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3,266,972

PROCESS FOR PRODUCING AN EXTENSIBLE PAPER

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This application is a continuation-in-part of U.S. application Serial No. 171,731, filed February 7, 1962, and now abandoned.

This invention relates to a novel and useful process for making paper. More specifically it is concerned with a process of making extensible papers from a cellulose-containing paper pulp.

Extensible papers have found a wide acceptance in the preparation of multiwall bags. While normally 3 or 4 plies of such paper are used in such bags, bags of comparable strength using fewer plies can be made from paper made in accordance with the present process.

It is an object of this invention to provide a novel and useful process for the preparation of extensible papers.

Another object is to provide extensible papers especially useful in the manufacture of bags.

The present invention provides an improvement in the process of producing an uncreped paper web of water-laid, adherent, cellulose fibers, with smooth, substantially parallel faces and substantial permanent extensibility in excess of the primitive elastic limit of the web, and which suffers no substantial decrease in thickness when elongated by stretching, which comprises forming the said water-laid web from a furnish of cellulose fibers containing from about 1% to about 10%, based on the total dry weight of the furnish, of an additive particle of highly swollen, water insoluble cellulose derivative containing a deep seated substituent from the class consisting of an ether, an acid, a nitrile, an ester and mixtures thereof, the degree of substitution of the said cellulose being from about 0.01 to about 0.8, the said furnish being characterized by a Canadian standard freeness at the headbox of from about 450 to about 650. By a "deep seated" substituent is meant a substituent distributed throughout the body of the additive particle as distinguished from an additive particle wherein substituents are largely restricted to fiber surface locations. While the degree of substitution need not necessarily be uniform throughout the cross-sectional area of the additive particles, it is essential that substitution not be concentrated upon surface locations and substantially uniform substitution is preferable. Cellulosic particles of such character can be produced by the direct reaction of a reactant capable of supplying the desired substituent upon a highly swollen form of alkali cellulose. Where these particles are of suitable size for paper making, i.e., not so large as to produce "shiners" nor so small that they will be lost through the drainage wire, they may be used directly in the process of the present invention. In addition to such particles, referred to hereinafter as "original morphology" particles, regenerated particles may be used. Preferred among the regenerated additive particles are the shear-

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precipitated particles of etherified cellulose of Belgian Patent 613,355, granted July 31, 1962, to Brody et al. and described more fully hereinafter.

In the process described above, the manipulative technique employed is that which is known in the trade as "Clupaking." This process is described and claimed in U.S. 2,264,245 to Cluett et al., dated January 6, 1953. Applicants' modification of this process provides extensible papers from which extremely durable multiwall bags can be constructed. While applicants do not wish to be bound by any theory of operation, it is postulated that the deformability of the additive particles interacts with the compaction of the paper sheet to afford excellent binding. Further improvement in product can be realized by practicing applicants' invention while operating the Clupak section necessary in the Clupak process at a slack draw (obtained by loosened felts), to permit a cross directional shrinkage of the sheet formed of at least about 3% and preferably from about 4% to about 6%. Cross directional shrinkage using the additive particles as a furnish component as taught in the present invention has also been found highly useful in paper formation, even without use of Clupaking as will be demonstrated hereinafter. Use of the etherified particles of the Belgian patent are preferred when cross directional shrinkage is desired.

PREPARATION OF THE CELLULOSE PARTICLES

The original morphology particle of the present invention can be formed from any cellulosic material such as cotton linters, wood chips kraft pulp, regenerated cellulose fiber or film or the like, by first steeping the material in dilute alkali to swell it and form the alkaline salt and thereafter form the desired derivative by the conventional reaction. It is essential in attaining the deep seated modification to swell the particle prior to derivative formation by steeping in aqueous alkali containing from about 14% to about 30% by weight caustic (preferably about 18% to 19%) under conditions generally employed in the viscose rayon industry. Use of very dilute aqueous alkali, i.e., from about 1% to about 3% is not adequate for deep seated modification, but leads invariably to surface reaction upon the particle. The temperature and period of steeping may vary widely. At room temperature a steeping period of 15 minutes is generally adequate for cotton linters although longer periods may be used. After steeping, the material is pressed to remove liquid until the weight of the pressed cellulose is about three times its dry weight. It is then shredded following conventional viscose rayon procedure and may be aged for as long as one or two weeks although use of the shredded product within 24 hours is preferred. Derivative formation is carried out in a baratte following conventional procedures. In the formation of cyanoethyl cellulose from cotton linters, for instance, the shredded alkali cellulose is charged to the baratte along with from about 0.05 to about 0.5% by weight based on the cellulose of acrylonitrile and permitted to react for from as short a period as 10 minutes at elevated temperatures to as much as 2 hours at low temperatures. The cyanoethyl cellulose can be hydrolyzed by known procedures to form the acid.

The particles may be used in the shape in which they are prepared, hence the designation "original morphology" of if desired the regenerated structure may be used. For attaining cross directional shrinkage according to the process of the present invention, a particular regenerated particle of cellulose ether is preferred which is referred to hereinafter as a "shear precipitated" particle.

The shear precipitated particles of etherified cellulose useful in the present invention are described in the Belgian patent to Brody et al. identified above. These products are hydrophylic, water insoluble and microscopically uniform and have a substantially non-crystalline but well ordered molecular structure having a high level of chain segment mobility. Such derivatives may be made by one of several processes. The cyanoethylated product is most conveniently produced by the addition of acrylonitrile and carbon disulfide to the barrette during the conventional xanthation process, sufficient acrylonitrile being added to provide a degree of substitution between about 0.2 and about 0.7. Generally from about 0.5 mole to about 3.0 moles of acrylonitrile may be used per mole to assist in solubilization of the etherified product, but it is not essential in the production of the cyanoethylated product. Thus alkali cellulose may be cyanoethylated by direct addition of acrylonitrile to it as exemplified hereinafter. This embodiment of the claimed product may require a more concentrated caustic to solubilize it, due to the absence of the xanthate groups. In addition to simultaneous xanthation and etherification, the xanthation may occur prior or subsequent to etherification to produce a more readily soluble embodiment.

The production of ethers other than cyanoethylated ethers is done by contacting the alkali cellulose in the solid form with the etherifying agent such as an alkylene oxide or ethylene chlorohydrin. When employing this technique with alkylene oxide as etherifying agent it is essential that the alkali cellulose have a caustic content less than about 30% by weight based on cellulose (and preferably from about 18% to about 22%) and that sufficient of the etherifying agent be added to provide at least about 30% by weight of alkylene oxide based on the weight of the cellulose employed in the reaction. The use of alkali cellulose of a higher caustic concentration and/or the use of a lesser amount of etherifying agent generally favors the production of a water insensitive, rayon type material.

The shear precipitated particles of Brody et al., which are useful in the present invention are formed by precipitating the cellulose ether from solution with a combination of shearing conditions and coagulation rate to provide a total shear value (R_s') as defined herein between about 3 and 10,000 and preferably between about 100 and 1600.

The dimension "total shear value" (R_s'), is defined by the formula

$$R_s' = \frac{V_p}{V_s R_p t}$$

wherein V_p and V_s are the viscosities of the precipitant and the cellulose ether solution respectively, in poises measured at their respective temperatures just prior to combining to form the precipitant, t is the time in microseconds during which the precipitate is deformable and R_p is the rate of shear for the precipitant. For use as a pulp component it is preferred that the length of the dewatered precipitated particles be between about 8 millimeters and 0.5 millimeter. Particles as long as 20 millimeters may be processed on some equipment however. Particles less than about 0.001 millimeter are generally too fine to be of practical value. Typical processes for preparation of these particles are included hereinafter.

Although each of the particle types described above will normally be used in the process of the present invention without drying, they are each characterized by a

high capacity for water absorption after being dewatered, for instance by solvent interchange or the use of salt solution to cause gel syneresis. In the water wet form, the particles are highly gelatinous.

TEST AND CHARACTERIZATION PROCEDURES

The test and characterization procedures employed in measuring various properties reported herein are listed in Table I below. Unless otherwise indicated the code letter numerals indicate standard TAPPI tests.

TABLE I

Property	Test Procedure
Canadian Std. Freeness.....	T227-58.
CSI Abrasion.....	ASTM D-1175-55T (Method A).
Elmendorf Tear.....	T414M49.
Elongation.....	T457.
MIT Fold.....	T423M50.
Mullen Burst.....	T403M53.
Porosity.....	T460M49.
Spencer Puncture.....	Thwing Albert Instrument Co., Phila., Pa. Directions for Spencer Puncture Tester.
Stiffness.....	T451M60.
Tensile Strength.....	Revised T404 (Proposed TAPPI method under TAPPI Project 760).
Work-to-Break.....	Do.

The progressive height flat drop test is used to evaluate bag performance. A bag is filled with 94 pounds (42.6 kg.) of cement, closed and then dropped flat on its face from a height of 24 inches (64 cm.), dropped on the opposite face for each successive drop and the height increased in 6 inch (15.2) increments for each drop to a maximum of 10 feet (3.05 m.). The bag is dropped in this manner until it fails. The bags are stored, filled and tested at 73° F. (23° C.) and 50% R.H.

Water absorption is determined by placing a sample of the material weighing approximately 1 gram in about 300 grams of water at room temperature and soaking for 30 minutes. The sample is removed and spread out to cover a 2" x 2" (5.1 x 5.1 cm.) square area on bleached sulfite blotter paper. The sample is placed between layers of blotter paper and loaded with a 3 kilogram weight to give a pressure of 1.6 lb./sq. in. (112.5 g./cm.²). Pressure is applied for five minutes after which the sample is removed and weighed, giving the wet weight. Then the sample is dried to constant dry weight using a Noble and Woods sheet dryer at 100° C. Absorbency equals wet weight minus dry weight divided by dry weight.

By the expression "extensible papers" is meant a paper having an increased elongation (generally a minimum of about 6%) in the machine direction. Such papers can be made by compacting during drying as taught by Cluett U.S. Patent 2,624,245, and other methods such as the creping procedures taught in Reissue Patent 25,335, 2,494,334 and others.

By "basis weight" is meant the weight of a ream (500 sheets) of 24 x 36" (61 x 92 cm.) paper.

The following examples are cited to illustrate the invention. They are not intended to limit it in any manner.

Example 1

Clupak papers are prepared on a Fourdrinier machine, the Clupak unit being located between the first and second dryers. Speed at the wet end is 91 feet per minute and after Clupaking 81½ feet per minute. The Clupak is operated at 20 lbs. per square inch. The dryer is maintained at 112° C. and the second at 121° C. Four runs are made, each using 1000 pounds of southern pine kraft pulp which has been beaten in a Hollander beater to the extent indicated in Table I below. Original morphology additive particles identified in the table, are introduced at the beater chest at a concentration of 5% by weight based on the weight of the pulp in the furnish.

TABLE I

Run	Additive	Beating Time (Min.)	Freeness	
			Beater	Headbox
1A	None	150	550	515
1B	Hydroxyethyl cellulose	135	550	515
1C	Cyanoethyl cellulose	140	600	490
1D	Carboxyethyl cellulose	95	650	495

The hydroxyethyl cellulose used has a degree of substitution of 0.15 and is available on the open market under the trademark "Ethyner" from Rayonier, Inc., of 161 East 42nd St., New York, N.Y. The cyanoethyl cellulose particle is prepared from cotton linters steeped in aqueous alkali to form alkali cellulose containing 15.5% sodium hydroxide, 53.3% water and 31.2% total cellulose. After aging at room temperature for 4 days, 0.127 g. of acrylonitrile per gram cellulose, is reacted with the cellulose in a baratte. The product is then added to an aqueous neutralizing bath containing 5% H₂SO₄ and 15% Na₂SO₄ and is thereafter drained and soaked in an aqueous dewatering and buffering bath containing 17% Na₂SO₄ and 3% Na₂HPO₄. The product is drained and centrifued. The cyanoethyl cellulose so produced contains about 4.65% nitrogen corresponding to 0.65 mole of cyanoethyl per glucose unit and 0.01 moles of carboxyethyl groups per glucose unit. To prepare the carboxyethyl cellulose particles, a portion of the cyanoethyl cellulose particles prior to neutralization, prepared as described above, is stored in plastic bags for two days at room temperature. The aged product is then neutralized and dewatered. It is observed to contain 0.19 mole of carboxyethyl group per glucose unit.

While it is not necessary to use a "dry" or dewatered particle to obtain the beneficial results of the process of the present invention, the water absorptive capacity of the particles has been found to provide an indication of the effectiveness of the additive particles, those possessing the higher water absorptive capacities being the more effective. Generally those particles with a water absorptive capacity of from about 1.7 grams to about 30 grams of water per gram of cellulose derivative are particularly effective. The water absorptive capacity (in grams/gram) of the three cellulose derivatives employed in this example is reported in Table II below.

TABLE II

Additive:	Absorptive cap.
Hydroxyethyl cellulose	1.7
Cyanoethyl cellulose	1.8
Carboxyethyl cellulose	6.5

In runs 1A and 1B of this example, rosin size (0.3% by weight based on the weight of plup) is added at the beater and the pH is adjusted to 4.5 with alum. The stock, having a consistency of 3.6% is dropped to the beater chest and is then pumped to a second chest, passed through a Jordan and continuously diluted with "white water" at the Fourdrinier headbox to a consistency of 0.3%. Properties measured on the various papers is reported in Table III. Each paper has a basis weight of from 49.4 to 50.3 pounds per ream.

TABLE III

Property		1A	1B	1C	1D
		Tensile (lbs./in.)	MD 15.6 CD 12.6	16.0 13.0	18.2 14.3
Elongation (percent)	MD 10.1 CD 3.7	11.2 4.3	9.9 4.4	9.7 4.6	
Work-to-break (in.-lbs./in. ²)	MD 1.01 CD 0.34	1.05 0.41	1.14 0.47	1.34 0.50	
MIT Fold	MD 380 CD 106	398 94	496 132	1,021 167	
CSI Abrasion (cycles)	MD 14 CD 7	-----	20 37	25 64	

Example 2

The paper making technique of Example 1, modified to provide paper with machine direction elongations of 1.4 and 11% respectively (Samples 2E and 2F respectively) and employing the furnish of Sample 1D, is followed. Two ply cement sacks of a commercial design (pasted valve) are made from the above papers. The bags are subjected to a progressive height flat drop test. The following results are obtained:

TABLE IV

Sample	Total basis weight (lb.)	Average safe drops	Average total inches of drop
2E	103	2.0	63
2D	105	10.2	564

Example 3

As demonstrated above, the additive particle of the present invention is of value as a furnish additive in conventional Clupaking. It has been found to be of particular value in a modification of the Clupak technique wherein cross directional shrinkage of the paper is facilitated by controlling the temperature of the dryer sections (front end about 270° C. and final end about 180° F.) and running at a relaxed draw (obtained by loosened felts). The cross-directional shrinkage technique is also valuable in upgrading the properties of non-extensible papers as will be demonstrated hereinafter. The preferred particle for use in the technique of cross-directional shrinkage is that of Belgian Patent 613,355 referred to above. In preparing such materials for use in the process of the present invention, conventional cotton linter sheets are steeped in 19% by weight caustic soda solution, and thereafter hydraulically pressed to a 3/1 (total/cellulose) press weight ratio. The sheets of alkali cellulose are then shredded, and held for subsequent processing in a refrigerated space at under 5° C. The cotton linter alkali cellulose so produced has the composition shown below:

	Percent by weight
Precipitable cellulose	31.2
Sodium hydroxide	15.75
Water	53.05

Twenty pounds of the above alkali cellulose are charged to a 12-gallon baratte. The baratte is rotated and warmed to an internal temperature of 25° C. at which time 2.13 pounds of carbon disulfide and 2.27 pounds of acrylonitrile is added over a ten minute interval. During the simultaneous xanthation and cyanoethylation the temperature of the reaction mass is maintained at about 30° C. The reaction requires about 30 minutes and its termination is indicated by a cessation of the evolution of heat by the reaction mass. The cyanoethyl cellulose xanthate product is then dissolved in a 4% sodium hydroxide solution and cooled to 5° C. Properties of the cyanoethyl cellulose viscose at this point are shown in the following table.

Salt index	18.
Viscosity	Range from 30 to 50 Du Pont seconds at 18° C.
Percent cellulose	5.0 (approx.).
Percent alkalinity	5.44.
Percent total sulfur	1.12.
Percent total nitrogen	0.43.
Degree of ether substitution ¹	0.42.

¹ Measured on precipitated and regenerated particle.

The solution is shear precipitated by feeding it from a manifold at 19° C. and under a pressure of about 80 pounds per square inch gauge through twelve holes of 0.02 inch diameter into a 1/8 inch tubing passing through the manifold, through which tube an aqueous precipitant containing 5% by weight sulfuric acid and 15% by weight sodium sulfate is being fed at a temperature of about 35° C. and under a pressure of about 120 pounds per square

inch gauge. The system provides a total shear value of about 351. The fibrous precipitated particles are collected on a wire screen and compressed with a squeeze roller into 1/2 inch thick mats. The mats are then stored at room temperature for at least 30 minutes to insure complete regeneration of the cyanoethyl cellulose and thereafter neutralized by immersion in a bath containing 17 percent by weight of sodium sulfate and 2 percent by weight of disodium monohydrogen phosphate, adjusted to a pH between 5.0 and 6.0. After draining to approximately 10 percent by weight of solids, the mass is centrifuged to about 30 percent by weight solids. The particles have a water absorbency of about 9 grams of water per gram of particle.

The additive particles, prepared as described above and referred to hereinafter as the "regenerated particles," are used to manufacture a series of papers. In the paper preparations, 1000 pounds of southern pine kraft are beaten in a Hollander beater for 130 minutes to a Canadian standard freeness of 550 cc. The stock has a pH of 9.0 and a consistency of 3.55%. It is transferred to a beater chest and through a pony Jordan to the Fourdrinier headbox where it is diluted to 0.28% consistency. Paper 3E, a non-extensible comparative control with a 45 pound basis weight, is processed under standard conditions at 90 ft./min. to give a 39" trim sheet. A second beater load is similarly processed with the additional step of Clupaking to give a machine direction elongation about at least 10%. The "Clupak" unit is located between the second and third dryers. The first dryer is at room temperature. Temperatures in the second and third dryers are in Table V. Speed at the dry end is 95 feet (29 m.)/min. and 86 ft. (26.2 m.)/min. after "Clupak" with a pressure of about 20 lbs. per square inch (140 g./cm.²) on the blanket. This paper, an extensible comparative control is labelled 3F.

In a third beater 1100 lbs. of southern kraft is taken down to 600 Canadian standard freeness in 155 minutes and 8% of the regenerated particles described above are added at the beater chest. The particle addition lowers the freeness to 410. The stock is then pumped to the headbox and diluted to give a consistency of 0.37% and a pH of 7.7. The sheet is processed under standard wet end conditions. The temperatures of the dryers sections is noted in Table V. The dryers are run at slack draw (i.e. with loosened felts). Relaxation and shrinkage in the cross direction are obtained, evidenced by a final 38" trim sheet. This non-extensible made using the cross directional shrinkage technique is labelled 3G. Another portion of the same stock is processed under the same conditions but employing, in addition, the "Clupak" attachment set to give machine direction elongation of about 10%. The extensible paper, formed with cross directional shrinkage is labelled 3H.

The four papers obtained above are tested for physical properties at 65% relative humidity at a temperature of 73° F. Observations are reported in Table V.

TABLE V

		3E	3F	3G	3H
5	Basis Weight (lbs./ream)-----	46.0	47.0	45.6	43.5
	Tensile (lbs./in.)-----	MD 26.0 CD 14.3	13.4 10.5	33.9 25.6	17.9 17.9
	Elongation (Percent)-----	MD 2.7 CD 5.8	16.2 6.6	4.4 11.1	18.8 11.0
	Work-to-break (in.-lbs./in. ²)-----	MD 0.42 CD 0.46	1.26 0.52	0.90 1.8	2.5 1.4
	Elmendorf Tear (gms.)-----	MD 107 CD 117	122 124	82 95	57 101
	Mullen Burst (p.s.i.)-----	25	29	49	52
10	Spencer Puncture (2 ply basis) (in.-lbs./in. ²)-----	2.4	3.2	3.9	6.5
	MIT Fold-----	MD 370 CD 180	560 70	1,660 3,110	1,140 2,940
	CSI Abrasion (Cycles)-----	MD 4 CD 9	2 10	25 130	104 122
	15	Temp. (° C.):			
2d dryer-----		101	104	103	107
3d dryer-----		101	111	115	111

Comparison of the two comparative controls, 3E and 3F, shows that the "extensible kraft" 3F sacrifices tensile strength for increased machine direction (MD) elongation. Also, MD work-to-break is increased, but cross direction (CD) work-to-break remains nearly constant. Tear strength is slightly increased, both MD and CD. Burst strength and puncture resistance (non-directional properties) are higher. Fold strength is improved in MD, but much poorer in CD, while abrasion resistance is cut in half.

Comparing the control non-extensible paper 3E, with the non-extensible paper made with cross directional shrinkage 3G, shows improvement in almost every physical property resulting from the cross directional technique. Tensile strength is increased in both directions. Elongation is up 50% MD, and up 80% CD. Work-to-break is doubled MD, and tripled CD. Increases in fold and abrasion properties are up by factors ranging from 4 to 15. Sheet 3G is considered to offer high potential as a bagging material comparing well with extensible control 3F.

Improvement in properties of the extensible paper made using cross-directional shrinkage 3H over the extensible comparative control 3F is obvious.

Example 4

The procedures of Example 3 are repeated in large scale runs involving the preparation of kraft papers suitable for manufacture of multi-wall bags. Five separate runs are made, the first, 4I, being a non-extensible control and the second being an extensible control, 4J, made under the same conditions as 4I except for use of Clupaking. In runs 4K, 4L, and 4M, extensible papers are made using the cross-directional technique of Example 3 with pulps containing 8%, 6% and 6% respectively of regenerated particles. Paper 4N, a non-extensible paper but made with cross-directional shrinkage contains 8% by weight of the regenerated particles. The papers are tested and the physical properties are summarized in Table VI below. These physical properties were determined at 50% relative humidity and 73° F.

TABLE VI

	4I	4J	4K	4L	4M	4N
Freeness kraft blend on wire-----	650	650	650	650	650	715
Basis Weight (lbs./ream-24x36-500)-----	49.6	50.6	52.1	48.7	98.9	48.3
Tensile (lbs./in.)-----	MD 23.8 CD 10.2	11.7 9.2	32.2 28.0	24.7 21.2	65.3 40.2	24.0 19.1
	MD 1.5 CD 3.1	11.9 3.8	12.8 6.6	10.5 6.1	10.0 6.9	9.8 5.0
Elongation (percent)-----	MD 0.23 CD 0.22	0.83 0.26	2.08 1.05	1.55 0.89	3.60 1.93	1.31 0.65
	MD 98 CD 91	89 127	100 116	98 107	191 273	101 122
Spencer Puncture (in.-lbs./in. ²)-----	1.17	1.96	6.20	4.82	>12.0	3.85
Mullen burst (p.s.i.)-----	22.8	20.8	55.0	49.0	108.0	42.0
MIT Fold (cycles)-----	MD 80 CD 25	130 30	3,050 940	1,880 840	2,640 1,270	1,970 630
	MD 3.0 CD 8.0	4.9 8.3	91.6 134	27.3 198	59.0 730	13.4 63
C.S.I. Abrasion (cycles)-----	MD 3.5 CD 1,720	5.8 18.1	163 42.6	132 40.2	580 199	65 41.7
	MD 62.6 CD 37.5		61.4	57.4	208	63.3

Multiwall bags of a commercial design with a sewn valve are made of papers 4I, K, L, and N by a commercial bag fabricator.

Thirty of each of the bags are loaded with 100 pounds of sand and submitted to the constant height drop test. In this test a loaded bag is dropped from a height of 3 feet on its face and turned over to drop on the alternate fact until the bag fails. The average number of drops to failure is reported in Table VII.

TABLE VII

Paper	Bag plies	Total basis wt. (lb.)	Drops
4I.....	4	194	1.0
4K.....	3	161	4.0
4L.....	2	97	1.9
4N.....	3	146	3.8

Example 5

While in conventional paper-manufacturing techniques it is standard practice to run the sheet taut on the felt in order to prevent cockle and wrinkle, as is demonstrated herein, the present invention provides a wet sheet which is capable of relaxation as it emerges from the wet press section, a sheet which does so relax, and a sheet which after relaxation exhibits substantial improvements in performance, specifically in toughness and isotropic strength. In the large-scale practice of the present invention, the wet sheet which emerges from the wet press section with a water content of about 65% by weight, is run on the felt with minimum machine direction tension to permit maximum cross-direction relaxation, and to permit some machine-direction relaxation as well. A minimum of 3% shrinkage in the cross direction is recommended, and 4%-6% is preferred. In operating with hand sheets, shrinkage up to 20% in each direction has been achieved, and is accompanied by beneficial results.

With unmodified papermaking machinery, the machine is preferably operated with the sheet slack, with zero draw or less. With festoon or tunnel drying machinery, the system permits taking as much as 10% relaxation in the machine direction. This provides a final sheet of maximum toughness.

To further demonstrate the highly beneficial nature of cross directional shrinkage at various concentration levels of the regenerated particle additive, non-extensible paper products are made employing southern pine kraft. A portion of the paper is made by the standard commercial process, while a second portion is wet-relaxed overnight during processing after which it is dried. Sample 5P is a comparative control containing no additive particle of the present invention. Samples 5Q and 5R contain 4% and 9% by weight respectively of the regenerated additive particle identified above. Samples 5P, Q and R are unrelaxed. Samples 5P', Q', and R' are relaxed. Properties of the papers are shown in Table VIII.

TABLE VIII

		5P	5P'	5Q	5Q'	5R	5R'
Tensile (Lb./in.).....	(MD.....)	29.1	26.1	36.3	39.0	43.9	45.2
	(CD.....)	14.2	13.9	18.8	18.7	24.2	21.6
Elongation (percent).....	(MD.....)	3.6	5.0	3.1	6.0	3.6	7.1
	(CD.....)	6.6	8.3	7.0	12.1	11.6	15.0
Burst (p.s.i.).....	(MD.....)	41.6	48.7	55.3	74.8	79.0	94.6
	(CD.....)	895	715	1,525	4,120	5,250	7,580
Fold (MIT) (cycles).....	(MD.....)	270	710	1,650	1,525	3,490	2,790
	(CD.....)	1.38	1.26	1.07	1.03	1.04	0.90
Elmendorf Tear (g./g./m. ²).....	(MD.....)	1.59	1.57	1.11	1.25	1.10	1.00
	(CD.....)	51	49	47	51	52	54
Ream wt. lbs. 24 x 36-500.....	(MD.....)	0.47	0.84	0.72	1.42	0.98	1.90
	(CD.....)	0.47	0.79	0.90	1.52	1.91	2.34

While applicant does not wish to be bound by any theory of operation, it is believed that relaxation as described above permits realignment of the cellulose fibers in a more random configuration. However, randomness of the fibers cannot alone account for the high toughness of the present products. Hand sheets of kraft pulp—necessarily completely random in fiber distribution—do not have such toughness. It is apparent that some synergistic and beneficial combination of effects is achieved in the present invention, even though the mechanism by which it operates is not fully known.

Example 6

This example illustrates the increased cross-directional shrinkage obtained when the regenerated additive particle is used in the furnish in the process of this invention.

Southern pine kraft pulp with a Canadian standard freeness of about 750 to 780 is continuously fed from a pulp mill to a Hollander beater (without a bed plate) where it is dispersed to a consistency of about 1 to 2%. This stock is beaten in 3 Jordans in series to provide a couch freeness of about 670 and transferred to a regulator box where it is diluted to the approximate consistency desired. This stock is then transferred to the Fourdrinier headbox where the consistency is adjusted to 0.3%.

The paper machine is a commercial design with a 104" wide wire and containing 30 drying sections in series. The process from headbox to dried paper takes about 2 minutes. The paper is a comparative control labelled 6S.

The same general process is used to make paper 6T except that 7.1% of the regenerated cyanoethyl cellulose particles of Example 3 above, are added to the Hollander beater with the pulp. A couch freeness (i.e. the Canadian standard freeness as measured on a sample of wet pulp removed from the felt immediately after the squeeze rolls) of 611 is obtained. The temperature of the steam in the dryers is maintained at about 149° C. A temperature of about 144 to 146° C. is used for 6S control and is about the maximum. Further operating details are reported in Table IX.

TABLE IX

	6S	6T
Paper machine speed feet/minute.....	520	530
Wet end width of paper, in.....	95.6	94.9
Dry end width of paper, in.....	92.7	90.1
Percent of wet width shrinkage.....	3.0	5.2

Properties of the two papers are shown in Table X.

TABLE X

Paper Properties		6S	6T
Basis weight, lbs.....	(MD.....)	46.4	52.4
	(CD.....)	1.2	2.0
Elongation, percent.....	(MD.....)	2.6	4.7
	(CD.....)	18.6	48.0
Tensile:	Lbs./in.....	12.1	21.6
	Lbs./in.....	18.6	48.0
Work-to-break:	In.-lbs./in ²	0.125	0.570
	In.-lbs./in ²	0.205	0.700

Suitable cellulose derivatives for use in the process of the present invention include the alkyl ethers, such as ethylcellulose; the carboxyalkyl ethers, such as carboxymethylcellulose and carboxyethylcellulose; the hydroxyalkyl ethers, such as hydroxyethylcellulose; the arylalkyl ethers, such as benzylcellulose; and other beta-substituted alkyl ethers, such as cyanoethylcellulose.

Mixed ethers may also be used. For example, some of the nitrile groups in cyanoethylcellulose may be hydrolyzed; part of these may stop at the amide stage and the remainder be converted to carboxyl groups. Thus, there would be three types of ether groups present. Mixed ether-ethers may also be used, e.g., one containing a mixture of acetate and ether groups. Salts of the derivatives may be used. Cellulose esters such as the acetate and nitrate may be used.

The original morphology cellulose derivative particles must be water-insoluble but water-swellaible. Although this combination of properties is a function of the substituent group, the molecular weight of the cellulose derivative and the degree of substitution it has been found that suitable particles can be selected based on the degree of substitution and the water absorbency values. The degree of substitution should range from about 0.01 to 0.8 mole of substituent per glucose unit and preferably from 0.1 to 0.8. The water absorbency should range from about 1.7 to 30 grams and preferably from about 6 to 20 grams.

Many equivalent modifications of the above described invention will be apparent to those skilled in the art without a departure from the inventive concept.

What is claimed is:

1. A process for producing an uncreped paper web of water-laid, adherent, cellulose fibers, with smooth, substantially parallel faces and substantial permanent extensibility in excess of the primitive elastic limit of the web, and which suffers no substantial decrease in thickness when elongated by stretching, which comprises depositing, upon a foraminous surface a furnish comprising (I) cellulose fibers and (II) from about 1% to about 10%, based on the total dry weight of the furnish, of an additive particle of highly swollen, water insoluble cellulose derivative containing a deep seated substituent from the class consisting of an ether, an acid, a nitrile, an ester and mixtures thereof, the degree of substitution of the said cellulose being from about 0.01 to about 0.8, the said particle having been formed from an alkali cellulose particle swollen by steeping in aqueous alkali containing from about 14% to about 30% by weight caustic prior to derivative formation, the said furnish being characterized by a Canadian standard freeness at the headbox of from about 450 to about 650, the web so formed being thereafter subjected to an after-treatment comprising moving said web in a direction lengthwise thereof, and while in the physical condition it possesses as it leaves the wet end of a paper making machine, slowly removing a part only of the moisture from said paper web, and uniformly pushing and crowding the fibers of the partially dried web together in the space between the faces of the web as laid, continuous through the web, and by forces acting in a direction parallel to the faces of the web, oppo-

site to the direction of movement, and throughout the pushing and crowding confining the web against creping by pressures on the web normal to said web faces.

2. The process of claim 1 wherein the said additive particle is unregenerated.

3. The process of claim 1 wherein the said additive particle is regenerated.

4. The process of claim 3 wherein the said particles are shear precipitated particles of a hydrophylic, water-insoluble, microscopically uniform etherified cellulose having a degree of substitution upon partially substituted cellulose polymer chains of from about 0.1 to about 0.7.

5. The process of claim 1 wherein the said cellulose derivative is an ethyl ether.

6. The process of claim 1 wherein the said cellulose derivative is cyanoethyl cellulose.

7. The process of claim 1 wherein the said cellulose derivative is carboxyethyl cellulose.

8. A process for preparing a sheet product which comprises depositing, upon a foraminous surface, an aqueous suspension of a composition comprising (I) cellulose pulp and (II) from about 2% to about 95%, based on the weight of solids in the said composition of shear precipitated particles of a hydrophylic, water-insoluble, microscopically uniform etherified cellulose having a degree of substitution upon partially substituted cellulose polymer chains of from about 0.1 to about 0.7, the web formed in a relaxed state during removal of water for a period of time sufficient to provide shrinkage in cross direction of at least about 3%.

9. The process of claim 8 wherein the said cellulose pulp is a sulfate pulp.

10. The process of claim 9 wherein the said etherified cellulose is cyanoethylated cellulose.

11. The process of claim 10 wherein the said web is subjected to an after-treatment comprising moving said web in a direction lengthwise thereof, and while in the physical condition it possesses as it leaves the wet end of a paper making machine, slowly removing a part only of the moisture from said paper web, and uniformly pushing and crowding the fibers of the partially dried web together in the space between the faces of the web as laid, continuous through the web, and by forces acting in a direction parallel to the faces of the web, opposite to the direction of movement, and throughout the pushing and crowding confining the web against creping by pressures on the web normal to said web faces.

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