 10 minutes). The samples were then placed in either of two air ovens at 40° C., or at 150° C., dried at that temperature, and the final product was tested to determine its loss in area due to shrinkage measured as a percentage of the original area of the wet sheet. At the 40° C. drying temperature, the shrinkage varied from about 30% to about 10% as the wet leaf pressing temperature varied from about 40° to 85° C. At the higher drying temperature (150° C.), the shrinkage varied from about 49% to about 30%, as the wet leaf pressing temperature varied from about 40° to about 85° C., although in some instances the shrinkage went through a maximum at a temperature of about 60° C. These data indicate that when the wet leaf is subjected to a pressing operation at elevated temperatures and pressures, enough bonding occurs in the non-woven structure to reduce the area shrinkage. Substantially all the shrinkage occurs during the final drying operation with very little occurring during the pressing of the wet leaf.

(3) Non-woven sheets prepared as described above in this example exhibited densities from about 19.5 pounds per cubic foot to about 40 pounds per cubic foot, depending upon the conditions of the wet leaf pressing and the final drying.

(4) Non-woven sheets prepared as described above in this example exhibited porosities which varied from about 140 to 20 cu. ft./min./sq. ft. (measured on Gurley air permeometer).

EXAMPLE 3

Blends of gel fibers with non-gel fibers

In this series of experiments, wet gel fibers of polyacrylonitrile were blended with other fibers which did not exhibit a gel network structure. The ability of the self-bonding gel fiber to act as a binder for other fibers which do not have self-bonding properties provides the possibility of producing non-woven materials of many different properties.

Polyacrylonitrile wet gel fiber was prepared as described in Example 1 and cut to ½-inch staple. The non-gel fibers of the blends were a polyamide (66 nylon), a polyester (polyethylene terephthalate), a polyolefin (polypropylene), and an irreversibly collapsed gel fiber of polyacrylonitrile. The properties of the various fibers is shown in the following tabulation.

TABLE III

	Denier	Grams/denier
Polyacrylonitrile gel fiber	3.0	3.7
Polyacrylonitrile dried fiber	3.0	4.3
Polyamide	6.0	5.5
Polyester	4.0	4.4
Polyolefin	8.0	3.9

Blends were prepared of various mixtures of the gel fiber and one of the other fibers (also cut to ½-inch staple) and formed into webs on a laboratory handsheet mold. The aqueous dispersions from which the webs were formed contained 0.3% (based on the dry fiber weight) of an acrylamide polymer as a dispersing agent and drainage assistant. The webs were made to have basis weights of 2.5 dry oz./wt. sq. yd. The handsheets, after preparation and couching, were transferred to a flat bed press where the sample was pressed for 2½ minutes at 85° C. and 100 p.s.i. Where the sample was pattern bonded, it was accomplished by passing the sample through patterned pressure rolls at 5 feet/minute to produce a square pattern of 1/32-inch spots on ⅛-inch x ⅛-inch centers. The pressed webs were suspended in a hot air oven and dried at 150° C. for 2½ minutes without restraining the webs in any way. The results are shown in the following tabulation.

TABLE IV.—WET LEAF—OVERALL BONDED

Weight percent gel fiber	Weight percent other fiber	Pressed wet leaf tensile strength, lb./in./oz./sq. yd.	Dry tensile strength, lbs./in./oz./sq. yd.	Dry tear strength, lb./oz./sq. yd.	Dry density, G/cc.	Dry fabric air permeability, cu. ft./min./s sq. ft.
100	0	3.68	6.25	0.162	0.347	25
75	25 dry polyacrylonitrile	3.76	5.10	0.280	0.313	35
50	50 dry polyacrylonitrile	2.56	3.14	0.360	0.303	55
25	75 dry polyacrylonitrile	1.40	1.45	0.275	0.313	85
75	25 polyamide	2.72	3.22	0.193	0.183	107
50	50 polyamide	1.64	1.75	0.118	0.132	215
25	75 polyamide	0.38	0.41	0.033	0.082	380
75	25 polyester	2.76	3.49	0.182	0.208	92
50	50 Polyester	1.68	1.91	0.089	0.130	190
25	75 polyester	0.60	0.45	0.046	0.106	335
75	25 polyolefin	2.36	2.97	0.174	0.205	102
50	50 polyolefin	1.36	1.49	0.115	0.125	250
25	75 polyolefin	0.44	0.42	0.033	0.112	355
	WET LEAF—PATTERN BONDED					
100	0	2.80	2.94	0.250	0.133	145
75	25 dry polyacrylonitrile	1.00	1.15	0.228	0.090	250
50	50 dry polyacrylonitrile	0.52	0.65	0.230	0.071	280
25	75 dry polyacrylonitrile	0.275	0.32	0.270	0.063	290
75	25 polyamide	1.20	1.31	0.180	0.091	245
50	50 polyamide	0.60	0.39	0.086	0.089	315
25	75 polyamide	0.05	0.11	0.029	0.062	430
75	25 polyester	1.32	1.54	0.200	0.099	215
50	50 polyester	0.68	0.64	0.098	0.090	290
25	75 polyester	0.13	0.11	0.014	0.091	390
75	25 polyolefin	1.68	1.49	0.212	0.108	260
50	50 polyolefin	0.84	0.73	0.081	0.094	295
25	75 polyolefin	0.20	0.13	0.024	0.083	420

EXAMPLE 4

Copolymers of acrylonitrile as gel fibers

Gel fibers were made from acrylonitrile homopolymer and copolymer at various spinning conditions to demonstrate that the self-bonding property is substantially independent of the chemical composition of the polymer. The copolymer was 91% by weight acrylonitrile, 7.6% by weight methyl acrylate, and 1.4% by weight sulfoethylmethacrylate. All polymers were spun from a solution of the polymer in zinc chloride. The wet leaf was prepared from ¼-inch staple in each instance. The following tabulation shows the spinning conditions and the resulting properties.

TABLE V.—HOMOPOLYMER SERIES

Spinning conditions										Pressed wet leaf tensile strength, lb./in./oz./sq.yd. at 200 p.s.i./3 min.		
Solution temp., ° C.	Coagulation bath temp., ° C.	Concentration $ZnCl_2$ in coagulation bath, percent	Stretch ratio	Wet gel weight ratio, water/fiber [1]	Denier	Tensile, a/d.	Elongation, percent	Young's Modulus, g./d.	Percent shrink on drying	40° C.	60° C.	85° C.
30	15	42.0	12.5	2.37	3.2	4.3	33	54	24	0.7	2.4	5.2
30	9	42.0	12.5	1.84	3.2	4.7	31	49	21	0.4	1.6	3.0
70	30	32.0	[2] 4.0		7.7	0.95	26	33	43	0.2	0.5	1.1
30	12.5	44.2	12.5	2.13	3.5	3.8	37	49				
COPOLYMER SERIES												
70	30	32.1	10.0	1.20	2.8	4.0	28	56	22	0.3	0.6	1.6
70	30	40.0	12.5	1.69	2.7	3.2	29	51	33	0.6	3.8	6.5
31	15	42.0	12.5	0.55	2.7	5.0	23	63	14	0.3	1.9	4.0
30	9	42.0	12.5	0.59	2.3	5.8	23	65	14	0.2	0.6	1.8
70	31	32.5	10.0	1.14	2.9	4.1	26	60	17.5			

[1] Ratio after stretching.
[2] Maximum stretch ratio for these conditions.

Blends were made of gel fibers of the last homopolymer and the last copolymer shown in Table V. The blends were made into webs by the papermaking procedure and each wet leaf was subjected to combinations of pressure, temperature, and time, and the pressed wet leaf tensile strength was measured. The results are shown in Table VI.

TABLE VI

Weight percent of polymer type		Pressed wet leaf tensile strength, lb./in./oz./sq. yd.		
Homopolymer	Copolymer	60° C./100 p.s.i./5 min.	85° C./100 p.s.i./5 min.	85° C./100 p.s.i./3 min.*
0	100	0.30	0.85	6.1
25	75	0.55	1.70	5.9
50	50	0.82	2.90	5.7
75	25	1.18	3.26	5.5
100	0	1.35	4.55	5.3

*Homopolymer was ⅜-inch staple and copolymer was that shown as the second copolymer sample in Table V (cut to ¼-inch staple).

These results clearly indicate that while bond strengths are modified by the blending, there is more than adequate self-bonding in all blend proportions.

EXAMPLE 5

Impregnation of webs with resin solids

A series of experiments was undertaken in order to demonstrate how to prepare impregnated fabrics employing the non-woven materials of this invention.

Wet gel fibers of acrylonitrile homopolymer were prepared, spun washed, and stretched as described in U.S. Pat. 2,790,700. These fibers were so sized to give 3 denier per filament (⅜-inch staple) and 1½ denier per filament (3/16-inch staple) on drying under unrestrained conditions.

An aqueous suspension of these wet gel fibers blended in a 1:1 ratio was prepared by dispersing the filaments at about 0.04% by weight of dry fiber in water containing 1% polyacrylamide (based on dry fiber weight) as a dispersing agent and drainage assistant. The wet leaf was then formed on a continuously moving screen and transferred at about 30% by weight of polymer (2½ oz. wet gel fibers/sq. ft.). Wet leaf thus formed was pattern bonded with 1/32-inch spots on a rectangular pattern of ¼-inch x ⅜-inch by passing the sheet through the nip of heated pattern bond rolls. Nip pressure was 10 pounds/linear inch of nip and temperature was 85°–100° C. The pattern bonded wet leaf was then dipped in an aqueous binder composition of "Hycar" 1571—a latex emulsion of butadiene/acrylonitrile. The solids in the aqueous latex system were varied from 10–40% to provide impregnated wet leaf samples with latex solid contents of 10–50%. To regulate the latex solids pickup in the sheets still further, they were sandwiched between blotter papers and passed through the nip of rubber squeeze rolls.

The samples thus prepared were dried 5 minutes at 150° C. in a forced air oven. The fiber web was unrestrained and a resulting shrinkage of about 35% occurred. These are samples 1–5 in Table VII.

In other samples the latex solids were coagulated in situ by dipping the impregnated sheet into a solution of aluminum sulfate (1% by weight), squeezing to remove excess water, washing and squeezing again to approximately 30% solids. The sheet was then dried as described above at 150° C. for 5 minutes. These are samples 6–10 in Table VII.

In other samples the latex was applied to the nonwoven sheet resulting from drying the wet leaf for 3 minutes at 150° C. in the manner described above. This treatment irreversibly collapses the gel fibers in the wet leaf. These dry sheets were then impregnated with latex as described and then redried for 5 minutes at 150° C. These are samples 11–15 in Table VII.

In still other samples the wet leaf was dried to cause irreversible collapsing of the gel fibers and the dry sheet product was impregnated with latex solids, followed by coagulation with aluminum sulfate as described above. The sheets were then redried 5 minutes at 150° C. These are samples 16–20 in Table VII.

All sheets were subjected to the TAPPI (Technical Association of the Pulp and Paper Industry) standard tensile and extension test using 1-inch strips on an Instron machine, and to the Elmendorf-type tear test. Other physical data includes basis weight in oz./sq. yd., and percent resin.

TABLE VII

Sample No.	Fabric wt. (dry basis) oz./sq. yd.	Impregnating solids, wt. percent	Dry tensile strength, lb./in./ oz./sq. yd.	Extension, percent	Tear strength, lb./oz./ sq. yd.
1	4.2	13	1.3	18	0.2
2	4.6	20	1.9	18	0.3
3	5.5	34	4.5	25	0.4
4	5.7	40	5.0	27	0.5
5	6.3	47	5.4	27	0.4
6	4.2	12	0.9	7	0.2
7	4.2	20	3.5	7	0.5
8	5.2	34	6.5	18	0.2
9	5.7	43	6.3	21	0.4
10	6.2	48	7.6	25	0.2
11	4.2	10	0.6	10	0.1
12	4.4	17	1.1	16	0.3
13	5.6	31	2.3	23	0.5
14	6.2	39	2.2	22	0.4
15	6.7	46	2.4	27	0.5
16	4.2	10	0.3	11	0.2
17	4.4	17	0.9	14	0.2
18	5.6	31	1.6	22	0.4
19	6.1	39	1.9	28	0.5
20	6.7	46	1.7	27	0.4

EXAMPLE 7

Comparison of impregnation before and after drying of web

In this series of experiments a comparison is made between the products produced by (1) impregnating the wet leaf with solids before drying, and (2) drying the wet leaf and impregnating the dried wet leaf. "Wet" means the former type of impregnation and "Dry" means the latter. All other processing conditions, including the type of impregnating latex, were the same as those employed in Example 5, except that the finished basis weight was 6 oz./sq. yd. of all cases. The amount of impregnating solids was approximately 20% by weight. In the description of the polyethylene terephthalate fibers "high tenacity" means tire cord quality of 11 denier/filament and approximately 8–9 grams/denier, while "normal tenacity" means textile quality of 6 denier/filament and approximately 5 grams/denier.

TABLE IX

Sample No.	Description of fiber in non-woven sheet	Extension, percent	Dry tensile strength, lb./in.	Tear strength, lb.
1	Wet, 100% polyacrylonitrile, 3 denier/filament, ¼-inch staple	11	19	1.6
2	Dry, 100% polyacrylonitrile, 3 denier/filament, ¼-inch staple	8	20	1.4
3	Wet, 80% polyacrylonitrile, 3 denier/filament, ½-inch staple; 20% polyethylene terephthalate, high tenacity, ¼-inch staple.	19	20	2.3
4	Dry, 80% polyacrylonitrile, 3 denier/filament, ¼-inch staple; 20% polyethylene terephthalate, high tenacity, ¼-inch staple.	8	13	1.7
5	Wet, 80% polyacrylonitrile, 3 denier/filament, ¼-inch staple; 20% polyethylene terephthalate, normal tenacity, ¼-inch staple.	24	13	2.5
6	Dry, 80% polyacrylonitrile, 3 denier/filament, ¼-inch staple; 20% polyethylene terephthalate, normal tenacity, ¼-inch staple.	11	10	2.2

EXAMPLE 6

Impregnation of webs made of blends of fibers

This example demonstrates the utility of other varieties of non-woven fibrous sheets in the preparation of impregnated fabrics. The same general procedure as described in Example 5 was employed on fibrous sheets made from polyacrylonitrile wet gel fibers of different lengths and properties, and on other sheets made from blends of different fibers. The results are shown in Table VIII in which the fibers employed in the non-woven sheet are characterized by chemical composition, denier, and staple length. In each instance the polyacrylonitrile fiber was a wet gel fiber, except for the "predried, high tenacity" fibers of Samples 13 and 14 which were wet gel fibers that had been irreversibly collapsed and dried before being used in the preparation of a wet leaf. The impregnating material was the same as that employed in Example 5.

EXAMPLE 8

Impregnation of webs with various types of resin solids

Wet leafs were formed, couched, and pattern bonded employing wet gel fibers of acrylonitrile homopolymer as described in Example 5. The webs were then impregnated by placing them between 20-mesh nylon screens and dipping the combination in one of several types of aqueous latices as described below. The web was then subjected to squeeze rolls to produce a web containing approximately 23% by weight resin solids and 77% by weight gel fibers on a dry basis. The impregnated webs were then dried by being placed for 5 minutes between two plates spaced 0.1-inch apart and maintained at 150° F. The web was not confined in the plane of the web, resulting in an area shrinkage of about 55% and a final fabric weight of 6 oz./sq. yd. As a comparison, identical webs were prepared and, before being impregnated, were dried to produce irreversible collapsing of the gel fiber. These dried sheets

TABLE VIII

Sample No.	Description of fiber in non-woven sheet	Impregnating solids, wt. percent	Dry impregnated fabric wt., oz./sq. yd.	Dry tensile strength, lb./in.	Tear strength, lb.
1	Polyacrylonitrile, 3 denier/filament, ⅜-inch staple	22	5.0	29	1.7
2	do	29	5.4	32	1.6
3	Polyacrylonitrile, ½ denier/filament, 3/16)-inch staple	27	4.6	34	1.0
4	do	36	5.3	47	1.0
5	do	42	5.9	52	0.9
6	Polyacrylonitrile, 6 denier/filament, ½-inch staple	18	5.3	19	1.7
7	Polyacrylonitrile, 70% 15 denier/filament, ¾-inch staple; 30% ½ denier/filament, ½-inch staple.	22	5.2	26	3.7
8	do	30	6.0	39	3.6
9	do	37	6.9	49	3.0
10	85% polyacrylonitrile, ½ denier/filament, 3/16)-inch staple; 15% polyhexamethylene adipamide, 11 denier/filament, 1-inch staple.	29	4.7	35	1.9
11	50% polyacrylonitrile, ½ denier/filament, 3/16)-inch staple; 50% polyhexamethylene adipamide, 11 denier/filament, 1-inch staple.	24	4.2	30	6.3
12	10% polyacrylonitrile, ½ denier/filament, 3/16)-inch staple; 90% polyhexamethylene adipamide, 11 denier/filament, 1-inch staple.	13	3.2	17	4.8
13	10% polyacrylonitrile, ½ denier/filament, 3/16)-inch staple; 90% polyacrylonitrile (predried, high tenacity), ½-inch staple.	24	3.3	19	1.2
14	50% polyacrylonitrile, ½ denier/filament, 3/16)-inch staple; 50% polyacrylonitrile (predried, high tenacity), ½-inch staple.	40	5.2	36	1.3

were then impregnated so as to produce the same content of resin solids and the same final fabric weight.

In still another comparison, sheets were prepared as described above, with the modification that immediately after impregnation the impregnated web was dipped in a 1%–2% solution of aluminum sulfate to coagulate the resin solids.

The properties of all sheets are shown in Table X. "Wet" refers to webs impregnated while in the wet leaf form before drying and irreversibly collapsing the gel fibers. "Dry" refers to webs impregnated after drying and irreversibly collapsing the gel fibers. The latices used to impregnate the fabrics are:

A—"Hycar"–1561; butadiene/high acrylonitrile latex emulsion—sold by B. F. Goodrich Company

B—"Hycar"–1571; butadiene/high acrylonitrile latex emulsion—sold by B. F. Goodrich Company

C—"Hycar"–1572; butadiene/medium acrylonitrile latex emulsion—sold by B. F. Goodrich Company

D—"Hycar"–2679; self-curing polyacrylic carboxylated polymer—sold by B. F. Goodrich Company

E—"Hycar"–2600 x 120; self-curing polyacrylic carboxylated polymer with high surface tension—sold by B. F. Goodrich Company

F—"Rhoplex" B–25; polyacrylic polymer—sold by Rohm & Haas Company

G—"Geon"–652; colloidal dispersion of polymers of vinyl/chloride—sold by B. F. Goodrich Company

H—"Geon"–450 x 167; colloidal dispersion of polymers of vinyl/chloride—sold by B. F. Goodrich Company

I—"PolyEm"; aqueous emulsion of polyethylene—sold by Spencer Chemical Company

TABLE X.—LATEX NOT COAGULATED

Sample No.	Impregnating latex	Porosity, ft.³/min./sq. ft.	Tear strength, lb.	Tensile strength, lb./in.	Elongation, percent	Tensile energy absorbed, ft. lb./lb.
1-Wet	A	55	1.3	27	17	1,063
1-Dry	A	60	1.6	27	33	1,842
2-Wet	B	70	1.3	21	7	330
2-Dry	B	105	2.1	20	22	921
3-Wet	C	65	1.2	22	8	421
3-Dry	C	75	1.9	22	14	609
4-Wet	D	55	1.1	32	12	774
4-Dry	D	110	1.8	34	26	1,526
5-Wet	E	60	1.2	33	14	940
5-Dry	E	75	2.0	39	31	1,914
6-Wet	F	90	1.4	15	5	267
6-Dry	F	120	2.0	15	49	1,082
7-Wet	G	100	0.8	27	7	445
7-Dry	G	100	0.8	26	8	540
8-Wet	H	102	0.9	26	8	478
8-Dry	H	145	1.1	30	11	722
9-Wet	I	48	0.8	20	4	156
9-Dry	I	108	2.1	24	9	292
LATEX COAGULATED						
10-Wet	A	17	2.8	30	14	812
10-Dry	A	17	4.0	33	27	1,645
11-Wet	B	20	2.6	24	11	646
11-Dry	B	20	3.3	34	22	1,462
12-Wet	G	100	2.0	18	5	184
12-Dry	G	115	2.1	36	15	1,049
13-Wet	H	110	1.8	24	5	278
13-Dry	H	165	2.4	40	14	918

EXAMPLE 9

Impregnation of pattern bonded webs of blended fibers with resin solids

Wet leafs were formed as described in Example 8, with the exception that the gel fibers (polyacrylonitrile homopolymer) were cut to ½-inch staple length and blended with various amounts of non-gel fibers also cut to ½-inch staple length. The non-gel fibers were:

11-denier nylon—polyhexamethylene adipamide
11-denier polyester—polyethylene terephthalate
6-denier polyethylene.

After formation the wet leafs were pattern bonded employing 1/32-inch spots on a square pattern of ⅛ x ⅛ inch. The bonding was performed by cooperating pressure rolls, the nip pressure being 2½ to 5 lbs. per inch of roll length and the temperature of the rolls was 85°–100° C. The bonded wet leaf was then impregnated by dipping into an aqueous latex emulsion of butadiene/high acrylonitrile ("Hycar"-1571, sold by B. F. Goodrich Co.), squeezed to produce 25% (dry basis) of resin solids in the web. These impregnated webs were then dried 5 minutes at 150° C. in a forced air oven without restraining the shrinkage. The dry web had exhibited an area shrinkage of about 40%. In Table XI the properties of these fabrics are shown.

TABLE XI

Sample No.	Fiber blend	Dry fabric weight oz./yd.²	Elongation, percent	Tear strength, lb.	Tensile strength, lb./in.
1	100% gel fiber	4.8	16	1.0	22
2	75% gel fiber, 25% nylon	4.9	17	2.0	14
3	40% gel fiber, 60% nylon	4.6	20	3.5	7
4	75% gel fiber, 25% polyester	4.6	15	1.4	16
5	40% gel fiber, 60% polyester	4.7	17	1.3	10
6	75% gel fiber, 25% polyethylene	4.9	17	1.3	17
7	40% gel fiber, 60% polyethylene	4.7	18	1.8	8

EXAMPLE 10

Area shrinkage produced by drying

In a series of experiments, gel fibers of acrylonitrile polymer were prepared by wet spinning polyacrylonitrile from an aqueous zinc chloride solution containing about 60% by weight zinc chloride into a coagulation bath (an aqueous zinc chloride solution containing about 43% zinc chloride) at about 12.5° C., washing the fibers substantially free of zinc chloride, and orienting them by stretching the gel filaments about 12 times their original length in an aqueous bath at 95°–100° C. These fibers were cut into ¼ to ⅜-inch staple, dispersed in water and formed into a wet leaf and couched, employing normal laboratory papermaking techniques. The wet leaf was then subjected to various combinations of temperature and pressure to provide interfiber self-bonding and

the pressed wet leaf was then dried between woven wire screens maintained at the drying temperature. The wet leaf and the dried sheet were tested for tensile strength and the dried sheet was tested for percent area shrinkage to show the differences obtained in using various combinations of interfiber bonding with various drying temperatures. The results are shown in Table XII.

TABLE XII

Wet leaf pressing conditions		Tensile strength, lb./in./oz./sq. yd.		Percent area shrinkage	
Temperature, °C.	Pressure, p.s.i.	Dried sheet at 40°C.	Dried sheet at 150°C.	40°C.	150°C.
25	5	(*)	.05	23.4	41.3
25	50	(*)	.16	17.8	41.3
25	100	.09	.5	30.2	41.3
25	250	.52	1.4	31.0	40.6
25	500	1.1	5.2	29.0	39.1
40	5	(*)	0.19	20.6	41.2
40	50	0.13	0.48	20.6	41.2
40	100	0.3	2.0	24.8	38.3
40	250	0.9	4.2	24.2	38.6
40	500	1.4	5.8	22.0	39.1
60	5	0.02	0.14	20.8	41.3
60	50	0.9	2.4	17.8	40.2
60	100	1.8	3.9	19.4	39.1
60	250	3.1	6.4	18.0	38.6
60	500	4.1	6.6	15.0	37.8
85	5	0.32	0.42	15.0	41.2
85	50	3.3	5.3	11.9	36.6
85	100	5.4	6.9	10.5	36.6
85	250	7.3	7.4	9.0	34.3
85	500	7.8	8.4	6.3	30.2

* Too weak to test.

EXAMPLE 11

Barrier drying of various webs

Wet gel fibers were prepared in substantially the same manner as described in Example 10 and were cut to various staple lengths and made into webs by wet leaf formation as described. In the first series, represented by samples 1, 2, and 3, the wet gel fiber was cut to ¼-inch staple, made into a wet leaf, felt-pressed to 28.5% solids, and then subjected to a drying operation to cause irreversible collapsing of the fibers. In sample 1, there was no restraint whatsoever on the drying fabric, while in samples 2 and 3, the spaced barriers of this invention were employed in the form of heated flat bed press platens, the temperatures of which were about 180° C. In samples 4, 5, and 6, the fiber was ¼-inch staple, was felt-pressed to 28.5% solids, and then calendered at 220 lbs./linear inch at 25° C. to produce a web having 57.4% solids, and this material was then dried so as to irreversibly collapse the gel fibers. In sample 4, the fabric was not restrained in any fashion during drying, while in samples 5 and 6, the fabric was dried between barriers as described above, about 180° C. In samples 7, 8, and 9, the gel fibers were cut to ⅜-inch staple, formed into a wet leaf, felt-pressed to 27.1% solids, and then dried to cause irreversible collapsing of the gel fiber. In each of these samples, the fabric was dried between two solid barriers in accordance with this invention. In sample 7, it should be noted that the thickness of the fabric before drying is greater than the distance between the barriers. In samples 10, 11, 12, and 13, the gel fiber was formed into a wet leaf and treated as described above with respect to samples 7, 8, and 9, with the additional treatment that the wet leaf was calendered at 120 lbs./linear inch at 25° C. to a fabric containing 50.5% solids and this material was then dried between barriers to cause irreversible collapsing of the fibers. The results are shown in Table XIII.

TABLE XIII

Sample No.	Weight, oz./sq. yd.		Thickness, mils		Barrier spacing, mils	Free space ratio [1]		Percent area shrinkage on drying	Volume percent fiber	Tensile strength, lb./in./oz./sq. yd.
	Wet leaf	Dry fabric	Wet leaf	Dry fabric		Wet leaf	Dry fabric			
1	2.5	--------	12.2	--------	∞	Too weak to test after drying				(2)
2	2.5	5.1	12.2	36	62.5	5.1	1.74	52	17	1.3
3	2.8	5.2	13.6	39	41	3.01	1.05	46	16	1.3
4	2.2	--------	4.1	--------	∞	Too irregular to test after drying				(3)
5	2.2	3.9	4.1	15	62.5	15.3	13.0	44	32	2.0
6	2.2	3.9	4.1	12	16	3.9	2.5	33	40	4.2
7	3.2	3.8	16.5	18	16	0.97	0.89	14	25	3.7
8	3.4	6.2	17.5	35	41	2.3	1.17	46	22	2.4
9	3.5	7.1	18.0	37	62.5	3.5	1.7	51	24	1.4
10	1.5	2.55	4.0	10	13	3.3	1.3	40	31	5.2
11	1.5	2.5	4.0	10	16	3.9	1.6	41	30	4.2
12	1.5	2.5	4.0	12	41	10.2	2.1	39	25	3.0
13	1.5	2.9	4.0	14	62.5	15.6	4.5	47	31	2.5

[1] Free space ratio = Distance between barriers / Thickness of fabric

[2] 0.1 wet leaf.

[3] 1.2 wet leaf.

EXAMPLE 12

Preparation of webs from continuous filament

An aqueous 60 weight percent zinc chloride solution containing about 10 weight percent dissolved polyacrylonitrile was extruded through a spinnerette containing 3500 8-mil holes into an aqueous 44 percent zinc chloride coagulation bath, washed essentially completely free from residual zinc chloride, and then stretched about 12 times in a hot water bath to produce about 3 denier per filament (dry basis) gel filaments, and a total tow denier of about 10,900 (dry basis). The degree of swelling or water content of the thus produced gel filaments was found to be about 233% (as measured by grams water in gel/grams dry filament × 100).

A portion of the tow or ribbon of the gel filaments was dried while restrained to constant length (i.e., no lineal or axial shrinkage) by wrapping it around and in contact with an 8-inch diameter roll dryer surface at 250° F. for 2½ minutes. Both ends of the ribbon were secured, thus making a hoop-like configuration. The surface tension of the gel fluid was about 74 dynes/sq. cm. The average shrinkage force developed in the drying filaments was determined to be an increasing force to 4.8 p.s.i. The total shrinkage generated resultant force against the roll was determined to be about 0.8 p.s.i., and about 0.4 p.s.i. average shrinkage generated resultant force between fiber layers, the ribbon being about 5 filament layers thick.

The irreversibly dried ribbon was observed to be a strong, coherent, self-bonded structure. The individual filaments could not be separated from one another when the ribbon was flexed and pulled. The filaments remained in a coherent, continuous ribbon. A microscopic examination of a cross-section of the ribbon showed that the filaments were excellently self-bonded to one or more adjacent filaments.

Ribbons 4½ inches wide and 1 inch wide were made according to the foregoing, with similar excellent results.

The foregoing procedure was repeated, except that the gel filament tow was dried in a relaxed and free-to-shrink condition. A free-filament, unbonded tow resulted. The physical properties of the free-filament tow and the 1 inch wide, self-bonded ribbon prepared according to this invention are set forth in Table XIV.

TABLE XIV

Sample form	Textile tow, free-filament bundle	Self-bonded ribbon, 1-inch wide ribbon
Denier	14,000	7,260
Ounces/square yard	1.81	.94
Tensile:		
Grams/denier	1.63	2.79
Pounds/square inch	25,200	43,200
Pounds/inch/ounce/square yard	39	48
Extension, percent	32	10
Initial modulus:		
Grams/denier/100% extension	10	162
Pounds/sq. in./100% extension	151,500	2,454,300

EXAMPLE 13

The procedure of Example 12 was repeated, excepting to utilize gel filaments of varying degrees of swelling, and to vary the surface tension of the gel fluid, the restraining force applied to the ribbon during drying, and the drying temperature. Drying was accomplished on a heated drum or hot air oven. These results are set forth in Table XV.

TABLE XV

Sample No.	Degree of swelling (parts water per 100 parts polymer)	Surface tension 25° C., dynes/cm.	Drying configuration of drying ribbon	Temperature (° F.) and drying medium	Applied degree of restraint (tension)	Product
1	225	74	(A)	250, drum surface	Full	Bonded ribbon.
2	225	74	(A)	300, drum surface	do	Do.
3	225	74	(B)	250, air oven	0	Textile fiber tow.
4	225	74	(C)	do	Full	Do.
5	225	34	(B)	do	0	Do.
6	225	74	(D)	150, air oven	Full	Do.
7	225	74	(D)	70, air oven	do	Do.
8	225	34	(D)	250, air oven	do	Weak bonded tow.
9	225	34	(D)	300, air oven	do	Yellow bonded ribbon.
10	100	74	(D)	250, air oven	do	Borderline ribbon or tow.
11	50	74	(D)	do	do	Textile fiber tow.
12	100	34	(D)	300, air oven	do	Weak bonded ribbon.
13	172	74	(D)	250, air oven	do	Do.
14 [1]	172	74	(D)	300, air oven	do	Do.
15	191	74	(D)	250, air oven	do	Bonded ribbon.
16	191	74	(D)	70, air oven	do	Textile tow.
17	1	74	(D)	300, air oven	do	Do.
18 [2]	102	74	(D)	250, air oven	do	Bonded ribbon.
19 [2]	102	74	(B)	do	0	Textile tow.
20	102	74	(C)	do	Full	Do.

[1] Copolymer of about 96% acrylonitrile.
[2] Copolymer of about 95% acrylonitrile.
Note:
(A) The gel filament ribbon was wrapped around a heated 8-inch diameter drum. A 100 mesh screen was pressed against the ribbon and drum surface, compressing the ribbon against the drum with about 4 p.s.i. compressive force.
(B) The gel filament ribbon was allowed to lay in a completely unrestrained condition on an open grid screen in a circulating hot air oven.
(C) The gel filament ribbon was firmly clamped in a parallel fiber array, and in a completely restrained from shrinkage position with a clamping unit placed in a circulating hot air oven. There was no side or edge contact with any solid surface (except adjacent filaments). Therefore, there was no direct or measurably significant resultant compressive force on the suspended ribbon segment.
(D) The gel filament ribbon was clampled and dried as in (C). In addition, the suspended ribbon segment was pressed between a solid metal block and a screen-faced metal block with an average resultant compressive force of about 4 p.s.i.

EXAMPLE 14

Hot wet treatment of wet leaf

Staple gel fiber (3/8-inch length) prepared substantially as described in Example 1 was formed into a wet leaf in a Williams handsheet mold (8" x 8"), couched between damp felts at room temperature and then pattern bonded by passing the wet leaf between patterned metal rolls heated with 50 p.s.i.g. steam. The pattern on the rolls was 1/32-inch pressure spots formed on 1/8-inch centers in a square pattern. The pressure between the rolls was 22 pounds per inch of roll length. Six comparative samples were prepared to show the advantages of a hot wet treatment of the pattern bonded wet leaf. The various treatments given these samples are as follows:

Sample 1—No further treatment after pattern bonding.
Sample 2—Same as sample 1, followed by drying without restraint on sheet at 140° F. in a circulating air oven.
Sample 3—Pattern bonded wet leaf boiled in water for 10 minutes.
Sample 4—Same as sample 3 followed by drying without restraint on sheet at 140° F. in a circulating air oven.
Sample 5—Pattern bonded wet leaf was dried without restraint on sheet at 140° C. in a circulating ai oven, impregnated by dipping in a latex containing 10% resin solids ("Hycar"–1571), squeezed, and redried in same manner as before.
Sample 6—Same as sample 5 except that pattern bonded wet leaf was boiled in water for 10 minutes before drying, impregnating, and redrying.

The results are shown in Table XVI. The hot wet treatment provided by boiling the wet leaf causes a shrinkage to take place before the drying step and, because of the relaxation of the fibers, produces a stronger sheet per unit of fabric weight (tensile strength x fabric weight).

TABLE XVI

Sample No.	Fabric weight, oz./sq. yd. (wet leaf)	Fabric weight, oz./sq. yd. (dried)	Impregnating resin wt., percent	Area shrinkage, percent	Tensile strength, lb./in./oz./sq. yd.	Elongation, percent
1	2.0	[1] 2.0	0	0	4.0	6.7
2	2.0	3.1	0	35	3.6	13.3
3	2.0	[1] 2.9	0	30	3.2	10.0
4	2.0	4.0	0	50	5.5	11.6
5	2.0	4.9	26	45	6.6	15.3
6	2.0	6.0	26	55	10.7	26.7

[1] Wet.

Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

What is claimed is:

1. In a process for preparing a dry, nonwoven fibrous sheet by forming a web of self-bonding nonfibrillated gel fibers of thermoplastic, fiber-forming polymer of acrylonitrile wherein the said gel fibers have a gel network structure that has never been completely collapsed by drying and that consists essentially of interconnecting capillary spaces intimately intertwined with a fibrillar structure of polymeric material, subjecting said web to a combination of superatmospheric pressure, a temperature of at least 25° C., and time, which combination is not sufficient to cause dry fibers of said polymer to fuse but which is

sufficient to produce a web having a rewet tensile strength of at least about 0.05 lb./in./oz./sq. yd., and subsequently drying the said web to produce the final product, the improvement which comprises subjecting said web to drying conditions which cause said gel fibers to collapse while maintaining said web substantially free of forces tending to restrain shrinkage of said web.

2. The process of claim 1 wherein said gel fibers are staple gel fibers and said combination of pressure, temperature of at least 25° C., and time, is applied to said web in the form of a pattern of spaced, heated pressure points spaced apart not greater than the staple length of said fibers, and wherein said drying conditions are imposed while maintaining said web substantially free of externally applied stresses other than those inherent in said pattern of spaced, heated pressure points.

3. The process of claim 1 wherein the recovered dry, nonwoven fibrous sheet is thereafter subjected to an annealing heat treatment in which the temperature of the dry sheet is raised to at least 30° C. above the glass transition temperature of said polymer of acrylonitrile.

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