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3,098,786

PAPER MAKING PROCESS

James R. Biles, Decatur, Ala., and Richard R. Holmes, Charlotte, N.C., assignors, by mesne assignments, to Monsanto Chemical Company, a corporation of Delaware

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This invention relates generally to the manufacture of paper from pulp comprised essentially of acrylic-type fibers. More precisely, the present invention is concerned with improving the uniformity of fiber distribution in paper products produced from acrylic fibers.

In the manufacture of most grades of paper from fibers of whatever source, it is customary to suspend previously beaten fibers, or what is generally known as pulp, in an aqueous medium for delivery to a sheet forming device, such as a Fourdrinier wire. This fiber containing aqueous dispersion is commonly referred to in the art as a furnish. One troublesome problem at this stage of papermaking, i.e. at a point after all operations designed to modify the fibrous constituents by mechanical means have been completed and during the step of sheet or web formation, is the tendency for the fibers to clump, coagulate or settle in the aqueous vehicle. This condition is generally referred to as flocculation, and greatly impedes the attainment of proper web formation. That is, flocculation causes a non-uniform distribution of fibers in the web, and the paper product produced therefrom manifests not only a mottled, uneven appearance but is also defective in such important physical properties as tear, burst and tensile strength.

In the manufacture of paper from conventionally used fibers, such as cellulose, methods are known for reducing and even preventing the occurrence of flocculation. One of the more effective means has been to add a small quantity of deacetylated karaya gum to the fiber furnish. Normally from about 2 to 10 percent on the weight of the fiber has been found to be a sufficient quantity for obtaining satisfactory results. However, this deflocculent of itself manifests so little dispersive or deflocculating potency with respect to acrylic-type fibers that only when used in massive amounts is it possible to avoid clumping of these fibers. In fact, it has been found that as much as 50 percent and sometimes 100 percent on the weight of the fiber is necessary to effect the deflocculation required for sheet formation. Obviously, the use of such large amounts of deflocculent is not economically practical. Furthermore, the presence of such an excessive quantity of non-fibrous material is detrimental to product quality.

Accordingly, it is a primary object of this invention to provide a method for achieving the maintenance of a uniform dispersion of acrylic-type fibers in water during the web formation step in papermaking.

It is a further object of this invention to provide a means wherein tolerable quantities of deacetylated karaya gum can be successfully employed to effect a satisfactory deflocculation of acrylic fibers in the aqueous dispersions which are employed in the papermaking process.

It is a still further object of this invention to provide an improved process for producing paper from acrylic fibers of excellent uniformity and with superior properties.

Other objects of this invention will become apparent from the following detailed description.

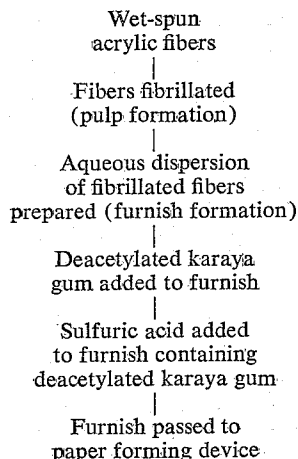
It has now been found that acrylic-type fibers can be maintained uniformly dispersed in an aqueous medium with modest quantities of deacetylated karaya gum when small amounts of sulfuric acid are used in combination therewith. Thus, satisfactory results can be obtained

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with from 3 to 20 percent karaya gum when from 4 to 10 percent of sulfuric acid is also present in the fiber dispersion or furnish, all percentages being based on the weight of the fiber. Generally speaking, best results are achieved by employing from 4 to 10 percent deacetylated karaya gum and from about 5 to 8 percent sulfuric acid based on the weight of the fiber present in the furnish. The order of addition has been found to be critical. That is, the sulfuric acid should be added to the fiber-containing furnish only after the karaya gum has first been introduced therein. Although the concentration of the sulfuric acid may vary in the solution thereof employed, generally it has been found convenient to add the sulfuric acid to the furnish in the form of a 1 N solution.

As in ordinary papermaking processes, the total concentration of solids present in the furnish may vary widely, for example, over a range of from 0.3 percent by weight or less up to 5 percent or more.

A simple flow diagram of the process is as follows:



As noted, it has not been possible previously to maintain acrylic-type fibers satisfactorily dispersed in an aqueous medium during sheet formation with less than 50 percent of deacetylated karaya gum, based on the fiber weight, and often as much as 100 percent was required. However, by the introduction of minor quantities of sulfuric acid into the fiber dispersion with the gum deflocculent it is now possible to reduce the requirement of this agent by a factor of up to 95 percent. Although the mechanism responsible for this effect is not fully understood, it is known that more than pH control is involved, since other strong acids, such as hydrochloric and nitric, have been found relatively ineffective.

As previously mentioned, the usefulness of deacetylated karaya gum as a fiber deflocculent has been known heretofore, and its nature and composition have been fully described in both the literature and patents. See, for example, U.S. Patents 2,069,766 and 2,088,479. Consequently, only a brief discussion of this material will be undertaken here.

Gum karaya is a natural product obtained from the plant *cochlospermum gossypium* and allied botanical species. The product in its natural state is not an effective dispersing agent, but is rendered so by either a complete or partial deacetylation, i.e. by substituting acetyl groups for hydroxyl groups. This can be accomplished in the following manner: First, take two parts by weight of the dry gum and form a jelly thereof in 98 parts of water. The gum may be advantageously granulated for this purpose but should not be subjected to excessive grinding because it is susceptible to degeneration by mechanical attrition, and when thus broken down will not

satisfactorily form the characteristic karaya jelly. On each 100 parts of this 2 percent karaya jelly, add 0.6 part of 26° Baumé aqueous ammonia. The ammonia is mixed with the water and dispersed gum, preferably by mild rather than vigorous agitation. This effects a gradual change in the jelly over a period of from 2 to 3 hours at room temperature, which converts it into the deacetylated derivative. Best results are attained when freshly prepared deacetylated karaya gum is employed. That is to say, this material is most desirably used on the same day that it is prepared.

Although the present invention is primarily directed to the particular problem posed by acrylic-type fibers when used in paper manufacture, the fibers which may be employed in the present invention are not restricted exclusively thereto. That is, other fibers may be blended with acrylics, such as those derived from cellulose and other sources.

By the term acrylic fibers as used herein and in the claims, there is meant those fibers which are formed from polyacrylonitrile or copolymers thereof which contain at least 80 percent acrylonitrile in addition to one or more mono-olefinic monomers copolymerizable therewith. There is also included blended polymers and copolymers in which the blend contains at least 80 percent acrylonitrile.

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 mono-olefinic monomers include acrylic, alpha-chloroacrylic and methacrylic 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, diethylcitrate, 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 blended polymers containing at least 80 percent acrylonitrile may, for example, comprise a major amount of a polymer (A) containing at least 85 percent acrylonitrile and up to 15 percent of one of the above-named mono-olefinic monomers copolymerizable therewith and a minor amount of a polymer (B) containing one of the vinyl-substituted alkyl pyridine monomers noted above and another of the above-named mono-olefinic monomers or acrylonitrile copolymerized therewith. These blended

polymer compositions preferably contain from 50 to 98 percent of polymer (A), containing at least 85 percent acrylonitrile and up to 15 percent of another mono-olefinic monomer copolymerizable therewith, and from 2 to 50 percent of polymer (B), containing at least 30 percent of a vinyl-substituted alkyl pyridine monomer and up to 70 percent of another mono-olefinic monomer copolymerizable therewith, polymers (A) and (B) being so proportioned that the polymer blend contains from 2 to 15 percent of the vinyl-substituted alkyl pyridine monomer in polymerized form. Fibers made from the just-described copolymer blend unexpectedly have a notably excellent propensity to fibrillate so that a superior paper can be manufactured therefrom.

The use of acrylic fibers formed from other than wet-spinning procedures, such as by melt or dry spinning techniques are not considered useful for papermaking, inasmuch as filaments produced by the latter two methods have little tendency to fibrillate under the conditions which are employed in conventional papermaking processes. Consequently, the acrylic fibers contemplated for the purposes of the present invention, are those formed by the so called wet-spinning process wherein a water coagulable solution of polymeric material is extruded through a spinneret and the extruded solution is thereafter coagulated in a precipitating bath to form continuous filaments.

The following series of runs were made to test the effectiveness of sulfuric acid in accentuating the dispersive power of deacetylated karaya gum with respect to dispersions of acrylic fibers in water. The fibers employed in each of the test samples were obtained by the wet spinning of a copolymer blend comprising 88 percent of one copolymer consisting of 94.6 percent acrylonitrile and 5.4 percent vinyl acetate and 12 percent of another copolymer consisting of 50 percent acrylonitrile and 50 percent methylvinyl pyridine. The fibers had an average length of one-quarter inch and a denier of 3 per filament.

Example 1

To a one liter beaker there was added a fiber-mix containing 0.05 gram of acrylic fiber in 500 ml. of water.

Example 2

To a second one liter beaker there was added 500 ml. of an aqueous slurry containing 0.05 gram of acrylic fiber and an amount of deacetylated karaya gum constituting 5 percent on the weight of the fiber.

Example 3

To another one liter beaker there was added 500 ml. of an aqueous slurry containing 0.05 gram of acrylic fiber and an amount of deacetylated karaya gum constituting 10 percent on the weight of the fiber.

Example 4

To another one liter beaker there was first introduced 500 ml. of an aqueous slurry containing 0.05 gram of acrylic fiber and an amount of deacetylated karaya gum constituting 5 percent on the weight of the fiber. There was then slowly added in dropwise manner a 1 N solution of sulfuric acid in an amount sufficient to provide 9.8 percent sulfuric acid based on the weight of the fiber.

Example 5

To another one liter beaker there was added 500 ml. of an aqueous slurry containing 0.05 gram of acrylic fiber and an amount of deacetylated karaya gum constituting 4 percent on the weight of the fiber. There was then slowly added a 1 N solution of sulfuric acid in an amount sufficient to provide 6.8 percent sulfuric acid based on the weight of the fiber.

Example 6

To still another liter beaker there was added 500 ml. of an aqueous slurry containing 0.05 gram of acrylic

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fiber and an amount of deacetylated karaya gum constituting 10 percent on the weight of the fiber. There was then slowly added a 1 N solution of sulfuric acid in an amount sufficient to provide 4.9 percent sulfuric acid based on the weight of the fiber.

After each of the above-described test samples had been prepared, they were agitated to form a dispersion. Each test sample was then examined to ascertain whether or not flocking had occurred. The results are given in the following tabulation:

Example	Percent karaya gum added	Percent sulfuric acid added	Result
1.-----	none-----	none-----	flocculation.
2.-----	5-----	none-----	Do.
3.-----	10-----	none-----	Do.
4.-----	5-----	9.8-----	uniform dispersion.
5.-----	4-----	6.8-----	Do.
6.-----	10-----	4.9-----	Do.

From the above the test results, it is evident that only in those instances where sulfuric acid was employed in combination with the deacetylated karaya gum was it possible to avoid the occurrence of flocculation.

In order to determine the extent of improvement in the formation of paper products produced in accordance with the present invention, another series of tests were run. In this test series paper handsheets were prepared and evaluated for formation quality. In each of the following test samples, the fibers used in preparing the handsheets were obtained by the wet spinning of a copolymer blend comprising 88 percent of one copolymer consisting of 94.6 percent acrylonitrile and 5.4 percent vinyl acetate and 12 percent of another copolymer consisting of 50 percent acrylonitrile and 50 percent of methylvinyl pyridine. The fibers employed had been fibrillated by a 40-minute beating cycle in a conventional laboratory beater.

Example 7

A paper furnish was prepared by dispersing 2.5 grams of fibrillated fibers of the above described type in sufficient water to give a consistency of about 0.03 percent. This furnish was then added to the sheet mold of a noble and wood hand sheet machine. The dispersion was de-watered on a 100 mesh wire screen, and the resulting handsheets were couched from the wires onto standard blotting papers. The handsheets were then pressed on a roller type press, and finally dried between blotters on a steam heated drying drum.

Example 8

To the sheet mold of a paper handsheet machine partially filled with water, there was first introduced a 0.5 stock solution of freshly prepared deacetylated karaya gum. Thereafter, 2.5 grams of fibrillated acrylic fibers were added. The resulting paper furnish had a karaya gum content of 15 percent on the weight of the fiber and a consistency of about 0.03 percent. Water was removed from the fiber dispersion by means of a 100 mesh wire screen. The resulting handsheets were then passed to standard blotting paper after which they were pressed and finally dried.

Example 9

To the sheet mold of a paper handsheet machine, having been partially filled with water, there was first introduced a 0.5 stock solution of freshly prepared deacetylated karaya gum. Thereafter, 2.5 grams of fibrillated acrylic fiber were added to the mold giving a paper furnish having a consistency of about 0.03 percent with a karaya gum content of about 20 percent on the weight of the fiber. Water was removed from the dispersion by means of a wire screen. The resulting handsheets were then passed to standard blotting paper after which they were pressed and finally dried.

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Example 10

To the sheet mold of a paper handsheet machine, having been previously partially filled with water, there was first introduced a 0.5 stock solution of freshly prepared deacetylated karaya gum. Thereafter, 2.5 grams of fibrillated acrylic fiber were added to the mold, and finally there was slowly added 3.5 ml. of a 1 N solution of sulfuric acid. The furnish thus prepared had a consistency of about 0.03 percent, and contained 4 percent karaya gum together with 6.8 percent sulfuric acid based on the weight of the fiber present.

Following removal of water from the furnish by means of a wire screen, the resulting handsheets were passed to standard blotting paper after which they were pressed and finally dried.

Example 11

To the sheet mold of a paper handsheet machine, having been previously partially filled with water, there was first introduced a 0.5 stock solution of freshly prepared deacetylated karaya gum. Thereafter, 2.5 grams of fibrillated acrylic fiber were added to the mold, and finally there was slowly added 3.0 ml. of a 1 N solution of sulfuric acid. The furnish thus prepared had a consistency of about 0.03 percent, and contained 5 percent karaya gum together with 5.8 percent sulfuric acid based on the weight of the fiber.

Following removal of water from the furnish by utilizing a standard wire screen, the resulting handsheets were passed to standard blotting paper after which they were pressed and finally dried.

Uniformity of sheet formation was objectively measured in each of the above examples by employing an instrument known as the Thwing-Albert formation tester. This device utilizes a beam of light and a photo-electric cell for measuring the quality of formation. Thus, the sample to be measured is moved at high velocity between a steady light source and the photo tube. The variation in opacity of the paper, which may be due to variations in either thickness or structure, cause a fluctuation in the photo-electric cell current. The fluctuations are amplified by means of an amplifier of suitable frequency characteristics, until they are of sufficient magnitude to operate a meter. The average steady photocell current is indicated on a second meter. The ratio of the readings of the two meters gives the formation value or number. The higher values or numbers are indicative of the greater uniformity in formation. The following table shows the results of the tests carried out on the above-described test samples. In the table, the use of the term "percent added" refers to the weight of the designated material added to the paper-making furnish based on the weight of the fiber present.

Example	Karaya gum, percent added	Sulfuric acid, percent added	Formation value
7.-----	none	none	16
8.-----	15	none	32
9.-----	20	none	35
10.-----	4	6.8	44
11.-----	5	5.8	52

From the above table, it is clearly evident that substantial improvement in paper formation is realized when small quantities of sulfuric acid are employed in combination with the deacetylated karaya gum as compared with the sole use of this deflocculent.

It should be understood that although the foregoing examples describe in detail the essential features of the invention, they are intended to be illustrative only and not limitative. Thus, for example, although the invention has been illustrated in connection with the production of hand formed sheets, it is likewise applicable to the continuous production of paper sheets of indefinite lengths. That is, the fibers may be beaten in a continuous manner

and then continually sheeted out on a Fourdrinier wire, rotary machine or an Oliver forming machine.

In summary, the method of this invention provides a means for maintaining acrylic fibers uniformly dispersed in an aqueous medium by employing small amounts of sulfuric acid in combination with deacetylated karaya gum to attain excellent deflocculation. The dispersing power of the karaya gum is so greatly enhanced by the presence of small amounts of sulfuric acid that acrylic fibers can be maintained in the uniform dispersion required for paper formation with from 3 to 20 percent of this dispersing agent based on the weight of the fiber present. Heretofore, this could be accomplished only by the use of prohibitive amounts of karaya gum, i. e. from 50 to 100 percent on the weight of the fiber.

Various modifications and changes may be made in the above described process and materials that come within the scope of the invention as defined in the appended claims.

We claim:

1. In a process for making paper from an aqueous suspension of wet-spun acrylic fibers, the step which comprises first adding, to said suspension after all operations designed to modify the fibrous constituents by mechanical means are completed and prior to the formation of the paper web, from 3 to 20 percent of deacetylated karaya gum and thereafter slowly adding as a further component from 4 to 10 percent of sulfuric acid, all percentages being based on the weight of the fibers present in said aqueous suspension, and finally passing said aqueous suspension to a paper web forming device.

2. The process of claim 1, wherein said acrylic fibers have been obtained by the wet-spinning of a polymer blend comprising from 50 to 98 percent of one copolymer consisting of at least 85 percent acrylonitrile and up to 15 percent of another mono-olefinic monomer copolymerizable therewith and from 2 to 50 percent of another copolymer consisting of at least 30 percent of a vinyl-substi-

tuted alkyl pyridine and up to 70 percent of another mono-olefinic monomer copolymerizable therewith.

3. The process of claim 1, wherein said acrylic fibers have been obtained by the wet-spinning of a polymer blend comprising 88 percent of one copolymer consisting of 94.6 percent acrylonitrile and 5.4 percent vinyl acetate and 12 percent of another copolymer consisting of 50 percent acrylonitrile and 50 percent methylvinyl pyridine.

4. In a process for making paper from an aqueous suspension of wet-spun acrylic fibers, the step which comprises first adding to said suspension after all operations designed to modify the fibrous constituents by mechanical means are completed and prior to the formation of the paper web, from 4 to 10 percent of deacetylated karaya gum and thereafter slowly adding as a further component from 5 to 8 percent of sulfuric acid, all percentages being based on the weight of the fibers present in said aqueous suspension, and finally passing said aqueous suspension to a paper web forming device.

5. A stage product in the manufacture of paper from an aqueous suspension of wet-spun acrylic fibers, comprising the product obtained by first adding to said suspension after all operations designed to modify the fibrous constituents by mechanical means are completed and prior to the formation of the web, from 3 to 20 percent of deacetylated karaya gum and thereafter slowly adding as a further component from 4 to 10 percent of sulfuric acid, all percentages being based on the weight of the fibers present in said aqueous suspension.

References Cited in the file of this patent

UNITED STATES PATENTS

2,069,766	Le Compte	Feb. 9, 1937
2,810,646	Wooding et al.	Oct. 22, 1957
2,930,106	Wrotnowski	Mar. 29, 1960
3,013,936	Iyengar	Dec. 19, 1961