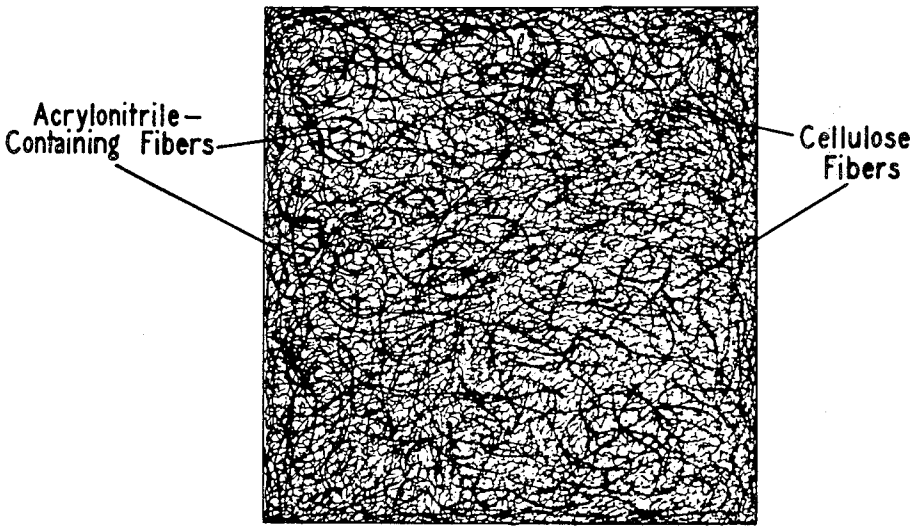
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PAPERS WITH IMPROVED ABSORBENT PROPERTIES

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PAPERS WITH IMPROVED ABSORBENT PROPERTIES

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The present invention relates to the production of novel cellulosic, i.e., cellulose-containing, paper products which demonstrate improved liquid absorption characteristics. In particular, this invention is concerned with the production of paper products from fiber blends containing both cellulose fibers and synthetic acrylonitrile-containing fibers such as acrylic and modacrylic fibers.

Over recent years the improvement of liquid absorption characteristics, and especially absorbency for water, in cellulosic paper products has received considerable attention from those skilled in the art. Such absorbent paper products find use, for example, as blotting paper, filter paper, paper toweling in hygienic applications and as saturating papers such as those employed in the production of resin-impregnated laminates and in chemical analytical procedures such as paper chromatography and the like.

A method heretofore commonly utilized to improve the liquid absorption characteristics of cellulosic paper products lies in the treatment of the cellulose fiber used to prepare the paper products with relatively large quantities of water-soluble wetting agents. Unfortunately, however, the paper products produced from cellulose fibers treated in such a manner may, in many instances, lose their absorption characteristics to a substantial extent when dried and rewetted, thus limiting the frequency with which the paper products can be used as an absorbent. In other instances, the wetting agent employed may lose its effectiveness upon prolonged storage. Still other wetting agents may be allergenic or toxic, thereby excluding the subsequent utilization of the treated paper products for hygienic purposes or in application such as those encountered in the food or pharmaceutical industries.

These disadvantages can now be overcome through the practice of the present invention which, in its broadest aspect, contemplates the production of highly absorbent cellulosic paper products in accordance with conventional paper-making techniques from blends of paper-making cellulose fibers with acrylonitrile-containing fibers such as acrylic and/or modacrylic fibers, the acrylonitrile-containing fibers being present in the fiber blends and paper products of this invention in a proportion of from about 25 percent to about 75 percent based upon the total weight of the fibers. The acrylonitrile-containing fibers suitable for use in accordance with this invention are also necessarily limited to those having a denier of from about 0.5 to about 25, or slightly higher, and a length of from about 1 millimeter to about 20 millimeters or slightly higher. In addition it is of salient importance to this invention that the novel paper products herein described be produced under conditions preventing or inhibiting the bonding or adhesion of the acrylonitrile-containing fibers with each other or with the cellulose fibers. Thus, the paper products of this invention are characterized by the fact that the acrylonitrile-containing fibers contained therein are essentially unbonded and non-fused and therefore retain their individuality in the paper products. The bonding that is present in the paper products of this invention is essentially conventional bonding between cellulose fibers common to paper products and in which the acrylonitrile-containing fibers play no part.

A fuller understanding of this invention may be facilitated by reference to the accompanying drawing, which

illustrates an enlarged section of a paper product of the invention composed of a blend of paper-making cellulose fibers and unbonded and non-fused acrylonitrile-containing fibers.

The highly absorbent paper products of this invention can be employed in substantially all of the conventional applications requiring an absorbent paper, and can be dried and rewetted indefinitely without loss in absorption characteristics. Moreover, the novel paper products are non-allergenic and non-toxic, and retain their absorption characteristics even after prolonged storage. The improved absorbency of the paper products of this invention, when compared with papers produced wholly from cellulose fibers, is evidenced, for example, by an increase in both the rate of liquid transport therein, i.e. wicking, and in the total amount of liquid absorbed thereby, as well as in the total area of paper ultimately wetted by the absorbed liquid.

The paper-making cellulose fibers utilized in accordance with this invention are well known to the art and can be defined more particularly as the vegetable fibers such, for example, as wood, rag cotton, flax, jute, straw or other fibers derived from plants of various kinds, and of any paper-making length. The invention also encompasses the use of appropriate mixtures of such cellulose fibers. The cellulose fibers can be prepared for paper-making by any suitable process, such, for example, as the sulfite process, sulfate process, soda process, kraft process or by suitable mechanical processes etc., and thereafter hydrated, bleached, washed, screened, beaten, aged or otherwise prepared for paper-making in known manner. It is to be noted in this respect that in the past cellulose fibers possessing relatively little added hydration such as is effected by the conventional beating of the fibers in water were frequently employed to produce absorbent paper products. The use of such fibers resulted in a minimal bonding of the fibers and therefore in the ultimate production of a more porous paper. Advantageously the cellulose fibers suitable for use in producing the paper products of this invention are not limited thereto, although such fibers can be employed with good effect. Thus, a wider range of cellulose pulp or other source of cellulose fibers can be made use of in accordance with this invention. The utilization of the more hydrated cellulose fibers that are produced by an extensive beating of the fibers in water may in fact be preferred in this invention when the blend thereof with acrylonitrile-containing fibers, as herein described, contains the latter type of fiber in relatively large proportions or when a tighter paper product is desired.

The acrylonitrile-containing fibers contemplated by this invention are also well known to the art and are the fibers designated as acrylic and modacrylic fibers in accordance with the definitions adopted by the Federal Trade Commission. The acrylonitrile-containing fibers suitable for use in this invention can be defined more particularly as the fibers produced by conventional fiber spinning operations from homopolymers of acrylonitrile and/or copolymers thereof with one or more other ethylenically unsaturated monomers polymerizable therewith, such copolymers containing the acrylonitrile component in a concentration of at least about 35 percent by weight based upon the weight of the copolymer. As employed herein, the term "copolymer" is meant to include the polymers produced by the interaction of two or more different monomers, the term "polymer" is meant to include both homopolymers and copolymers.

As illustrative of the ethylenically unsaturated compounds which can be polymerized with acrylonitrile to produce fiber-forming polymers from which the acrylonitrile-containing fibers of this invention can be obtained there can be mentioned the following:vinyl chloride,

vinylidene chloride, vinyl pyridine, vinyl pyrrolidone, styrene, methyl methacrylate, methacrylamide, methyallyl alcohol, allyl cyanide, methallyl cyanide, vinyl acetate and the like. Of these, the acrylonitrile-containing fibers produced from copolymers of acrylonitrile and either vinyl chloride, vinylidene chloride or both are preferred.

The acrylonitrile-containing polymers and the fibers produced therefrom can be obtained in well known manner, such for example, as by the processes disclosed in U.S. Patents 2,420,565, 2,603,620 and 2,868,756 or by any other convenient means, which disclose suitable acrylonitrile-containing polymers and fibers for use in the present invention.

As previously indicated the acrylonitrile-containing fibers are incorporated in the fiber blends and paper products of this invention in a proportion of from about 25 percent to about 75 percent by weight based upon the total weight of the fibers. Within this range, the combination of cellulose fibers with acrylonitrile-containing fibers has been found to engender the production of absorbent paper products evidencing an exceptionally rapid rate of wicking when brought into contact with a liquid such as water.

In addition, as further indicated above, the acrylonitrile-containing fibers contemplated by this invention have a denier of from about 0.5 to about 25 or slightly higher and a machine-cut length of from about 1 millimeter to about 20 millimeters or slightly higher. In this connection, it has been found that greater quantities of liquid are absorbed by the paper products of this invention containing the longer and/or the thinner, i.e. lower denier, acrylonitrile-containing fibers within the above-mentioned ranges. It has also been found that a more rapid rate of liquid absorption is evidenced by the paper products containing the shorter and/or the thicker acrylonitrile-containing fibers. Thus, where a paper product characterized by a maximum absorbency for liquids is desired, the acrylonitrile-containing fibers employed in accordance with this invention are preferably those having a length of from about 5 to about 20 millimeters and a denier of from about 0.5 to about 12. On the other hand where a maximum in both the rate of wicking and in the ultimately wetted area of the paper product is desired, acrylonitrile-containing fibers having a length of from about 1 to about 5 millimeters and a denier of from about 12 to about 25 are preferably employed.

In an embodiment of this invention the cellulose fibers and the acrylonitrile-containing fibers are blended or admixed and paper products are produced therefrom in any conventional manner known to the art. In a typical procedure, the acrylonitrile-containing fibers and papermaking cellulose fibers having the desired degree of hydration engendered by a previous conventional beating of the fibers in water in an apparatus such as a Valley laboratory beater, are dispersed in an aqueous dispersion medium in proportions as hereinabove described. To this dispersion there can be added, if desired, small quantities of a dispersing or antifoaming agent although such addition is not essential. Frequently, commercially available acrylonitrile-containing fibers will have a coating containing a quantity of dispersing agent such that the addition of further quantities of the dispersing agent, where desired, is not necessary. The advantages accruable in accordance with this invention have been realized with and without the presence of a dispersing agent. The adequate blending of the fibers in the dispersion is then assured by introducing the dispersion to a conventional agitator or mixer such as a TAPPI (Technical Association of the Pulp and Paper Industry) standard disintegrator wherein the fibers are mixed. The beating of the cellulose fibers to effect the desired degree of hydration can also be carried out during or subsequent to the formation of the cellulose-acrylonitrile-containing fiber blend. However, such a procedure may damage the acrylonitrile-containing fibers also present and is therefore generally not preferred. Thereafter, paper products are produced from the fiber blend by conventional water-laying techniques such for example, as by introducing the aqueous dispersion to a machine such as a Noble and Wood handsheet machine wherein a paper product is formed. The paper product is then removed from the forming apparatus and dried.

It is to be noted that this invention is in no way limited by the particular method for forming the fiber blends or paper products or by the apparatus used therein. Of critical importance thereto, however, is the maintenance of conditions preventing or inhibiting the bonding or adhesion of the acrylonitrile-containing fibers with each other or with the cellulose fibers. Thus, the drying of the paper products is necessarily carried out at a temperature below that at which the acrylonitrile-containing fibers become "tacky" and tend to coalesce and therefore preferably kept below about 250° F. The maximum operable temperature for drying the paper products in accordance with this invention will vary, naturally, depending for the most part upon the chemical composition of the acrylonitrile-containing fibers employed, but can readily be determined by those skilled in the art in light of this disclosure.

The present invention can be illustrated further by the following specific examples of its practice but is not intended to be limited thereto.

EXAMPLE I

In a series of experiments, sheets of paper were prepared from both paper-making cellulose fibers and blends thereof with acrylonitrile-containing fibers in the following manner. In each run, a total of 2.5 grams of fiber were dispersed in water to which there was added several drops of a dispersing agent, viz. Ethomeen 5/15, a product of the Armour Company, the aqueous fiber dispersion placed in a TAPPI standard disintegrator and mixed therein for 600 counts. The blended dispersion was then introduced to the deckle box of a Noble and Wood handsheet machine wherein a square sheet of paper eight inches on a side was formed. The sheet of paper was subsequently couched and pressed to remove water and dried at a temperature of 220° F. for two minutes at which temperature the acrylonitrile-containing fibers did not bond or adhere to each other or to the cellulose fibers present. The cellulose fibers employed in each run were obtained from unbleached sulfite paper pulp manufactured by the Marathon Corporation and which was beaten in water in a Valley laboratory beater to a Canadian standard freeness of 132. The acrylonitrile-containing fibers employed in each run were obtained by conventional fiber spinning operations from a copolymer containing approximately 60 percent by weight of acrylonitrile, the remaining component of the copolymer being vinyl chloride, and had a length of 3 millimeters and a denier of 2. In run No. 1, the paper product was produced entirely from the cellulose fibers; in run No. 2, the paper product was produced from a blend containing 75 percent by weight (1.875 grams) of the cellulose fibers and 25 percent by weight (0.625 gram) of the acrylonitrile-containing fibers; in run No. 3, the paper product was produced from a blend containing 50 percent by weight (2.25 gram) of each of the fibers; and in run No. 4, the paper product was produced from a blend containing 25 percent by weight (0.625 gram) of the cellulose fibers and 75 percent by weight (1.875 grams) of the acrylonitrile-containing fibers. Specimens of the paper sheets thus prepared were tested to measure both the rate and distance of liquid transport therein as well as the amount of liquid absorbed thereby using water as the liquid. The water transport measurements were made by immersing vertically-held strips of the paper ½ inch wide by 8 inches long to a depth of ⅛ inch in a container of water. Observations were made of the height to which the water had risen in the paper strip at one-minute intervals to a

total of 5 minutes. The amount of water absorbed was determined by weighing the paper strips before immersion and after five minutes. The results obtained from this series of experiments are tabulated below in Table A. In the table, the time during which transportation of water in the paper strips took place, i.e. wicking time, is indicated in minutes. The distance that the water was transported, i.e., the distance wicked, at the conclusion of each time interval is indicated in inches. The total amount of water absorbed by the paper strips after 5 minutes is indicated in percent by weight based upon the original weight of the paper strips.

Table A

Run No.	Time	Distance Wicked	Total Amount of Water Absorbed
1	1	¼	
	2	⅜	
	3	½	
	4	¾	
	5	⅞	22
2	1	¾	
	2	1	
	3	1¼	
	4	1⅝	
	5	1¾	54
3	1	1½	
	2	2¼	
	3	2½	
	4	3	
	5	3¼	107
4	1	1¼	
	2	2	
	3	3½	
	4	4	
	5	4¾	170

From the above table, it can be seen that the paper products of this invention demonstrate improved absorption characteristics, viz. in both the rate of liquid transport and in the amount of liquid absorbed, when compared with paper products produced entirely from cellulose fibers.

EXAMPLE II

In a manner similar to that described in Example I, except where hereinbelow indicated, a series of paper sheets were prepared from blends of the paper-making cellulose fibers described in Example I with acrylonitrile-containing fibers produced by conventional fiber spinning operations from a copolymer containing approximately 40 percent by weight of acrylonitrile, polymerized therein, the remaining component of the copolymer being vinyl chloride, and having a length of 3 millimeters and a denier of 2. A total of 5 grams of fiber were used to produce each paper sheet. In run No. 1, the fiber blend employed contained 90 percent by weight of the cellulose fibers and 10 percent by weight of acrylonitrile-containing fibers; in run No. 2, the fiber blend employed contained 75 percent by weight of the cellulose fibers and 25 percent by weight of the acrylonitrile-containing fibers; in run No. 3, the fiber blend employed contained 50 percent by weight of each of the fibers; in run No. 4, the fiber blend employed contained 25 percent by weight of the cellulose fibers and 75 percent by weight of the acrylonitrile-containing fibers; and in run No. 5, the fiber blend employed contained 10 percent by weight of the cellulose fibers and 90 percent by weight of the acrylonitrile-containing fibers. In each run, the sheet of paper formed in the Noble and Wood machine was subsequently washed to remove any dispersing agent present and dried at room temperature. The specimens for testing were made by cutting the paper sheet into strips ½ inch wide by 6 inches long. The paper strips were then suspended from a horizontal bar and brought into contact with an aqueous stain solution. Measurements were made of the time required for the aqueous solution to wick 1 inch of the paper strips and of the total distance of water transport and amount of water absorbed after five minutes. The amount of water absorbed was determined by weighing the strips before immersion and after five minutes. The results obtained from this series of experiments are tabulated below in Table B from which the advantages accruable in accordance with this invention can readily be seen. In the table, the time required to wick the first 1 inch of the paper strips is indicated in seconds. The total distance wicked at the end of 5 minutes is indicated in inches. The total amount of water absorbed by the paper strips is indicated in percent by weight based upon the original weight of the paper strips.

Table B

Run No.	Time To Wick the First Inch	Total Distance Wicked	Total Amount of Water Absorbed
1	62.1	1.87	54.1
2	22.8	3.01	103
3	10.2	3.95	171
4	6.5	4.56	310
5	47.5	1.75	235

It can be seen from the above table that maximum effects are realized by the incorporation of the acrylonitrile-containing fiber in the fiber blends and paper products of this invention in a proportion of from about 25 percent to about 75 percent by weight based upon the total weight of the fibers.

EXAMPLE III

In a manner similar to that described in Example II, a series of experiments were conducted using however, as the acrylonitrile-containing fibers, commercially available Orlon acrylic fibers said to be made principally from polyacrylonitrile polymer. The runs were carried out using both the same cellulose fiber and proportions of cellulose and acrylonitrile-containing fibers as described in Example II. The results obtained from this series of experiments were measured and are tabulated below in Table C as described in Example II.

Table C

Run No.	Time To Wick the First Inch	Total Distance Wicked	Total Amount of Water Absorbed
1	99.6	1.55	37.2
2	28.5	2.82	102
3	7.3	4.18	289
4	9.1	3.40	385
5	77.8	1.19	302

EXAMPLE IV

In a manner similar to that described in Example II, a series of experiments were conducted to observe the effect that a change in the length and denier of the acrylonitrile-containing fibers has upon the absorption characteristics of the paper products of this invention. Run Nos. 1 to 5, the cellulose fibers and the acrylonitrile-containing fibers were the same as those described in Example II, save in the length and denier of the latter, and were employed in each instance a proportion of 75 percent by weight of the acrylonitrile-containing fiber and 25 percent by weight of the cellulose fiber based upon the total weight of the fibers. The length and denier of the acrylonitrile-containing fibers varied in each run. For comparison, one run (run No. 6) was conducted using commercially available blotting paper for testing purposes. The results obtained from this series of experiments were measured and are tabulated below in Table D as described in Example II. The length of the acrylonitrile-containing fiber is indicated in inches.

Table D

Run No.	Acrylonitrile-Containing Fiber		Time To Wick the First Inch	Total Distance Wicked	Total Amount of Water Absorbed
	Length	Denier			
1	½	2	16	4.0	265
2	¾	6	14.8	4.0	255
3	½	24	11.4	3.8	224
4	⅛	2	10.5	4.1	235
5	½	2	25.6	3.4	245
6			28	3.12	143

From the above table it can be seen that the more rapid rates of liquid transport, i.e. wicking, are obtained using the thicker and/or shorter length acrylonitrile-containing fibers while greater quantities of liquid are absorbed by the paper products incorporating the thinner and/or longer length acrylonitrile-containing fibers. In each instance, however, the paper products of this invention were superior with respect to both the rate of liquid transport and the amount of liquid absorbed when compared with commercial blotting paper produced entirely from cellulose fibers.

What is claimed is:

1. An absorbent paper product composed of a blend of paper-making cellulose fibers and unbonded and non-fused acrylonitrile-containing fibers selected from the group consisting of acrylic and modacrylic fibers, said

acrylonitrile-containing fibers (*a*) containing at least about 35 percent by weight of acrylonitrile, (*b*) having a length of from about 1 millimeter to about 20 millimeters, (*c*) having a denier of from about 1 to about 25 and (*d*) being present in said paper product in a proportion of from 25 percent to 75 percent by weight based upon the total weight of the fibers present.

2. An absorbent paper product as claimed in claim 1 wherein the acrylonitrile-containing fibers are composed of a copolymer of acrylonitrile with at least one member selected from the group consisting of vinyl chloride and vinylidene chloride.

3. An absorbent paper product as claimed in claim 1, wherein the acrylonitrile-containing fibers are composed of a copolymer containing from about 40 percent to about 60 percent by weight of acrylonitrile polymerized therein, the remaining component of said copolymer being vinyl chloride.

References Cited in the file of this patent

UNITED STATES PATENTS

2,477,000	Osborne	July 26, 1949
2,603,620	Walter et al.	July 15, 1952
2,810,646	Wooding et al.	Oct. 22, 1957
2,899,351	Morse	Aug. 11, 1959

FOREIGN PATENTS

674,577	Great Britain	June 25, 1952