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MANUFACTURE OF PAPER PRODUCTS FROM FIBERS WET SPUN FROM POLYMER BLENDS

Pompelio A. Ucci and Nealie T. Anderson, Decatur, Ala., assignors, by mesne assignments, to Monsanto Chemical Company, St. Louis, Mo., a corporation of Delaware

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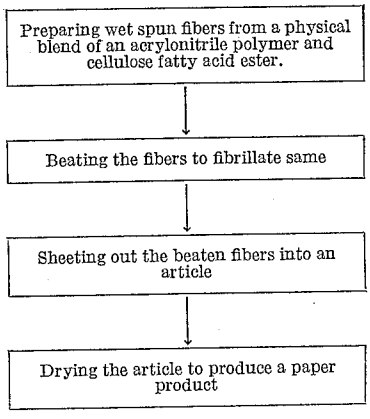
This invention relates to the manufacture of paper, non-woven products and the like comprising randomly intermingled discontinuous fibers which are at least in part composed of highly fibrillated fibers wet spun from a blend of polymers. More particularly, the invention relates to the manufacture of paper products composed of highly fibrillated thermoplastic fibers wet spun from a blend of polymers comprising a long chain synthetic polymer from which an acrylic fiber can be formed and a cellulose ester polymer of the fiber-forming type.

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, natural unmodified cellulosic fibers such as those derived from wood pulp and other natural cellulosic fibers of similar properties are beaten in an aqueous medium to disperse the fibers therein and to reduce them to a length and fineness suitable for use in paper making in a conventional manner. During the beating operation these cellulosic fibers fibrillate, the fibrillation manifesting itself by a fraying of the surfaces and ends of the fibers to produce minute tendrils or fibrils which serve subsequently 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 of the paper is attained through the interlocking of large numbers of fiber branches or fibrils during sheet formation and drying.

It was only recently possible to manufacture sufficiently strong paper containing 100% synthetic hydrophobic fibers which are arranged heterogeneously as in the case of ordinary paper made from natural cellulosic fibers. The drawback to the utilization of said synthetic fibers has been due to the fact that it previously was regarded that synthetic or artificially formed fibers do not fibrillate satisfactorily when they are beaten in water. Prior efforts, therefore, toward the utilization of these synthetic fibers have been directed to producing paper or non-woven 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 the 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 ultimate products. Furthermore, some attempts have been made to prepare paper from a mixture of natural cellulosic fibers and varying amounts of regenerated cellulosic fibers and/or cellulose ester fibers. Webs formed from a blend of these fibers are treated with a solvent or heat, or in some cases both to cause the fibers to coalesce. This treatment, as well as other prior methods which serve to bind the fibers together, is costly and difficult to control.

However, some recent developments in the paper-making art have opened interesting aspects as to the utilization of synthetically formed fibers in the manufacture of paper products and the like without recourse to the use of adhesives and expensive bonding procedures. A familiar procedure for manufacturing water-laid webs, including paper, from synthetic fibers without the use of bonding chemicals and the like involves 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. According to this known procedure the thus-fibrillated fibers formed from the acrylic polymer are deposited on a screen, for instance, to form a web with heat subsequently being applied to the web thereby to dry and develop an interlocking of the fibers. In the known procedure for making paper products from wet-spun acrylic fibers when the fibers regarded as non-fibrillatable are combined with wet-spun acrylic fibers and beaten in aqueous suspension for an extended time, the sheets formed are so weak that in many instances they cannot be removed from the sheeting out means. Specifically, when polymeric ethylene terephthalate fibers, nylon fibers, cellulose acetate fibers, vinyl chloride fiber and the like are beaten with wet-spun acrylic fibers, examination of the beaten fibers under a microscope shows that no significant fibrillation takes place on these fibers, excluding the wet-spun acrylic fibers which, of course, are fibrillated. Hence, the addition of non-fibrillatable fibers to wet-spun acrylic fibers for the production of water-laid webs therefrom impairs the wanted properties of the synthetic fiber paper as the same has drawbacks, including greatly reduced strength, resistance to tear and burst, and the like. While this recent disclosure represents a notable advance in the art, it is desirable to improve the strength and the resistance to tearing and burst, shrinkage and stretchability, electrical performance, and other physical properties in both the dry and wet states of paper made from synthetic fibers.

One object of this invention is to provide a highly fibrillated fiber formed by wet-spinning a blend of polymers comprising a long chain synthetic polymer from which an acrylic fiber can be formed and a cellulose ester polymer of the fiber-forming type. Another object is to provide paper products and the like exhibiting improved and valuable physical properties. A further object is to provide a method of making said paper products wherein the material costs and processing costs are appreciably lower, the reduction in cost and improvements in physical properties opening new fields for the application of synthetic fiber-containing paper. Other objects

and advantages will become apparent from the following detailed description of the invention.

Briefly stated, it has been found that a highly fibrillatable fiber providing strong paper products and the like is obtained by blending a base acrylonitrile polymer, i.e., along chain synthetic polymer from which an acrylic textile fiber can be formed and containing at least 85 percent by weight of combined acrylonitrile with from 5 to about 25 percent by the weight of the blend of a modifying cellulose ester polymer of the fiber-forming type, the resulting blend being capable of forming a solution of at least 5 percent concentration of weight in N,N-dimethylacetamide, and by processing the resulting solution into fibers by conventional wet spinning procedures. In the wet spinning method the blend of polymers is dissolved in a suitable solvent, such as N,N-dimethylacetamide, N,N-dimethylformamide or the like and the solution is extruded through small orifices in a spinneret into a liquid in which the solvent dissolves but in which the polymer is insoluble. The fibers are produced under conditions that they are a predetermined paper-making quality and are generally characterized by a valuable tendency to fibrillate when beaten in an aqueous suspension. These products are prepared by wet abrading the fibers wet-spun from the just described polymer blends in an aqueous medium, depositing the abraded fibers from the medium after same are sufficiently fibrillated to obtain a satisfactory paper product, and thereafter drying the product with application of heat to obtain a finished paper-product. Unexpected results and results which could not have been foreseen are obtained in the manufacture of paper products from fibers made from a polymer blend containing the composition above-described in view of the fact that cellulose ester fibers per se, either wet spun or dry spun, are regarded as being substantially non-fibrillating.

The polymer blends of this invention have an average specific viscosity of not less than 0.10 or greater than 0.40, calculated from conventional viscosity measurements for 0.1 gram of the polymer blend in 100 mls., of N,N-dimethylacetamide.

As just indicated the base polymer is an acrylic fiber-forming substance consisting of a long chain synthetic polymer composed of about at least 85% by weight combined acrylonitrile units. Therefore, the base polymeric material is an "acrylonitrile polymer" which term refers to polyacrylonitrile, including binary and ternary polymers containing about at least 85 percent by weight of acrylonitrile combined in the polymer molecule, or a blend comprising polyacrylonitrile or copolymers comprising polymerized acrylonitrile with 2 to 50 percent by weight of another combined monomer, the blend having an overall polymerized acrylonitrile content of about at least 85 percent by weight.

For example, the polymer may be a copolymer of from 85 to 98 percent acrylonitrile and from 2 to 15 percent of another monomer containing the >C=C< grouping and copolymerizable with acrylonitrile. Suitable monoolefinic monomers include acrylic, alpha-chloroacrylic and methacrylic acids; the acrylates, such as methylmethacrylate, ethylmethacrylate, butylmethacrylate, methoxymethyl methacrylate, betachloroethyl 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; alphachloroacrylamide, or monoalkyl substitution products thereof; methyl vinyl ketone; vinyl carboxylates, such as vinyl acetate, vinyl chloroacetate, vinyl propionate, vinyl stearate; N-vinylimides, such as N-vinylphthalimide and N-vinylsuccinimide; methylene malonic esters; itaconic acid and itaconic esters; N-vinylcarbazole, vinyl furane; alkyl vinyl esters; vinyl sulfonic acid; ethylene alpha, beta-dicarboxylic acids and 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-1-vinylimidazole, and other >C=C< containing polymerizable materials.

The polymer may be a ternary 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 85 to 97 percent of acrylonitrile, from 1 to 10 percent of a vinylpyridine or a 1-vinylimidazole, and another substance, such as methacrylonitrile or vinyl chloride.

The base polymer can be a blend of polyacrylonitrile or a binary interpolymer of 85 to 99 percent by weight acrylonitrile and from 1 to 15 percent of at least one other >C=C< containing substances with from 2 to 50 percent by 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. Preferable, when the base polymeric material comprises a blend, it will be a particular blend of a copolymer of 90 to 98 percent by weight of acrylonitrile and from 2 to 10 percent of another monoolenfinic monomer, such as vinyl acetate, with a sufficient amount of a copolymer of from 10 to 70 percent by weight of acrylonitrile and from 30 to 70 percent by weight of a vinyl-substituted tertiary heterocyclic amine, such as 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.

The modifying polymer of cellulose ester of the polymer blend may be any suitable cellulose lower fatty acid ester such as, for example, cellulose acetate, cellulose propionate, cellulose acetate-formate, cellulose acetate-butyrate, and the like. The degree of substitution of the cellulose ester may vary, according to the particular ester utilized and the desired effect. For example, in the case of cellulose acetate, its combined acetic acid content may be within the range from about 48.5 percent to that corresponding to the normally obtainable tri-ester, namely about 61 percent, the preferred value being in the range from about 52 to 57 percent acetic acid. For other cellulose lower fatty acid esters, a somewhat equivalent degree of substitution is suitable.

In general, the blends of the invention are characterized by the unexpected ease of water-fibrillating of fibers produced therefrom; and paper products formed from the fibrillated fibers exhibit improved physical properties.

The base acrylic polymer and the modifying cellulose ester polymer are preferably blended by intimately mixing them in the required amounts with a common solvent with stirring to obtain a solution of the blend which can be spun through orifices in a conventional spinneret immersed in a coagulating bath. The physical form of the base acrylic polymer, as well as the cellulose ester polymer, is preferably that of fine, dense grains or powder. The base polymer is soluble in N,N-dimethylacetamide, and in blends with the modifying cellulose ester forms a solution in N,N-dimethylacetamide, which can be formed into fibers by conventional wet spinning procedures. The blends may be prepared by forming an intimate mixture of the base acrylic polymer and modifying cellulose ester polymer in N,N-dimethylacetamide, for instance. However, the characteristic solubility of the base polymer in N,N-dimethylacetamide does not preclude the use of other solvents in which the blend of the base polymer and cellulose ester polymer forms a solution which can be formed into fibers in preparing spinnable solutions thereof. However, one of the advan-

tages of the blends of the invention resides in their property of forming wet spinnable solutions in N,N-dimethylacetamide, a solvent which is especially useful in large scale production of fibers. The blends may be prepared by mixing solid polymeric materials in conventional mechanical mixers in the presence of the solvent; or they can be mixed dry and then dissolved in the selected solvent.

The spinning solution containing the polymer blend of an acrylic polymer and cellulose ester is extruded through small orifices in a spinneret; and the polymer in the extruded solution is precipitated in a coagulating bath, thereby forming continuous filaments of any desired diameter which can later by cut into any desired lengths. Examples of suitable coagulating baths for wet spinning the polymer blends include mixtures of the spinning solvent and water, such as mixtures of N,N-dimethylformamide and water and N,N-dimethylacetamide and water. Other suitable bath compositions may also be employed.

It is known that during coagulation in a wet spinning operation there is an inward diffusion of bath liquid into the coagulating filaments, as well as a corresponding outward movement of solvent into the bath. Ordinarily, 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 filaments and corresponding collapsed filaments show a pronounced difference therebetween, the extent to which the filament is uncollapsed or collapsed being indicated by these measurements. Obviously, the densities of the collapsed filaments are greater than the densities of corresponding uncollapsed filaments. In accordance with the present invention it is preferred that the density of the fiber used to make paper products or the like be at least 15 percent and 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 of the porous fiber structure 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 filaments wet spun from the polymer blend of the instant invention 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 natural cellulosic fibers commonly used to make paper. More specifically, superior fibers for use in paper-making can be produced by spinning a water coagulable solution of a polymer blend composed of an acrylic fiber-forming polymer and a cellulose ester of the fiber-forming type in certain proportions into an aqueous coagulating 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 or totally removing the water content from the filaments without appreciably destroying said uncollapsed structure.

The wet spun filaments of the present invention which are produced with a view to being utilized in accordance with the invention 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. The stretch given is ordinarily at least 200% at an elevated temperature. This stretching preferably is performed after the residual spinning solvent carried by the filaments has been reduced to not less than 2 percent by weight and preferably to not more than 10 percent by weight. During the stretching the fiber may be subjected to temperatures in the range of from 90° C. to about 250° C. or higher as long as the porous structure is not destroyed. The filaments may be stretched while they are passing through a heated liquid such as water. The filaments may also be heated during stretching in an atmosphere of hot air or steam, which may be dry, saturated or supersaturated. 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 can be reduced by partially or completely drying with air, steam, or the like by centrifuging same, by use of vacuum means, and the like without substantial reduction of the propensity of the filaments to fibrillate. It should be borne in mind that a prerequisite to the best practice of the invention is that the uncollapsed structure of the fibers not be destroyed before they are processed into paper and the like.

After the porous filaments have been purified and partially or totally dried they are cut to staple lengths. Fibers in length shorter or longer than the length of ordinary staple textile fibers can be used. When short fibers are 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 fibers 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 fibers of the present invention 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 the blend of polymer is spun under conditions producing a high tenacity fiber.

While the fibers wet spun from the polymer blend of an acrylic fiber-forming polymer and a cellulose ester can be used as the sole fibrous material to manufacture strong sheet-like materials, it will be appreciated that such fibers may be combined with other fibrillatable fibers including synthetic, artificial and natural fibers to manufacture satisfactory sheet-like materials. For example, the fibers of the present invention are compatible with natural cellulosic fibers over a wide range of proportions and paper of improved physical properties is obtainable therefrom.

In accordance with the invention at least the amount of the fibers as used herein necessary for providing a desired paper product is beaten or battered in the presence of water in acqueous 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 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 collapsed fibers of like composition or ordinary wet-spun acrylic fibers. Thus, the uncollapsed fibers wet spun from the polymer blend herein can be subjected comparably to less severe beating action and yet be fibrillated sufficiently. Avoidance of severe beating action is desira-

ble in some instances since a harsh beating action produces fibers of undesirably short lengths. Furthermore, for a given severity of beating under conditions where collapsed wet-spun acrylic fibers of the ordinary textile type would be comminuted or broken into undesirably short lengths and having broom-like ends and very short fibrils along the fiber length, the uncollapsed fibers wet spun from the polymer blend as used in the instant invention advantageously are 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 to the aqueous beating medium, if desired. The suspension of fibers 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. Although not required, the fibers may be sized by the beater addition method or water laid webs of the fibrillated fibers may be sized. Although the additional cost may be unwarranted in some instances, it is within the purview of the invention to use a resinous substance or a potentially resinous substance on the fibers or webs formed from the fibers.

The beaten fibrillated fibers wet spun from the polymer blend of the present invention are thereafter formed into a paper product by any suitable process. For example, such product can be formed into self-supporting continuous webs or sheets 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 paper may be passed under a battery of drying lamps; or other heating means can be used to dry the product.

The drying temperature may be and usually is in the same range ordinarily used for drying natural cellulosic fiber-containing paper and is determined to a considerable extent by the properties desired in the ultimate paper product. The paper products herein may be dried at room temperature and up to the temperature at which the fiber degrades considerably or melts. The drying temperature affects the properties of the paper product. It has been found in this regard that the physical properties with reference to tensile strength, tear and burst resistance usually are related directly to the drying temperature. That is to say, when a higher drying temperature is employed, one may expect improvements in these properties. For example, properties of handsheets 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 papermaking lengths 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 I

A 1½ lb. Valley laboratory beater was charged with 150 grams of oriented acylic fibers in 20 liters of water (0.75 percent consistency). The fibers were approximately 3 denier per filament cut to an average length of ¼" and had been prepared by wet spinning from a copolymer compound of 94.6 percent acrylonitrile and 5.4 percent vinyl acetate. The fibers had little void volume therein as seen by microscopic examination thereof. The density of the fiber was 1.17 grams per cubic centimeter and the fibers were commercial textile grade type of acrylic fibers.

The severity of 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 fibers are drawn between the beater bars and bedplate by the circulatory action therein. The 150 gram sample of the fibers was processed in the Valley beater using a 12 lb. counterweight. Samples to be formed into handsheets were taken every 10 minutes. The handsheets which weighed approximately 2.5 grams were formed and dried by using a Noble and Wood laboratory handsheet machine. The machine includes an 8" square mold, press rolls, and felt, as well as a steam heated drying drum with felt. The handsheets were dried supported on a wire by being passed around a drying drum at 198° F. The data of the physical properties of these handsheets having an average thickness of 0.008 inch are given below in Table 1. Handsheets were weighed on a weight scale basis. 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

Beating Time (mins.)	Tear (gms.)	Bursting (p.s.i.)	Tensile Strength (lbs./in.)
30	4	(1)	(1)
50	8	0.8	(1)

[1] Values too low for measurement.

EXAMPLE II

Ninety-nine parts of a polymer prepared by polymerizing 94.6 percent acrylonitrile and 5.4 percent vinyl acetate (base polymer) were blended with 1 part of cellulose acetate (modifying polymer) having a combined acetic acid content of 52 percent. The blend was prepared by dissolving the base copolymer and the modifying cellulose polymer each in powdered form in N,N-dimethyl-acetamide to produce an 18 percent spinning solution. The solution was then extruded through a spinneret into an aqueous coagulating bath containing 60 percent dimethylacetamide and 40 percent water by volume maintained at a temperature of 32° C. to form a hundle of filaments. The bundle was withdrawn from the bath and given a stretch of 400 percent in boiling water containing a small amount of dimethylacetamide. 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 lengths of ¼ inch. Examination under an electron microscope of the cut fibers revealed that the fibers were porous, having a sponge-like structure. In other words the fibers possessed what is known as an uncollapsed structure. These uncollapsed fibers had an average density of only 0.75 gram per cubic centimeter.

A 1½ lb. Valley laboratory beater was charged with a 150 gram sample of the uncollapsed fibers in 20 liters of water. The fibers were approximately 3 denier. The sample was beaten in the beater using a 12 lb. counterweight. Handsheet samples were taken at intervals indicated below in Table 2 and handsheets were prepared as outlined in Example I. The properties also listed in the table below were measured as outlined above in Example I.

Table 2

Beating Time (mins.)	Tear (gms.)	Bursting (p.s.i.)	Tensile Strength (lbs./in.)
40	8	1.1	0.3
50	6	0.8	1.0

EXAMPLE III

Various parts of a polymer prepared by polymerizing 94.6 percent acrylonitrile and 5.4 percent vinyl acetate (base polymer) were blended with various parts of cellulose acetate (modifying polymer) having a combined acetic acid content of 52 percent, the parts being given in Table 3 below. The resulting polymer blends were separately dissolved in N,N-dimethyl-acetamide to form a like number of spinning solutions, each containing about 18 percent solids. The solutions were spun into fibers in accordance with the procedure outlined in Example II to produce wet spun fibers having an uncollapsed structure and an average density of 0.75 gram per cubic centimeter.

The fibers produced from these solutions were processed separately in the Valley beater, again using a 12 lb. counterweight. Samples were taken every 10 minutes with sheets being produced in accordance with the handsheet method described above in Example I. The physical properties of the handsheets are listed in the Table 3 below and were measured as outlined in Example I.

Table 3

Blend Composition (percent acrylic—percent cellulose ester)	Beating Time (mins.)	Tear (gms.)	Bursting (p.s.i.)	Tensile Strength (lbs./in.)
95—5	20	28	1.7	1.8
95—5	30	15	2.1	1.6
95—5	40	9	1.5	1.6
90—10	10	47	4.0	1.3
90—10	20	61	4.7	2.8
90—10	30	58	4.6	3.5
90—10	40	28	4.0	3.6
90—10	50	20	3.7	2.0
88—12	10	102	12.3	3.3
88—12	20	129	13.0	5.0
88—12	30	95	11.9	6.1
88—12	40	56	9.9	6.1
88—12	50	26	7.4	5.5
85—15	10	124	13.7	5.0
85—15	20	142	14.2	6.4
85—15	30	92	13.2	7.2
85—15	40	45	10.0	6.5
85—15	50	27	8.5	6.4
75—25	20	35	2.9	1.4
75—25	30	28	2.9	2.6
75—25	40	15	2.6	2.8
75—25	50	9	2.2	2.6

The beaten fibers were examined visually under a microscope and compared with the beaten fibers produced in Examples I and II. 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 of the fiber beaten in accordance with the example were tougher and adhered more tenaciously to the fiber body.

EXAMPLE IV

Handsheets were prepared from collapsed fibrillated fibers wet spun from a solution of a polymer blend composed of 90 percent of a copolymer of 94.6 percent acrylonitrile and 5.4 percent vinyl acetate and 10 percent cellulose acetate having a combined acetic acid content of 52 percent. The spinning conditions were similar to those used in Example II except that the freshly spun filaments were completely dried while being passed around the assembly of drying drums to cause the resulting filament structure to be collapsed. The properties of the handsheets are listed in Table 4 below and were measured as above.

Table 4

Beating time (mins.)	Tear (gms.)	Bursting (p.s.i.)	Tensile Strength (lbs./in.)
20	29	2.2	1.0
30	21	1.7	1.4
40	18	2.0	1.8
50	12	1.8	2.2

It can be seen by comparing the data in Example III given for a similar fiber (90% acrylic polymer–10% cellulose acetate) but uncollapsed fiber with the data for the collapsed fiber of this example, that the uncollapsed fiber can be used to form the better paper.

EXAMPLE V

Handsheets were prepared from uncollapsed fibrillated fibers wet spun from a solution of a polymer blend composed of 88 percent of a copolymer of 94.6 percent acrylonitrile and 5.4 percent vinyl acetate and 12 percent cellulose acetate having a combined acetic acid content of 60.4 percent (cellulose tri-acetate). The spinning conditions were similar to those used in Example II with the resulting fibers having an uncollapsed structure. The properties of the handsheets made from these fibers are listed in Table 5 below and were measured as above.

Table 5

Beating Time (mins.)	Tear (gms.)	Bursting (p.s.i.)	Tensile Strength (lb./in.)
20	12	1.4	1.2
30	7	1.3	1.5

EXAMPLE VI

Handsheets were prepared from uncollapsed fibrillated fibers wet spun from a solution of a polymer blend composed of 88 percent of a copolymer of 94.6 percent acrylonitrile and 5.4 percent vinyl acetate and 12 percent of commercially obtained cellulose propionate. The spinning conditions were similar to those used in Example II with the resulting fibers having an uncollapsed structure. The fibers were processed in the Valley beater using a 3 lb. counterweight. The properties of the handsheets made from these fibers are listed in Table 6 below and were measured as above.

Table 6

Beating Time (mins.)	Tear (gms.)	Bursting (p.s.i.)	Tensile Strength (lb./in.)
30	34	4.7	1.3
45	71	4.1	2.2
60	63	5.0	2.7
75	49	4.6	2.8
105	45	4.9	3.6

EXAMPLE VII

This example illustrates an attempt to form a paper handsheet from wet spun cellulose acetate fibers, as well as a handsheet from a blend of wet spun acrylic fibers and wet spun cellulose acetate fibers.

Cellulose acetate having a combined acetic acid content of 52 percent was dissolved in N,N-dimethylacetamide in an amount sufficient to give a resulting spinning solution of 15 percent solids. The solution was extruded through a spinneret into a coagulating bath composed of water and maintained at a temperature of 30° C. to form a bundle of filaments. The bundle was washed with water and given an afterstretch of 170 percent. Next, the filaments were partially dried by being passed around an assembly of drying drums. When the filaments were dried to the point where they were only slightly damp,

they were withdrawn from the drums and cut into ¼ inch lengths. The fibers had an uncollapsed structure, a tenacity of 1.3 gms./denier, and an elongation of 5 percent. The Valley beater above mentioned was charged with a 150 gram sample of these wet spun cellulose acetate fibers in 20 liters of water. The fibers were approximately 3 denier. The sample was beaten in the beater using a 12 lb. counterweight. Handsheet samples were taken at appropriate intervals with sheets being produced in accordance with the hand sheet formation method described above in Example I. The physical properties of the handsheets, including tear, bursting, and tensile strength, were too low for measurement.

Eighty-five parts of the wet spun acrylic fibers produced in accordance with Example I except that the fibers during formation were dried as in Example II so that same had an uncollapsed structure was blended with 15 parts of wet spun cellulose acetate fibers produced as above in this example. The Valley beater was charged with a 150 gram sample of the resulting fiber blend in 20 liters of water. The same was beaten in the beater using a 12 lb. counterweight. Handsheet samples were taken at appropriate intervals with sheets being produced in accordance with the handsheet formation method above described. The physical properties of the handsheets, including tear, bursting, and tensile strength, were too low for measurement.

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 out on a Fourdrinier machine, for instance. In such case, the sheet would be dried such as by passing same over drying cans and taken up in roll form. Likewise, when the base blending polymer made from other acrylonitrile polymers and when the modifying cellulose ester polymer made from other esters of cellulose 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 fibers which have been produced by wet spinning techniques from particular blends of polymers may be fibrillated more easily and to a much greater extent than ordinary wet spun acrylic fibers. Moreover, such improved fibrillation is even more significant when the fibers of the present invention are produced under conditions causing a porous or uncollapsed structure. The number of fibrils per fiber is increased and the ease of severance of the fibrils from the fiber is reduced. Furthermore, the cost of the resulting fibers is less expensive.

The fibers of the present invention are 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 a conventional paper-making machine. 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 can be separated from the fibers by any suitable means while forming the fibers 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 paper articles, of course, can be made by other similar methods.

Tough paper products having a substantial degree of flexibility and being relatively soft to the touch can be made; other products may be relatively stiff and resilient. The products have a high resistance to bursting and tearing both in the wet and dry state. An important feature of the paper products is their inherent ability to resist the action of certain chemicals. The products are, in general, readily wettable 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 chemicals which do not attack the fibers under the conditions employed, and filters for other purposes. As indicated, while excellent paper products may be produced without the using of bonding agents, sizes, 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 fiibrillated fibers produced in accordance with the instant invention are particularly useful in blending with ordinary cellulose pulp from wood, cotton linters, and the like. For example, a paper composed of a blend of only 10 percent of the fibers of the present invention with the remainder being natural unmodified cellulosic fibers has markedly superior dimensional stability, better ageing properties, etc., than paper composed 100 percent of such cellulosic fibers. In view of these improved properties, the fibers of the present invention 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, filters, and the like.

The present invention makes possible the production of a fiber that is feltable and eminently suitable for use in paper-making. 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 cohering of the fibrils to the fiber body contributes significantly to a higher resistance to breaking upon being flexed. The fibrillated fiber is particularly characterized as having been wet spun from blends of certain polymers and having a porous, sponglike structure, the fibrils thereof being tough, pliable, and tenaciously adhered to the fiber surfaces and ends.

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. A process for the manufacture of a paper product comprising the steps of preparing wet spun fibers from a solution containing a physical blend of about 95 to 75 percent by weight of a base polymer of a long chain synthetic polymer from which an acrylic textile fiber can be formed and containing at least 85 percent by weight combined acrylonitrile and about 5 to 25 percent by weight of a modifying polymer of a cellulose lower fatty acid ester of the fiber forming type, said blend being capable of forming a solution of at least 5 percent concentration by weight in N,N-dimethylacetamide, beating said fibers in an aqueous slurry to fibrillate same, sheeting out the beaten fibers into a predetermined shape and thickness, and drying the resulting sheeted out material to form a strong coherent paper product.

2. The process of claim 1 wherein the base polymer in the blend is a copolymer containing at least 85 percent by weight of combined acrylonitrile and up to 15 percent by weight of another mono-olefinic monomer copolymerized therewith.

3. The process of claim 2 wherein the other mono-olefinic monomer is vinyl acetate.

4. The process of claim 3 wherein the cellulose ester is cellulose acetate, the combined acetic acid content of which is within the range of 48.5 to 57 percent by weight.

5. A process for the manufacture of a paper product

comprising the steps of forming a solution from a physical blend of about 95 to 75 percent by weight of a base polymer of a long chain synthetic polymer from which an acrylic textile fiber can be formed and containing at least 85 percent by weight combined acrylonitrile and up to 15 percent by weight of another mono-olefinic monomer copolymerizable therewith and about 5 to 25 percent by weight of a modifying polymer of a cellulose lower fatty acid ester of the fiber forming type, said blend being capable of forming a solution of at least 5 percent concentration by weight in N,N-dimethylacetamide, spinning the resulting solution into an aqueous coagulating bath to produce filaments therefrom, cutting said filaments into short length fibers, beating said fibers in an aqueous slurry to fibrillate same, sheeting out the beaten fibers into a predetermined shape and thickness and drying the sheeted out material to form a strong coherent paper product.

6. The process of claim 5 wherein the other mono-olefinic monomer is vinyl acetate.

7. The process of claim 6 wherein the cellulose ester is cellulose acetate, the combined acetic acid content of which is within the range of 48.5 to 57 percent.

8. The process for the manufacture of a paper product comprising the steps of forming a solution from a physical blend of from 95 to 75 percent by weight of a base polymer of a long chain synthetic polymer from which an acrylic textile fiber can be formed and containing at least 85 percent by weight combined acrylonitrile and up to 15 percent by weight of another mono-olefinic monomer copolymerizable therewith, from 5 to 25 percent by weight of a modifying polymer of cellulose lower fatty acid ester of the fiber-forming type, said blend being capable of forming a solution of at least 5 percent concentration by weight in a solvent selected from the group consisting of N,N-dimethylformamide and N,N-dimethylacetamide, spinning the resulting solution into an aqueous coagulating bath containing a proportion of said solvent to produce filaments therefrom under conditions wherein the solvent and the bath liquid interchange to impart an uncollapsed structure to the filaments such that the density thereof is 15 to 65 percent less than the density of corresponding collapsed filaments, stretching and purifying the filaments, reducing the water content of the filaments without appreciably destroying said uncollapsed structure, cutting said filaments into short length fibers, beating said fibers in an aqueous slurry to fibrillate same, sheeting out the beaten fibers into a predetermined shape and thickness, and drying the sheeted out material to form a strong coherent product.

9. The process of claim 8 wherein the solvent is N,N-dimethylacetamide.

10. The process of claim 8 wherein the other mono-olefinic monomer is vinyl acetate.

11. The process for the manufacture of a paper product comprising the steps of forming a solution from a physical blend of from 95 to 75 percent by weight of a base copolymer of from 85 to 98 percent by weight combined acrylonitrile and 15 to 2 percent by weight combined vinyl acetate and from 5 to 25 percent by weight of modifying polymer of cellulose acetate of the fiber-forming type, the combined acetic acid content of which is in the range of 48.5 to 57 percent by weight, said blend being capable of forming a solution of at least 5 percent concentration by weight in N,N-dimethylacetamide, extruding the resulting solution through orifices in a spinneret immersed in an aqueous coagulating bath containing a proportion of N,N-dimethylacetamide to produce filaments having an uncollapsed structure such that the density thereof is 15 to 65 percent less than the density of corresponding collapsed filaments, withdrawing the filaments from the coagulating bath, passing the filaments through a second aqueous bath maintained at a temperature in the range of 90–250° C., stretching the filaments during their passage through said second bath by at least 200 percent, partially drying the filaments, cutting the filaments into paper-making lengths, beating said fibers in an aqueous slurry to fibrillate same, sheeting out the beaten fibers from said aqueous slurry into a predetermined shape and thickness, and heating the sheeted out material until dry to form a strong coherent product.

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