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FIBROUS SHEET MATERIAL

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This invention relates to the art of papermaking and particularly to the production of a paper web having an improved combination of tear and burst properties. More particularly, the invention relates to a paper web and a method of making the same wherein the product has an exceptional combination of high tear strength and high mullen or burst strength, being composed of uniformly intermingled fibers of polyvinyl alcohol and of papermaking cellulose.

The paper web of the present invention has particular utility in those uses for paper in which a high tear strength combined with high mullen or bursting strength are particularly desired, as for example, in bags, bread wrappers and overwrappers for boxes or cartons of frozen foods, napkin and towel stock, paper book covers and the like.

Previous attempts have been made to reinforce and improve the tear and burst properties of paper made from cellulose fibers by the incorporation of various natural and synthetic fibers in the pulp from which the web is formed but these attempts have not met with signal success. This lack of success is apparently due to the fact that these fibers, including spun glass, Dynel (a synthetic resin made by polymerization of vinyl compounds), nylon (a synthetic polyamide fiber) silk, polyacrylonitrile and the like, have no natural affinity for the cellulose pulp fibers and do not become sufficiently bonded thereto to form a web of adequate strength without the addition of certain binding agents which increase the difficulties and the expense inherent in the manufacture of the paper web from the pulp and detract from the overall utility of the product. Fibers of polyvinyl alcohol have not previously been considered for incorporation in papermaking furnishes since polyvinyl alcohol resins are normally considered to be water soluble and it has been believed that they would not remain as fibers after being processed in cellulose pulp slurries on papermaking equipment.

It has now been found, however, that synthetic fibers of polyvinyl alcohol are compatible with papermaking cellulose fibers and that these two types of fibers mutually assist in maintaining the individual fibers of each type as a uniform and controlled suspension in the aqueous paper making pulp slurry, preventing premature clumping of the fibers so that a coherent web of excellent formation and unusual strength properties may be obtained by passing a pulp slurry containing a mixture of these fibers over a conventional papermaking machine. From the improved strength characteristics inherent in the resulting paper web, it is evident that the synthetic polyvinyl alcohol fibers exert a strong bonding effect on the cellulose fibers.

Without wishing to be limited by the theory, we believe that the bonding effect herein noted is probably due to certain intermolecular forces of the hydrogen bond type which result from the many hydroxyl groupings present in polyvinyl alcohol and the hydroxyl and carboxyl groupings which form a portion of the cellulose molecule. Groups of this nature would, on the one hand, account

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for the repulsive forces in the aqueous slurry which result in excellent dispersion of the individual fibers and, on the other hand, also account for the strong bonding force which is evident in the dried, intimately co-mingled fibers of the finished paper. The lack of these active, hydrogen-bonding groupings in such materials as nylon, polyvinyl chloride and spun glass would account for the poor formation and inadequate strength properties of papers prepared from mixtures of these materials with cellulose pulp.

The cellulose fibers used in the present invention may be those prepared by any of the conventional methods for the production of papermaking pulp, including chemical, semi-chemical or mechanical pulp fibers prepared by, for example, the kraft, sulfite or soda processes or the ground-wood process. They may be bleached or unbleached stock and may be a stock which is unrefined or has been moderately refined in a beater or other refining device.

Polyvinyl alcohol fibers suitable for our use may be prepared by any suitable conventional methods such as described in The Textile Manufacturer, December 1956, pages 636-643. According to one such method, polyvinyl alcohol is dissolved in water to a concentration of 15-20% and then extruded through a spinneret into a coagulating aqueous salt bath (suitably saturated aqueous sodium sulfate) as continuous filaments which may then be stretched or tensilized and dried at elevated temperature to make them relatively insensitive to water. Polyvinyl alcohol fibers which have not been insensitized to water by heat treatment may also be used, but require close control in drying the resulting paper sheet to avoid dissolution of the polyvinyl alcohol fibers in the water retained by the semi-dried sheet. The polyvinyl alcohol from which the fibers are formed is suitably synthesized by catalyzed reaction of acetylene and acetic acid and subsequent alcoholysis of the resulting polyvinyl acetate to form polyvinyl alcohol.

The polyvinyl alcohol fibers for use in our invention are preferably cut to a relatively uniform length which can vary from about 1/4 inch (about 6 mm.) up to about 1/2 inch (about 12 mm.) or slightly longer and can range in diameter from about 10 microns up to about 40 microns. A length of about 3/8 inch and a diameter of 20 microns are quite satisfactory. For comparison, most papermaking cellulose fibers range from 20 to 50 microns in diameter and from about 1/16 inch to about 1/8 inch in length. Thus, the polyvinyl alcohol fibers suitable for use in the present invention are substantially longer than the normal papermaking cellulose fiber.

Paper made from blends of cellulose pulp with from about 5% to about 50% polyvinyl alcohol fibers based on the dry weight of the furnish exhibit the improved properties which result from the practice of our invention. If the percentage of polyvinyl alcohol fibers is increased to more than about 50%, the pulp blend cannot be satisfactorily formed into paper on conventional papermaking machinery by normal papermaking procedures without the addition of special pulp dispersants and a large portion of the advantage attendant on our invention is sacrificed. Blends containing from about 5% to about 50% polyvinyl alcohol fibers may be formed into paper webs having excellent formation and unusual strength characteristics using perfectly conventional equipment and techniques, without the addition of any dispersing or bond-

ing agents and at normal machine speeds. The formation of paper of equally desirable characteristics from blends of cellulose fibers with fibers of materials other than polyvinyl alcohol has not hitherto been attainable on conventional papermaking equipment.

Papers made from fiber blends containing relatively small amounts of polyvinyl alcohol fibers are of particular value in the manufacture of food wrappers and the like since they are relatively dense sheets having high tear and burst strength, while papers made from pulp blends containing from 20–50% polyvinyl fibers exhibit greater bulk while maintaining excellent tear and burst strength, and are of particular value as napkin and towel stock.

In normal papermaking operations, high burst strength or mullen is developed refining the cellulose pulp in beaters, and in general, increased beating results in an increase in mullen value. Beating of cellulose fibers, however, results in a serious decrease in tear strength, and hitherto it has been impossible to attain and maintain a high tear strength in paper from stock which has been beaten sufficiently to attain a desirably high burst strength or mullen.

By the practice of our invention, however, normal papermaking cellulose fibers may be refined by beating to a degree commensurate with the production of a desired value of burst strength in the finished paper sheet while the tear strength resulting from the addition of minor amounts of polyvinyl alcohol fibers in the papermaking pulp blend attains hitherto unprecedented values.

A series of experiments was conducted in which nylon fibers, Dynel (a co-polymer of 60% acrylonitrile and 40% vinyl chloride) fibers and polyvinyl alcohol fibers of one-quarter inch in length and about 18 microns in diameter were added in varying percentages to softwood sulfate pulp in dilute aqueous suspension which had been beaten to a degree commonly referred to in the trade as 300 ml. Canadian Standard freeness. Handsheets were prepared from the pulp slurries by standard papermaking test procedures and tested for burst strength (mullen) and tear strength by standard TAPPI methods. The results of these tests are recorded in Table I below.

Table I

Synthetic Fiber Content in percent by Wt. of Dry Fiber	Dynel		Nylon		Polyvinyl Alcohol	
	Burst ¹	Tear ²	Burst	Tear	Burst	Tear
0-----	155	147	170	155	144	170
5-----	155	136	164	197	124	222
10-----	148	171	147	251	115	303
20-----	134	182	107	256	106	439
50-----	55	198	46	258	67	810

¹ Mullen points/100 lb. per ream sheet. (1 ream=3000 sq. ft.).

² Gm./100 lb. per ream sheet.

The data in Table I indicate that significant increases in tear strength are obtained with as little as 5% of polyvinyl alcohol fibers in the furnish, and outstanding tear strengths are developed at higher polyvinyl alcohol percentages. Dynel and nylon, by comparison, are significantly less effective in improving the desired strength properties of the finished paper.

In a further series of experiments, a dilute aqueous slurry of softwood kraft pulp was refined to varying degrees by beating to various freeness values, polyvinyl alcohol fibers one-quarter inch in length and 18 microns in diameter were added to the extent of 20% based on the dry weight of cellulose fibers and handsheets were made and tested for tear and burst strength. In papermaking art, increased beating produces lower freeness values, increased burst strength values, and hitherto has always resulted in decreased tear strength. The results of this series of tests are recorded in Table II below.

Table II

Furnish	Canadian Freeness of Cellulose Pulp Slurry					
	300		150		75	
	Strength Tests on Finished Paper					
	Burst*	Tear*	Burst	Tear	Burst	Tear
20% Polyvinyl Alcohol Fiber, 80% Softwood Kraft Pulp-----	90	450	137	440	148	440
100% Softwood Kraft Pulp-----	155	200	176	150	194	139

* Units as in Table I.

It will be noted that, contrary to the expected result as exemplified by the data on sheets made from 100% softwood kraft fibers, the tear strength of the test sheets containing polyvinyl alcohol fibers remained at a very high level despite the varying degrees of refinement by beating, while the mullen was increased in the expected manner with increased beating.

It was found in further experimentation that paper having very high tear strength could be obtained from mixtures of papermaking cellulose fibers with polyvinyl alcohol fibers of a length as great as one-half inch or slightly more. The data recorded in Table III, following, were obtained on handsheets produced from blends of softwood sulfate papermaking pulp with polyvinyl alcohol fibers of one-quarter inch, three-eighths inch and one-half inch in length. The cellulose pulp was beaten to various degrees of freeness prior to the addition of the polyvinyl alcohol fibers.

Table III

PVA ¹ Fiber Length, In.	Softwood Sulfate Pulp Can. Free., Ml.	Burst, Mullen Pts./100 lb. Sheet PVA ¹ Fiber Content, Percent					Tear, g./100 lb. Sheet PVA ¹ Fiber Content, Percent				
		0	5	10	20	50	0	5	10	20	50
1/4-----	300	144	124	115	106	67	170	222	303	439	810
1/4-----	150	176	176	175	137	95	150	240	285	440	813
1/4-----	75	194	166	163	148	89	139	215	302	440	850
3/8-----	300	153	146	128	111	66	152	241	339	539	1,038
3/8-----	150	142	128	121	103	76	171	236	345	515	1,103
3/8-----	75	154	138	126	105	89	148	202	340	474	1,140
1/2-----	300	134	135	117	91	75	156	242	317	620	1,255
1/2-----	150	142	136	120	102	92	171	236	351	574	1,492
1/2-----	75	154	133	119	109	103	148	222	322	509	1,582

¹ PVA—Polyvinyl alcohol.

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It will be noted from Table III that inclusion of up to 50% of polyvinyl alcohol fibers of three-eighths inch and one-half inch in length impart exceptionally high tear strength to paper made from cellulose fibers. It was also found that if polyvinyl alcohol fibers appreciably longer than one-half inch were used, or if substantially more than 50% of such fibers were used, the formation of the resulting sheet suffered and the pulp blends became more difficult to handle on conventional papermaking equipment by normal papermaking procedures.

When papermaking cellulose pulp is beaten together with added polyvinyl alcohol fibers, a further unexpected result is obtained, in that the time required to reach a given freeness value for the production of paper sheets of a desired burst strength is drastically reduced, enabling significant economies in power and in the size of equipment necessary for refining a given quantity of pulp in a specified time.

Pulp blends containing up to 50% polyvinyl alcohol fibers may be processed on standard papermaking machinery at normal machine speeds using regular papermaking techniques. Blends containing more than 50% polyvinyl alcohol fibers are not as readily maintained in the uniformly distributed dilute aqueous slurry required for high quality paper production and the resulting paper tends to suffer from poor formation.

Papers exhibiting outstanding fold endurance have been obtained by treating the product of our invention containing blended fibers of wood cellulose and polyvinyl alcohol with from about 10% to about 30% of a plasticizing agent such as glycerine, ethylene glycol or other low molecular weight polyhydric alcohol and calendering the plasticized paper. Fold endurance is of particular value in papers subject to repeated flexing, examples being paperbound book covers and manila file folders.

Paper handsheets were prepared in the customary manner from aqueous slurries of papermaking pulp containing varying percentages of polyvinyl alcohol fibers. The resulting paper sheets were impregnated with 20% of glycerine based on the fiber weight and then subjected to a pressure of 5000 p.s.i. at 150° C. The fold endurance of the resulting pressed sheets was measured by the TAPPI standard method No. T423m-50 using a fold tester of the type developed at the Massachusetts Institute of Technology. The results of these tests are recorded in Table IV, following.

Table IV

Percent Polyvinyl Alcohol Fibers in Furnish	M.I.T. Fold Endurance Unplasticized	M.I.T. Fold Endurance Plasticized
0.....	1,600	3,000
5.....	1,620	16,000
10.....	1,700	41,000
20.....	1,870	47,300

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Remarkable increases in fold endurance such as those recorded in Table IV are obtained when the sheets of our invention are treated with from 10 to 30% based on total fiber weight of a polyhydric alcohol plasticizer followed by pressing or calendering at elevated temperatures.

Having now disclosed several of the preferred modifications of our invention, it is evident that various other modifications may be made within the spirit of our invention.

We do not wish to be limited in the interpretation of our invention except as distinctly set forth in the appended claims.

We claim:

1. Paper sheet material of improved burst and tear strength comprising a blend of papermaking cellulose pulp fibers and a minor amount of polyvinyl alcohol fibers.

2. Paper sheet material of improved burst and tear strength comprising a blend of papermaking cellulose pulp fibers and from about 5% to about 50% of fibers of tensitized polyvinyl alcohol.

3. Paper sheet material of improved burst and tear strength comprising a blend of papermaking cellulose pulp fibers and from about 5% to about 50% of water-insensitized polyvinyl alcohol fibers.

4. Paper sheet material of improved burst and tear strength comprising a blend of papermaking cellulose pulp fibers and from about 5% to about 50% of water-insensitized polyvinyl alcohol fibers, said polyvinyl alcohol fibers having a fiber length substantially greater than the average length of said cellulose fibers.

5. Paper sheet material of improved burst and tear strength and improved fold endurance comprising a blend of papermaking cellulose fibers, a minor amount of water-insensitized polyvinyl alcohol fibers and from about 10% to about 30% based on the total fiber weight of a low molecular weight polyhydric alcohol plasticizer.

6. Paper sheet material as described in claim 5 wherein the polyhydric alcohol plasticizer is glycerine.

References Cited in the file of this patent

UNITED STATES PATENTS

1,829,585	Dreyfus	Oct. 27, 1931
2,648,635	Brown et al.	Aug. 11, 1953
2,962,762	Hartmann et al.	Dec. 6, 1960

FOREIGN PATENTS

1,083,697	France	June 20, 1954
572,962	Great Britain	Oct. 31, 1945

OTHER REFERENCES

"The Textile Manufacture," December 1956, pages 636-643.