United States Patent Office

3,047,455
Patented July 31, 1962

3,047,455

PAPER MANUFACTURE FROM SYNTHETIC NON-CELLULOSIC FIBERS

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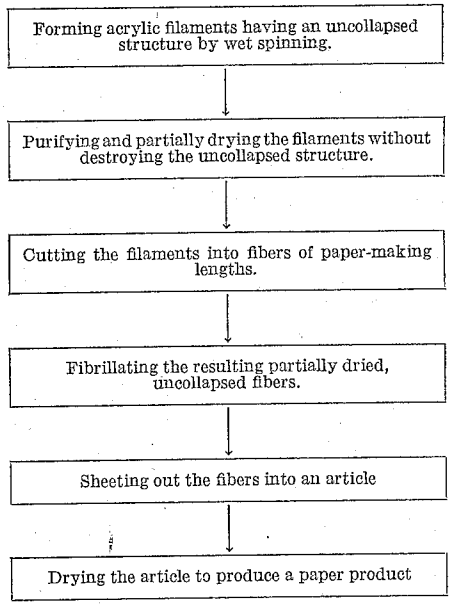
No Drawing. Filed Mar. 13, 1959, Ser. No. 799,080
3 Claims. (Cl. 162—157)

This invention relates to the manufacture of paper or nonwoven products comprising randomly intermingled discontinuous fibers which are at least in part composed of highly fibrillated synthetic non-cellulosic fibers of paper-making length. More particularly, the invention relates to paper products comprising randomly intermingled discontinuous fibers which are at least in part composed of highly fibrillated wet-spun thermoplastic products of a polymerized mass composed mainly of polymerized acrylonitrile, to such fibers, and to a method of producing said paper products.

The following flow diagram is given in order that the understanding of the method of the present invention can be better facilitated:



In the normal manufacture of paper, cellulosic fibers such as those derived from wood pulp are beaten in water to disperse the fibers therein and to reduce them to a length and fineness suitable for use in paper-making. During the beating operation the cellulosic fibers fibrillate, the fibrillation manifesting itself by a fraying or shedding of the surfaces and ends of the fibers to produce minute tendrils or fibrils which serve to interlock the fibers together when they are deposited on the forming screen of a paper-making machine to make a sheet therefrom and dried. The interlocking of these fibrils projecting from the deposited fibers imparts coherency and strength to the paper. In other words, the strength in the paper is attained through the interlocking of large numbers of fiber branches or fibrils during sheet formation.

While some success has been attained in the use of synthetic non-cellulosic fibers in paper manufacture by adding extremely long synthetic fibers to a standard cellulosic water dispersion at the end of the beating cycle and casting the resulting dipersion on a wire screen, it previously was regarded that synthetic fibers, such as those produced from polycaprolactam, polyhexamethyleneadipamide, polymeric ethylene terephthalate, and the like are not particularly useful in the manufacture of paper by ordinary techniques since these fibers do not fibrillate readily when they are beaten in water. Prior efforts towards the utilization of these synthetic fibers have been directed to producing paper or nonwoven structures therefrom by effecting fiber bonding in various manners. One way to effect fiber bonding involves the application of heat and pressure to soften and fuse the fibers together. The fiber bonding can be achieved also by the inorganic salt fiber fusion method which requires the use of inorganic chemicals to swell the fiber surface in conjunction with heat and/or pressure. A further method of effecting fiber bonding of synthetic fiber is by organic solvent fiber fusion technique wherein the fibers are swollen by or partially dissolved in the solvent. Moreover, the fibers can be bonded by the use of adhesives. Each of these methods has inherent disadvantages and deficiencies in regard to the specific manufacturing steps involved and to the properties of the ultimate product.

However, recently there has been disclosed a process for manufacturing water-laid webs, including paper, from synthetic fibers without the use of bonding chemicals by beating wet-spun fibers of acrylic polymers, viz., polymers made from polymerized acrylonitrile or a copolymerized mixture of acrylonitrile and up to about 15 percent by weight of another monomer copolymerizable therewith, in an aqueous suspension until the fibers have fibrillated to a sufficient extent. The thus-fibrillated fibers are deposited on a screen, for instance, to form a web with heat subsequently being applied to the web to dry and develop an interlocking of the fibers. While this recent disclosure represents a notable advance in the art, it is desirable to improve the strength and the resistance to tearing and bursting, as well as other physical properties, in both the wet and dry states of paper made from acrylic fibers.

One object of this invention is to provide a highly fibrillated fiber formed from wet-spun thermoplastic products of the polymerization of a polymerizable mass comprising mainly acrylonitrile and being suitable for use in the manufacture of paper, nonwoven articles and the like. Another object is to provide paper products having improved strength and resistance to tear and burst and formed from the just-described fibrillated fibers. A further object is to provide a method of making said paper products. Other objects will become apparent from the following detailed description of the invention.

According to a preferred modification of the invention, paper products having improved tear and burst properties are made by fibrillating a predetermined quantity of paper-making, wet-spun, gel, oriented, crystalline, uncollapsed, synthetic fibers composed mainly of polymerized acrylonitrile by abrasion thereof in an aqueous medium, depositing the fibers after same are sufficiently fibrillated to obtain a paper product of predetermined shape and

thickness, and thereafter drying the product to obtain a finished paper product.

As just indicated the fibers are made from thermoplastic fiber-forming materials of polymerization of a polymerizable mass comprising mainly acrylonitrile. Therefore, the fibers include the so-called "acrylic" fibers. The polymeric materials from which the fibers of the instant invention are produced are "acrylonitrile polymers" which refer to polyacrylonitrile, including binary and ternary polymers containing about at least 80 percent by weight of acrylonitrile in the polymer molecule, or a blend comprising polyacrylonitrile or copolymers comprising polymerized acrylonitrile with from 2 to 50 percent of another combined monomer, the blend having an overall polymerized acrylonitrile content of about at least 80 percent by weight.

For example, the polymer may be a copolymer of from 80 to 98 percent acrylonitrile and from 2 to 20 percent of another monomer containing the >C=C< linkage and copolymerizable with acrylonitrile. Suitable monoolefinic monomers include acrylic, alpha-chloroacrylic and metacrylic acids; the acrylates, such as methylmethacrylate, ethylmethacrylate, butylmethacrylate, methoxymethyl methacrylate, beta-chloroethyl methacrylate, and the corresponding esters of acrylic and alpha-chloroacrylic acids; vinyl chloride, vinyl fluoride, vinyl bromide, vinylidene chloride, 1-chloro-1-bromoethylene; methacrylonitrile; acrylamide and methacrylamide; alpha-chloroacrylamide, or monoalkyl substitution products thereof; methyl vinyl ketone; vinyl carboxylates, such as vinyl acetate, vinyl chloroacetate, vinyl propionate, and vinyl stearate; N-vinylimides, such as N-vinylphthalimide and N-vinylsuccinimide; methylene malonic esters; itaconic acid and itaconic ester; N-vinylcarbazole; vinyl furane; alkyl vinyl esters; vinyl sulfonic acid; ethylene alpha, beta-dicarboxylic acids or their anhydrides or derivatives, such as diethylfumarate, diethyl maleate, diethylcitraconate, diethylmesaconate; styrene; vinyl naphthalene; vinyl-substituted tertiary heterocyclic amines, such as the vinylpyridines and alkyl-substituted vinylpyridines, for example, 2-vinylpyridine, 4-vinylpyridine, 5-methyl-2-vinylpyridine, etc.; 1-vinylimidazole and alkyl-substituted-1-vinylimidazoles, such as 2-, 4-, or 5-methyl-2-vinylimidazole, and other >C=C< containing polymerizable materials.

The polymer may be a tertiary interpolymer, for example, products obtained by the interpolymerization of acrylonitrile and two or more of any of the monomers, other than acrylonitrile, enumerated above. More specifically, and preferably, the ternary polymer comprises acrylonitrile, methacrylonitrile, and 2-vinylpyridine. The ternary polymers preferably contain from 80 to 97 percent of acrylonitrile, from 1 to 10 percent of a vinylpyridine or a 1-vinylimidazole, and from 1 to 18 percent of another substance, such as methacrylonitrile or vinyl chloride.

The polymer can also be a blend of polyacrylonitrile or of a binary interpolymer of from 80 to 99 percent acrylonitrile and from one to 20 percent of at least one other >C=C< containing substance with from 2 to 50 percent on the weight of the blend of a copolymer of from 10 to 70 percent of acrylonitrile and from 30 to 90 percent of at least one other >C=C< containing polymerizable monomer. Preferably, when the polymeric material comprises a blend, it will be a particular blend of a copolymer of 90 to 98 percent of acrylonitrile and from 2 to 10 percent of another monoolefinic monomer, such as vinyl acetate, with a sufficient amount of a copolymer of from 10 to 70 percent of acrylonitrile and from 30 to 90 percent of a vinyl-substituted tertiary heterocyclic amine, such as a vinylpyridine or 1-vinylimidazole, to give a blend having an overall vinyl-substituted tertiary heterocyclic amine content of from 2 to 10 percent, based on the weight of the blend. Fibers made from the just-described blend of copolymer unexpectedly have a notably excellent propensity to fibrillate so that a superior paper can be manufactured therefrom.

The invention is limited to the use of synthetic fibers that have been wet-spun and does not contemplate the use of fibers produced by melt spinning and dry spinning since synthetic continuous filaments produced by the latter two methods have substantially no strong tendency to fibrillate under wet abrasive conditions employed in conventional paper-making processes. The term "wet spun synthetic fiber" as used herein refers, therefore, only to those fibers which are manufactured by truly synthetic methods wherein a water coagulable solution of a polymer (acrylonitrile polymer in this instance) is extruded through very small orifices as in a spinneret and then the extruded solution is coagulated in a precipitating bath, thereby forming continuous filaments of any desired diameter which can later be cut into any desired lengths.

Ordinarily, in a wet spinning operation coagulation is accomplished in an aqueous bath sometimes containing a percentage of solvent or dissolved salt. During coagulation there are an inward diffusion of bath liquid into the coagulating filaments and a corresponding outward movement of solvent into the bath. The solvent and bath liquid interchange in such a manner that the resulting filaments may contain voids or unfilled spaces along their lengths. Expressed another way, the filaments have a coarse, sponge-like structure that can be clearly seen with an electron microscope. Fibers having such structure are known as "uncollapsed" fibers. Ordinarily, in order to produce satisfactory textile fibers positive steps are taken to collapse or cave in these voids in the filaments in order to form a dense, consolidated structure, this usually being accomplished by highly tensioning the filaments and drying same at a relatively high temperature under considerable pressure or by other known techniques, thereby to form a more compact filamentary structure having a low void volume. Measurements by standard methods of the densities of uncollapsed fibers and corresponding collapsed fibers show a pronounced difference therebetween, the extent to which the fiber is uncollapsed or collapsed being indicated by these measurements. Obviously, the densities of the collapsed fibers are greater than the densities of corresponding uncollapsed fibers. In accordance with the present invention it is preferred that the density of the fiber used be at least 15 percent up to about 65 percent less than the density of a corresponding collapsed fiber.

In contrast to the prior art teaching in regard to the requisite collapsing to produce a satisfactory textile fiber, an important aspect of the present invention is based on the discovery that if care is taken that the wet-spun acrylic filaments are not substantially collapsed before they are utilized in a paper-making process, an improved paper can be made therefrom and the uncollapsed filaments can be fibrillated readily and easily by the same equipment and techniques and within comparable times as the cellulosic fibers used to make paper. More specifically, superior acrylic fiber for use in paper making can be produced by spinning a water coagulable solution of an acrylonitrile polymer containing at least 80 percent acrylonitrile in the polymer into an aqueous precipitating bath under controlled conditions wherein the solvent and the bath liquid interchange in such a manner to produce filaments having a sponge-like or uncollapsed structure and by purifying the filaments and by partially removing the water content from the filaments without appreciably destroying said uncollapsed structure.

The wet-spun acrylic filaments which are produced with a view to being utilized in accordance with the instant invention preferably are subjected to a stretching operation while they are in a gel state to attain a desired attenuation and molecular orientation according to various techniques. In addition to the stretching operation other treating and processing steps may be given the coagulated filaments, such as washing, crimping, cutting,

and the like. Furthermore, the water content in the filaments or fibers can be reduced by partially drying with air, steam, or the like by centrifuging same, by use of vacuum means, and the like without substantial reduction of the propensity to fibrillate. However, it is important that these freshly spun filaments or fibers should never be dried below the point where they contain less than 1–2 percent water before they are subjected to the action of the beater in a paper-making machine. Ordinarily, the water content of the fibers before being fibrillated is not decreased below 5 percent with good results being obtained. Hence, a prerequisite to the proper practice of the invention is that the uncollapsed and gel structure of the fibers or filaments not be destroyed before they are processed in accordance with the present invention. It will be perceived that the gel life can be prolonged by maintaining the gel fibers in contact with water or in the presence of a humectant if desired.

Next, the wet-spun, gel, synthetic filaments of an acrylonitrile polymerization product used in practicing this invention are cut to staple lengths. Fibers shorter or longer than commercially available staple fibers can be used. When short staple is used, it is possible to charge the beater quickly. If longer staple is employed, the fibers should be charged slowly to avoid clogging of the beater. The relationships between the count of long and short fibers or the fiber ratio in regard to the number of thick and thin fibers (i.e., of various deniers) are governed by the desired properties of the ultimate product. Hence, the acrylic fibers employed in making paper can be of any suitable denier or a mixture of fibers of different deniers can be used. For instance, fibers having deniers between 0.3 to 20 or more can be employed. On the basis of the data obtained, it has been found that best paper is produced when a high tenacity acrylic fiber stock is employed, i.e., a tenacity of at least 4.5 grams per denier, this value being much greater than the 2.5 grams per denier of normal textile grade acrylic fibers.

It should be understood that other fibers including synthetic, artificial, and natural fibers in proportions, say from 0–99 percent by weight, can be used in conjunction with the wet-spun gel thermoplastic fibers of acrylonitrile containing polymers as above defined; and still, one can produce therefrom a satisfactory paper product.

In accordance with the invention at least the amount of acrylic fibers as used herein necessary for providing a desired paper product is beaten or battered in the presence of water as in aqueous suspension, whereby the fibers are fibrillated and become dispersed. Means for beating commonly used in the paper-making art are satisfactory. Obviously, the time to which the fibers are subjected to the beating action depends, among other things, on the particular beater employed. Generally speaking, the fibers should be beaten sufficiently so that they become fibrillated to such an extent the fibrils produced will serve to interlock together subsequently in the paper-making process to produce a satisfactory paper product. Surprisingly, the uncollapsed, gel acrylic fiber used in the present process will fibrillate to a much greater extent and in a shorter period of time for a given severity of beating action than the collapsed fiber of like composition. Thus, the uncollapsed fiber can be subjected comparably to a less severe beating action and yet be fibrillated sufficiently. Avoidance of severe beating action is desirable in some instances since a harsh beating action produces fibers of undesirably short lengths.

Moreover, for a given severity of beating under conditions where collapsed fibers would be comminuted or broken into undesirably short lengths and having broom-like ends and very short fibrils along the fiber length, the uncollapsed, gel fiber as used in the instant invention advantageously is contused with less cutting thereof, whereby longer fibrils along the fiber length are produced that contribute to a more tenacious interlocking of the fibers in the ultimate product.

While excessive foaming is not ordinarily encountered during beating, anti-foaming agents such as octyl alcohol and the like may be added, if desired. The fiber suspension may be made more uniform by known suspending agents such as freshly deacetylated karaya gum. If such is used properly, the fibers do not settle or flocculate excessively and proper sheet formation is facilitated thereby.

The beaten fibrillated acrylic fibers are thereafter formed into a paper product by any suitable process. For example, such product can be formed into a self-supporting continuous web or sheet by the use of standard paper mill equipment of various types. The self-supporting paper sheet is then carried through a drying process. The drying of the paper can be carried out by continuously passing the paper over heated drums in a known manner. Also, a moving web of the paper may be passed across a battery of infra-red lamps or other heating means.

The drying temperature may be in the same range ordinarily used for drying cellulosic fiber-containing paper and is determined to a considerable extent by the properties desired in the ultimate paper poduct. The paper products herein may be dried at room temperature or lower and up to the temperature at which the acrylic polymer degrades or melts. The drying temperature affects the properties of the acrylic paper. It has been found in this regard that the physical properties with reference to tensile, tear, and bursting strengths usually are related directly to the drying temperature employed. That is to say, when a higher drying temperature is employed, one may expect improvement in these properties. For example, properties of a handsheet dried at 70° F. are usually inferior to a second identical handsheet dried at 200° F. which in turn is usually inferior to a third identical handsheet dried at 400° F.

By the term "paper products" is meant products comprising a multiplicity of discontinuous fibers of paper-making length associated together to form a coherent product which may be flexible or stiff, thick or thin, soft or hard, and including sheets, boards, filters, and molded paper articles of all kinds.

The following examples will further illustrate the practice and improvement of the instant invention. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

A 1½ lb. Valley laboratory beater was charged with 150 grams of oriented fibers in 20 liters of water (0.75 percent consistency). The fibers were approximately 3 denier per filament cut to an average of ¼" lengths and had been prepared by wet spinning from a polymer having the composition of a bland of (*a*) a copolymer of 97 percent acrylonitrile and 3 percent vinyl acetate and (*b*) a copolymer of 50 percent acrylonitrile and 50 percent vinylpyridine, said blend containing 6 percent vinylpyridine based on the total weight of the blend. The fibers had been dried during their manufacture and had little void volume therein as seen by microscopic examination thereof. The density of the fibers was 1.17 grams per cubic centimeter. The fibers had a tenacity of 5.2 grams per denier and an elongation of 9 percent.

The beating action of the Valley beater is regulated by the bedplate load or counterweight that urges the bedplate against the rotatable beater bars. During operation of the beater the fiber is drawn between the beater bars and bedplate by the circulating action therein. Three 150 gram samples of the fibers were processed separately in the Valley beater using 12 lb., 5 lb., and 3 lb. counterweights. Handsheets were taken every 10 minutes using the 12 lb. counterweight and every 15 minutes when using the 5 lb. and 3 lb. counterweights. The handsheets which weighed

approximately 2.50 grams were formed and dried using a Noble and Wood laboratory handsheet machine. The machine includes an 8" square mold, press rolls, and felt and a stream heated drying drum with felt. The handsheets were dried between blotters on the drying drum at 198° F. The physical properties of these handsheets are given below in Table 1. Handsheets were weighed on a weight scale basis and thickness was measured with a gauge micrometer. Physical strengths of the handsheets were measured on an Elmendorf tearing tester, a Mullen bursting strength tester, and a Scott model DH tensile tester, following TAPPI standards. All values were normalized to an 8" x 8" handsheet (44 lbs. per ream, 25 x 40–500).

Table 1

Counterweight (lbs.)	Beating Time (hrs.—mins.)	Tear (gms.)	Bursting (p.s.i.)	Tensile Strength (lbs./in.)
12	40	16	2.0	1.2
12	50	26	2.3	1.9
12	1—00	33	3.4	2.5
12	1—10	27	3.6	3.4
12	1—20	23	4.3	3.8
12	1—30	21	4.8	4.2
12	1—40	13	4.4	4.7
5	1—15	46	2.8	1.5
5	1—30	48	4.0	2.6
5	1—45	57	5.3	3.2
5	2—00	72	6.4	4.7
5	2—15	59	8.1	5.3
5	2—30	48	8.5	6.3
5	2—45	41	9.8	6.8
5	3—00	36	11.1	7.8
5	3—15	27	12.5	8.1
3	1—30	29	2.6	0.5
3	1—45	48	3.5	1.6
3	2—00	52	4.9	2.5
3	2—15	61	5.7	3.2
3	2—30	71	5.6	3.9
3	2—45	79	7.0	4.4
3	3—00	81	8.2	5.3
3	3—15	91	7.9	6.1
3	3—30	88	10.0	6.3
3	3—45	85	11.0	6.7
3	4—00	71	10.0	7.0
3	4—15	54	12.0	7.2

EXAMPLE II

A spinning solution was prepared from a blend of (*a*) a copolymer of 97 percent acrylonitrile and 3 percent vinyl acetate and (*b*) a copolymer of 50 percent acrylonitrile and 50 percent vinylpyridine, said blend containing 6 percent combined vinylpyridine based on the total weight of the blend in N,N-dimethylacetamide. The solution was then extruded into an aqueous coagulating bath to form a bundle of filaments. The filaments were withdrawn from the bath and given an orientation stretch. Next, the filaments were partially dried by passing same around an assembly of drying drums. When the moisture content of the filaments had been reduced to about 10 percent, they were withdrawn from the drums and cut into length of ¼ inch. Examination under an electron miscroscope of the cut fibers revealed that the fibers were porous, having a sponge-like structure. In other words, the fiber possessed what is known as an uncollapsed structure. Moreover, these uncollapsed fibers had a density of only 0.5 gram per cubic centimeter. The fibers had a tenacity of 5.2 grams per denier and an elongation of 9 percent.

A 1½ Valley laboratory beater was charged with three separate samples of 150 grams of the uncollapsed fibers in 20 liters of water (0.75 percent consistency). The fibers were approximately 3 denier per filament. The samples were beaten in the Valley beater using 12 lb., 5 lb., and 3 lb. counterweights. Handsheets were taken at intervals indicated below in Table 2. The properties also listed in the table below were measured as outlined above in Example I.

Table 2

Counterweight (lbs.)	Beating Time (hrs.—mins.)	Tear (gms.)	Bursting (p.s.i.)	Tensile Strength (lbs./in.)
12	30	72	10	6.1
12	40	82	12	7.9
12	50	94	14	10
12	1—00	69	15	11
12	1—10	63	17	13
12	1—20	40	19	14
5	1—00	159	11	6.5
5	1—15	152	14	9.5
5	1—30	112	18	12
5	1—45	99	20	13
5	2—00	92	23	14
5	2—15	90	27	15
5	2—30	80	33	16
5	2—45	76	33	17
3	1—00	116	8	2.5
3	1—15	132	10	3.6
3	1—30	193	11	5.3
3	1—45	189	12	7.1
3	2—00	186	15	8.8
3	2—15	175	16	9.8
3	2—30	166	19	12
3	2—45	154	23	13
3	3—00	145	30	14
3	3—15	114	33	15
3	3—30	107	34	16
3	3—45	87	35	18

The beaten fibers were examined under a microscope and compared with the beaten fibers produced in Example I. For the same beater adjustment and same beating time, the fibers of the instant example were more pronouncedly fibrillated. That is to say, that the count of fibrils projecting from the fiber body was greater. Furthermore, the number of fibrils that had been severed from the body of the fiber of the instant example was significantly less. This indicated that the fibrils on the fibers beaten in accordance with this example were tougher and adhered more tenaciously to the fiber body. Additionally, it can be seen from the above data that for a given beating time a smaller counterweight can be used and yet produce a resulting handsheet of comparable physical properties.

EXAMPLE III

One hundred and fifty grams of wet-spun, oriented fibers prepared from a polymer blend having the composition of a blend of 80.4 percent (*a*) a copolymer of 97 percent acrylonitrile and 3 percent vinyl acetate and (*b*) 19.6 percent polyvinyl chloride was charged to the 1½ lb. Valley beater having a 12 lb. counterweight. The fibers had been dried during their manufacture and were collapsed as evidenced by the fact that there was little void volume therein. Handsheets of about 0.007 inch thickness formed from these fibers as above after same were beaten for 30 minutes had a tear value of 33 grams, a bursting strength of 4.2 pounds per square inch, and a tensile strength of 1.2 pounds per inch.

A spinning solution was prepared from a polymer having the composition of a blend of 80.4 percent (*a*) a copolymer of 97 percent acrylonitrile and 3 percent vinyl acetate and (*b*) 19.6 percent polyvinyl chloride. The solution was spun into uncollapsed filaments as described in Example II. Handsheets of about 0.007 inch thickness formed from these fibers after same were beaten for 30 minutes in the Valley beater with a 12 lb. counterweight had a tear value of 56 grams, a burst resistance of 8.1 pounds per square inch, and a tensile strength of 2.4 pounds per inch. Whereas many loose fibrils were found associated with the beaten collapsed fibers, that is, fibrils had broken from the body of the fiber, no noticeable loose fibrils were found associated with the beaten uncollapsed fibers.

EXAMPLE IV

One hundred and fifty grams of wet-spun, oriented fibers of 3 denier per filament prepared from a polymer blend having the composition of 10 percent polystyrene and 90 percent of a blend of (*a*) a copolymer of 97 per-

cent acrylonitrile and 3 percent vinyl acetate and (*b*) a copolymer of 50 percent acrylonitrile and 50 percent vinylpyridine, said polymer blend containing 5.4 percent vinylpyridine based on the total weight of the blend was charged to a Valley beater having a 3 lb. counterweight. The fibers had not been collapsed or fully dried during their manufacture. Handsheets of 0.008 inch thickness formed from these fibers after same were beaten for 60 minutes had a tear value of 123 grams, a bursting strength of 21.7 pounds per square inch, and a tensile strength of 7.6 pounds per inch.

EXAMPLE V

Handsheets were prepared from collapsed fibrillated fiber wet spun and composed of a polymer of 93 percent acrylonitrile and 7 percent vinyl acetate. The properties of these handsheets were compared with a similar product made from gel, uncollapsed fibrillated fibers of like compositions. The comparison data are given in Table 3 below.

Table 3

COLLAPSED

Counterweight (lbs.)	Beating Time (mins.)	Tear (gms.)	Bursting (p.s.i.)	Tensile Strength (lbs./in.)
12	50	29	1.6	1.3
12	60	22	2.4	2.0
UNCOLLAPSED				
12	40	30	3.3	3.7
12	50	23	4.5	4.7

It should be understood that although the foregoing examples describe in detail some of the more specific features of the invention, they are given primarily for the purpose of illustration and the invention in its broader aspects is not limited thereto. For example, although the invention has been illustrated in the specific examples in connection with the production of hand formed sheets, it is applicable to continuous production of paper sheets of indefinite lengths. Thus, the fibers may be beaten in a continuous manner and the resulting beaten fibers sheeted on a Fourdrinier machine, for instance. Next, the sheet is passed over drying cans and taken up in roll form. Likewise, when uncollapsed acrylic fibers made from other acrylonitrile polymers described above are used in the manufacture of paper products, similar noteworthy improvements in regard to physical properties of the paper are obtained.

Therefore, it is seen that an important aspect of the invention is based on the discovery that gel uncollapsed acrylic fibers which have been produced by wet spinning techniques may be fibrillated more easily and to a much greater extent than wet-spun fibers of the same compositions that have been dried and subjected to conditions causing collapsing of the porous structure thereof. The number of fibrils per fiber is increased and the facility of severance of the fibrils from the fiber is reduced. Moreover, the flex life of the fibril is increased, that is to say, that the fibril can be flexed a greater number of times without breakage thereof from the fiber. It was quite surprising and unexpected that such wet-spun gel fibers which have been molecularly oriented but not collapsed would be especially amenable for papermaking, since the collapsing of the porous fiber structure is thought to be necessary in the production of satisfactory yarns and fabrics.

The fiber of the present invention is particularly applicable to the preparation of paper by the wet process or water laid technique, by sheeting out of the beaten highly fibrillated fibers from an aqueous medium onto any conventional paper machine. Sheeting out, of course, refers generally to a method by which fibers in an aqueous medium are converted into a predetermined shape by removal of water. As indicated above, this sheeting out can be accomplished on a Fourdrinier machine. Alternatively, the fibers can be water laid on a porous frame as is employed in the preparation of handsheets. The water may be separated by any suitable method and means while forming the fiber into its desired shape. The sheets made in any of the aforesaid ways may be just a few thousandths of an inch or several inches thick or more. Shaped articles can be made by other similar methods.

Tough paper products having a substantial degree of flexibility and relatively soft to the touch may be made, or the products may be relatively stiff and resilient, and they have a high resistance to bursting or tearing both in the wet and dry state. An important feature of the paper products is their inherent ability to withstand the action of certain chemicals. The products are, in general, readily wetable having a high strength and are porous. Filters produced from the paper herein have improved filtration efficiency and thus may be efficaciously used in the manufacture of filters for cigarettes, filters for certain chemical acids, alkalies, and oxidizing agents which do not attack the fibers under the conditions employed and filters adapted for other purposes. While excellent paper products may be produced without the use of bonding agents, resins, potentially resinous materials, or the like, it is understood of course that these can be employed also in the present process if desired.

The fibrillated acrylic fiber produced in accordance with the instant invention is particularly useful in blending with other pulp materials, such as ordinary cellulose pulp. For example, a paper composed of a blend of only 10 percent of the acrylic fiber with the remainder being cellulosic fibers has markedly superior dimensional stability, better ageing properties, and better electrical properties. In view of these improved properties the acrylic fibers can be employed advantageously as the sole type of fiber in or with a blend of other fibers in selected paper end uses such as currency paper, abrasive paper, tabulating card stock, photographic base stock, blueprint and similar stock, map and chart stock, impregnating paper, condenser tissue, electrical insulating paper and board, filter, cable paper, and the like.

The present invention makes possible the production of an acrylonitrile polymer fiber that is feltable and eminently suitable for use in the paper-making art. The highly fibrillated fiber realized in the present invention is desirable in that the paper products made therefrom are stronger and more able to absorb energy without bursting. In addition, the strength arising from a tenacious adhering of the fibrils to the fiber body contributes greatly to a higher resistance to breaking upon being flexed. The fibrillated fiber is particularly characterized as being formed from wet-spun thermoplastic products of polymerization of polymerizable mass comprising mainly acrylonitrile and having a porous, sponge-like structure, the fibrils thereof being tough, pliable, and tenaciously adhering to the fiber surfaces and ends.

Briefly stated, the present invention in broad outline provides a method including the steps of fibrillating gel acrylic fibers which are wet-spun and uncollapsed by beating same an an aqueous slurry, matting out said fibers from the slurry into a sheet and removing substantially all of the water from the sheet produced, whereby a flexible or stiff coherent paper product is formed.

Since it is apparent that many changes and modifications can be made in the above-described detailed specification without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited except as set forth in the appended claims.

What is claimed is:

1. In the process for the manufacture of a paper product wherein: filaments are wet-spun from an acrylonitrile

polymer containing at least 80 percent by weight of acrylonitrile and up to 20 percent by weight of a monoolefinic monomer copolymerized therewith; the said filaments are cut into fibers of paper-making lengths; the said fibers are fibrillated in an aqueous slurry to develop interlockable fibrils projecting therefrom; the fibrillated fibers are sheeted out into an article of a predetermined shape and thickness; and the resulting article is dried to form a paper product; the improvement comprising fibrillating the said fibers when same have a gel and an uncollapsed structure.

2. In the process for the manufacture of a paper product wherein: filaments are wet-spun from an acrylonitrile polymer containing at least 80 percent by weight of acrylonitrile and up to 20 percent by weight of a monoolefinic monomer copolymerized therewith; the said filaments are cut into fibers of paper-making lengths; the said fibers are fibrillated in an aqueous slurry to develop interlockable fibrils projecting therefrom; the fibrillated fibers are sheeted out into an article of a predetermined shape and thickness, and the resulting article is dried to form a paper product; the improvement comprising fibrillating the said fibers when same have a gel structure and an uncollapsed structure of a density of at least 15 percent to about 65 percent less than the density of corresponding collapsed fibers.

3. The process as defined in claim 2 wherein the polymer is a blend of a copolymer of 80 to 99 percent acrylonitrile and 1 to 20 percent of vinyl acetate and a copolymer of 10 to 70 percent acrylonitrile and 30 to 90 percent of a vinyl-substituted tertiary heterocyclic amine, said blend having an overall vinyl-substituted tertiary heterocyclic amine content of from 2 to 10 percent, based on the weight of the blend.

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