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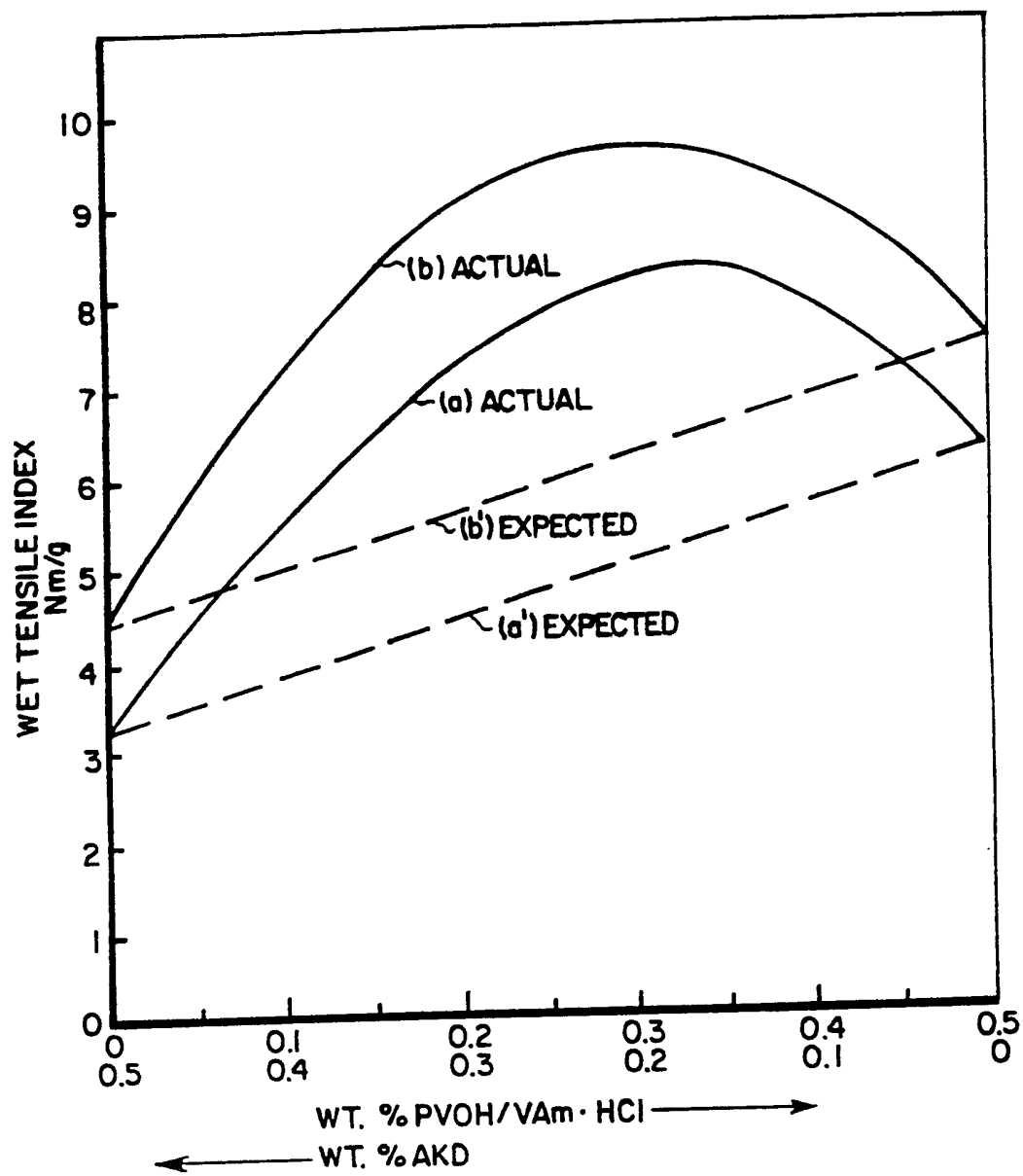
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## (54) Paper wet-strength improvement

(57) The wet strength of cellulosic paper is improved by wet- or dry-end addition of an amine-functional poly(vinyl alcohol) and a cellulose reactive size which is a 4 or 5 membered cyclic ester or anhydride having one or more alkyl or alkenyl substituents of 4 or more carbon atoms and having a total of at least 8 carbon atoms in said substituent(s). The amine-functional polymer is preferably a hydrolyzed copolymer of vinyl acetate and N-vinyl formamide or acetamide, and the cellulose reactive size is preferably an alkyl ketene dimer or an alkenyl succinic anhydride.

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## PAPER WET-STRENGTH IMPROVEMENT

This invention relates to a method of improving the wet-strength properties of cellulosic paper. In another aspect it relates to paper containing the combination of a cellulose reactive size and an amine functional poly(vinyl alcohol).

In order to improve paper properties and reduce manufacturing costs in papermaking, various additives are applied to the pulp slurry prior to sheet formation or after an initial drying of the paper. Those additives applied to the pulp in an aqueous slurry are known as wet-end additives and include retention aids to retain fines and fillers, for example, alum, polyethylene imine, and cationic starches; drainage aids, such as polyethylene imine; defoamers; and pitch or stickies additives, such as microfibers and adsorbent fillers. Other wet-end additives include polymers such as, cationic polyarylamides and poly(amide amine/epichlorohydrin) which are added to improve wet strength as well as dry strength of the paper. Starch, guar gums, and polyacrylamides are also added to yield dry strength improvements. Sizing agents are occasionally added to impart hydrophobic character to the hydrophilic cellulosic fibers. These agents are used in the manufacture of paper for liquid containers, for example, milk or juice, paper cups and surfaces printed by aqueous inks where it is desired to prevent the ink from spreading. Such sizing agents include rosin sizes derived from pine trees, wax emulsions and, more recently, cellulose-reactive sizes.

The application of additives to paper after an initial drying of the sheet by, for example, spraying, capillary sorption, immersion, and roll-coating, is often referred to as a dry-end addition. Poly(vinyl alcohol), acrylic or

vinyl acetate emulsions, starches, sizing agents, polyurethanes, and SBR latex are commonly added at the dry end.

5           Improvements are continually sought in wet-strength additives for paper. Improved speed of wet-strength development is desired and many wet strength additives require both time and temperature to develop their wet strength properties. Initial wet strength is desired to  
10 improve the wet web strength during paper formation. A review of the utility of paper additives is given by G. G. Spence, Encyclopedia of Polymer Science and Technology, Second Edition, Wiley-Interscience, Vol. 10, pgs. 761-786, New York (1987).

15

          The use of functional polymers of various types has been known for many years as a means to improve papermaking processes and paper properties. Several of these resins for improving wet strength of the paper have involved  
20 products derived from epihalohydrin. US-A-3,535,288 Lipowski, et al. (1970) discloses an improved cationic polyamide-epichlorohydrin thermosetting resin as useful in the manufacture of wet-strength paper. US-A-3,715,336 Nowak, et al. (1973) describes vinyl alcohol/vinyl amine  
25 copolymers as useful flocculants in clarification of aqueous suspensions and, when combined with epichlorohydrin, as useful wet-strength resins for paper. The copolymers are prepared by hydrolysis of vinyl carbamate/vinyl acetate copolymers made by copolymerization  
30 of vinyl acetate and vinyl isocyanate followed by the conversion of the isocyanate functionality to carbamate functionality with an alkanol. Additionally, CA-A-1,155,597 (1983) discloses wet-strength resins used in papermaking, including polymers of diallylamine reacted  
35 with epihalohydrin and a vinyl polymer reacted with epihalohydrin wherein the vinyl polymer is formed from a

monomer prepared by reacting an aromatic vinyl alkyl halide with an amine, such as dimethylamine.

Functional polymers derived from amides have also been  
5 used to improve paper processes. US-A-3,597,314 Lanbe, et al. (1971) discloses that drainage of cellulose fiber suspensions can be enhanced by the addition of a fully or partially hydrolyzed polymer of N-vinyl-N-methyl carboxylic acid amide. US-A-4,311,805 Moritani, et al. (1982)  
10 discloses paper-strength additives made by copolymerizing a vinyl ester, such as vinyl acetate, and an acrylamide derivative, followed by hydrolysis of the ester groups to hydroxy groups. The presence of the remaining cationic groups enables the polymer to be adsorbed on pulp fibers.  
15 Utilities for the polymers as sizing agents, drainage aids, size retention aids and as binders for pigments are disclosed but not demonstrated. US-A-4,421,602 Brunnmueller, et al. (1983) describes partially hydrolyzed homopolymers of N-vinyl formamide as useful as retention  
20 agents, drainage aids and flocculants in papermaking. EP-A-0,331,047 (1989) notes the utility of high molecular weight poly(vinyl amine) as a wet-end additive in papermaking for improved dry strength and as a filler retention aid.

25

More recently, vinyl amide copolymers have been disclosed as useful in papermaking to improve the properties of the product. US-A-4,774,285 Pfohl, et al. (1988) describes amine functional polymers formed by  
30 copolymerizing vinyl acetate or vinyl propionate with N-vinyl formamide (NVF) followed by 30-100% hydrolysis to eliminate formyl groups and the acetyl or propionyl groups. The copolymer contains 10-95 mole% NVF and 5-90 mole% vinyl acetate or vinyl propionate. The hydrolyzed copolymers are  
35 useful in papermaking to increase dry strength and wet strength when added in an amount of 0.1 to 5 wt% based on

dry fiber. The polymer can be added to the pulp or applied to the formed sheet. The two polymers used to show dry and wet strength improvements are said to contain 40% and 60% N-vinyl formamide before hydrolysis. Lower levels of amine functionality in poly(vinyl alcohol) are not demonstrated to be effective.

US-A-4,808,683 Itagaki, et al. (1989) describes a vinyl amine copolymer such as a copolymer of N-vinyl-formamide and N-substituted-acrylamide, which is said to be useful as a paper strengthening agent and EP-A-0,251,182 (1988) describes a vinyl amine copolymer formed by hydrolysis of a copolymer of N-vinyl formamide and acrylonitrile or methacrylonitrile. The product is said to be useful in papermaking as a drainage aid, retention aid and strength increasing agent. Examples presented to demonstrate the paper strengthening effect of the polymer used a pulp slurry containing cationic starch, alkyl ketene dimer as a sizing agent and a filler retention improving agent, but there is no indication of any cooperative effect between the polymer and the sizing agent.

On the other hand, certain combinations of additives have been found to be useful as paper additives. US-A-4,772,359, Linhart, et al. (1988) discloses utility of homopolymers or copolymers of N-vinyl amides, such as N-vinyl formamide (NVF), in combination with phenol resin as a drainage aid in pulp slurries for production of paper. In this service unhydrolyzed poly NVF is said to function cooperatively with the phenol resin, while a partially hydrolyzed poly NVF does not (see Example 6). EP-A-0,337,310 (1989) describes improving moist compressive strength of paper products using the combination of hydrolyzed poly(vinyl acetate-vinyl amide) and an anionic polymer such as carboxymethyl cellulose or anionic starch. The hydrolyzed polymer can contain 1-50 mole% vinyl amine

units and examples are given of polymers having amine functionality of 3-30%.

5       The contribution of Spence to the Encyclopedia of  
6       Polymer Science and Engineering, noted above, provides a  
7       comprehensive survey of paper additives describing the  
8       functions and benefits of various additives and resins used  
9       in the manufacture of paper. Wet-end additives are  
10      discussed at length. Resins containing amine groups that  
11      provide cationic functionality and have low molecular  
12      weights ( $10^3$  to  $10^5$ ) e.g., polyethylene imine, are used to  
13      aid retention of fines in the paper. Acrylamide-based  
14      water soluble polymers are used as additives to enhance dry  
15      strength of paper while a variety of resins, such a  
16      melamine-formaldehyde resins, improve wet strength.  
17      Polyethylene imine, however, is said not to be commercially  
18      significant as a wet-strength resin. Sizing agents are  
19      used to reduce penetration of liquids, especially water,  
20      into paper which, being cellulosic, is very hydrophilic.  
21      Sizing agents disclosed are rosin-based agents, synthetic  
22      cellulose-reactive materials such as alkyl ketene dimer  
23      (AKD), alkenyl succinic anhydrides (ASA) and anhydrides of  
24      long-chain fatty acids, such as stearic anhydride, wax  
25      emulsions and fluorochemical sizes. Cationic retention  
26      aids, such as alum, cationic starch or aminopolyamide-  
27      epichlorohydrin wet-strength resin, are used to retain the  
28      size particles in the sheet.

29       Marton, TAPPI J., pages 139-43 (Nov. 1990) discusses  
30      alkyl ketene dimer reactions and points out that hydrolysis  
31      is a competing reaction to the esterification reaction  
32      between AKD and cellulose, reducing the effectiveness of  
33      the size. The AKD size emulsions were stabilized with  
34      cationic starch or polyamine amide-epichlorohydrin resin,  
35      the latter exhibiting much higher hydrolysis rates. Both  
36      AKD and ASA form covalent ester bonds with cellulose-OH

groups, but react also, depending upon conditions, with other OH groups in the surrounding medium, foremost through hydrolysis with water.

5           Zhou, Paper Technology, pages 19-22 (July 1991) discusses AKD sizing studies which suggest that AKD sizing increases over a period of time after application, particularly at elevated temperatures.

10           We have discovered an unexpected synergistic cooperation between amine-functional poly(vinyl alcohol) polymers and cellulose reactive sizes in the production of cellulosic paper having improved wet-strength properties. The cellulose-reactive size is a compound which is a 4 or 5  
15   membered cyclic ester or anhydride having one or more alkyl or alkenyl substituents, each of which contains at least 4 carbon atoms and having a total of at least 8 carbon atoms in said substituent(s). The polymers are preferably made by copolymerization of vinyl acetate and N-vinyl formamide  
20   followed by hydrolysis to form a copolymer having a relatively low amine functionality of 1-25 mole% based upon the incorporated monomer. The preferred sizing agents are alkyl ketene dimers or alkyl succinic anhydrides.

25           According to our invention a cellulosic paper product having improved wet-strength is provided containing products formed by the addition to the paper during manufacture of the combination of an amine-functional poly(vinyl alcohol) resin and a cellulose reactive size  
30   which is a 4 or 5 membered cyclic ester or anhydride having one or more alkyl or alkenyl substituents containing at least 4 carbon atoms and having a total of at least 8 carbon atoms in said substituent(s).

35           The sole figure of the drawings is a graph comparing wet tensile properties of paper products of the invention



containing various combination levels of alkyl ketene dimer (AKD) and polyvinyl alcohol/vinyl amine copolymer (PVOH/VAm•HCl) with expected additive results based upon values obtained using the amine functional poly(vinyl alcohol) alone and the alkyl ketene dimer alone.

It has been found that amine-functional poly(vinyl alcohol), in particular poly(vinyl alcohol/vinyl amine) copolymers, in combination with a cellulose-reactive size such as an alkyl ketene dimer or alkenyl succinic anhydride offer synergistic wet strength properties when incorporated into paper. The wet strength of the mixture (at constant solids) is higher than expected from the added effects of the copolymer and size when used alone. The intermediate mixtures offer higher wet strength than either of the constituents, even at the same total additive level. This improved wet strength obtained by combining a wet-strength polymer with a sizing agent was unexpected.

Poly(vinyl alcohol) (PVOH) is not effective as a wet strength additive or as an additive in the wet-end of a paper process because it is not substantive to paper and is removed in the presence of water. Surprisingly, low levels of amine functionality in poly(vinyl alcohol), preferably 1 to 25 mole percent based upon the incorporated monomers, show substantive characteristics with retention in the presence of water, leading to improved physical properties under both wet-end and dry-end addition to paper. At higher levels of amine functionality in poly(vinyl alcohol), the economics are generally less favorable and in some cases random copolymers are difficult to synthesize using procedures similar to those employed for producing poly(vinyl acetate). In fact, incorporation of more than 10 mole % N-vinyl formamide in poly(vinyl acetate) is difficult, as composition variation leads to the formation of non-homogeneous products. This can be alleviated by

proper delayed feed of the more reactive monomer (NVF).

5 The preferred routes to amine functional poly(vinyl alcohol) are to synthesize vinyl acetate/N-vinyl amides (e.g. N-vinyl formamide, N-vinyl acetamide) copolymers followed by hydrolysis of both the vinyl acetate (to vinyl alcohol) and the vinyl amide (to vinyl amine). Based on reactivity ratios and economics, incorporation of 5 to 20 mole % of the N-vinyl amide is desired. Another preferred  
10 route is to react poly(vinyl alcohol) with an aminoaldehyde or aminoacetal. The aldehyde (or acetal) reacts with the hydroxyls of PVOH yielding pendant amine groups. Up to 25 mole % of the aldehyde can be incorporated using this route.

15

Poly(vinyl alcohol) can be prepared from the hydrolysis of poly(vinyl acetate). The preparation of poly(vinyl acetate) and the hydrolysis to poly(vinyl alcohol) are well known to those skilled in the art and are  
20 discussed in detail in the books "Poly(vinyl alcohol): Properties and Applications," ed. by C. A. Finch, John Wiley & Sons, New York, 1973 and "Poly(vinyl alcohol) Fibers," ed. by I. Sakurada, Marcel Dekker, Inc., New York, 1985. A recent review of poly(vinyl alcohol) was given by  
25 F. L. Marten in the Encyclopedia of Polymer Science and Engineering, 2nd ed., Vol. 17, p. 167, John Wiley & Sons, New York, 1989.

Poly(vinyl acetate) can be prepared by methods well  
30 known in the art including emulsion, suspension, solution or bulk polymerization techniques. Rodriguez in "Principles of Polymer Systems," p. 98-101, 403, 405 (McGraw-Hill, NY, 1970) describes bulk and solution polymerization procedures and the specifics of emulsion  
35 polymerization. Amine functional poly(vinyl alcohol) can be prepared by copolymerization of N-vinyl amides (e.g.

N-vinyl formamide or N-vinyl acetamide), N-allylamides (e.g. N-alkyl formamide), or allyl amine (including acid salts) with vinyl acetate using methods employed for poly(vinyl acetate) polymerizations. Above 10% (mole) incorporation of the N-vinyl amides leads to product variations unless delayed feed of the N-vinyl amides is employed. With allyl amine, about 10 mole % leads to lower molecular weight than desired, thus the desired vinyl alcohol polymers would contain up to 10 mole % allyl amine.

10

When preparing poly(vinyl acetate) by suspension polymerization, the monomer is typically dispersed in water containing a suspending agent such as poly(vinyl alcohol) and then an initiator such as peroxide is added. The unreacted monomer is devolatilized after polymerization is completed and the polymer is filtered and dried. This procedure for preparation of poly(vinyl acetate) can also be employed for the vinyl acetate copolymers (as precursors for amine functional poly(vinyl alcohol)) of this invention.

20

Poly(vinyl acetate) can also be prepared via solution polymerization wherein the vinyl acetate is dissolved in a solvent in the presence of an initiator for polymerization. Following completion of the polymerization, the polymer is recovered by coagulation and the solvent is removed by devolatilization. The vinyl acetate copolymers (as precursors for amine functional poly(vinyl alcohol)) can be prepared via this procedure.

30

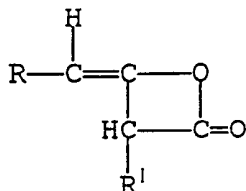
Bulk polymerization is not normally practiced in the commercial manufacture of poly(vinyl acetate) or vinyl acetate copolymers, but can be used if proper provisions are made for removing heat of polymerization.

35

The hydrolysis of the vinyl acetate/N-vinyl amide copolymers of this invention can be accomplished using

methods typically employed for poly(vinyl alcohol) as noted in the reference supra. Either acid or base hydrolysis can be conducted to yield the amine functional poly(vinyl alcohol) desired. In the case of acid hydrolysis, the amine group is protonated to yield a positive charge neutralized with an anionic group (e.g.  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{HSO}_4^-$ , and  $\text{H}_2\text{PO}_4^-$ ). Both the amine ( $-\text{NH}_2$ ) or protonated versions ( $\text{NH}_3^+\text{X}^-$ ) are suitable in this invention.

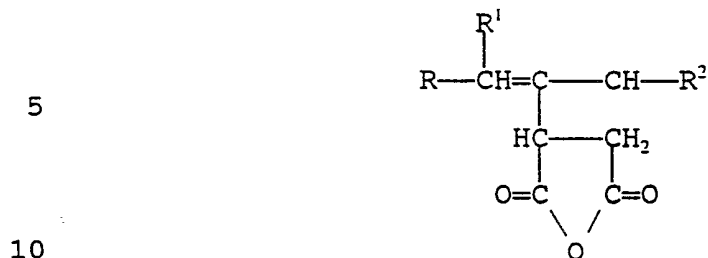
The cellulose reactive sizes of greatest interest for this invention are alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA). The alkyl ketene dimer can be represented by the structure:



where  $\text{R}$  and  $\text{R}'$  are independently straight or branched chain alkyl or alkenyl groups containing 4 to 20 carbon atoms.

Preferably  $\text{R}$  and  $\text{R}'$  are identical. In addition to the references given in the Background section, AKD technology is discussed by Gess and Lund, TAPPI J., p. 111 (Jan. 1991) and Cates et al. "The Sizing of Paper", ed. by W. F. Reynolds, TAPPI Press, Atlanta (1989). Such materials are well known to comprise an equilibratable mixture of vinyl  $\beta$ -lactones and 2,4-substituted cyclobutane-1,3-diones.

Alkenyl succinic anhydride (or acid) (ASA) has the structure of



where R, R<sup>1</sup> and R<sup>2</sup> are independently H, CH<sub>3</sub> or C<sub>2</sub>-C<sub>18</sub> alkyl, and R + R<sup>1</sup> + R<sup>2</sup> have 5-30 carbon atoms. ASA is generally prepared by reaction of an iso-alkene with maleic anhydride. ASA sizing for paper is discussed by Hatanaka et al. TAPPI J., p. 177, (Feb. 1991) and by Farley and Wasser, "The Sizing of Paper", ed. by W. F. Reynolds, TAPPI Press, Atlanta (1989) in addition to G. G. Spence (cited above).

20 The additives are generally mixed together as aqueous suspensions and can be incorporated into the paper by addition either to the wet-end of the process, adding the suspensions to the paper pulp slurry, or by application of the additives to the paper sheet in the dry-end of the papermaking. The total amount of additives including both the polymer and the size is normally in the range of 0.05 to 4.0 wt% based upon the dry paper pulp.

30 Other advantages and features of our invention will be apparent to those skilled in the art from the following Examples which are illustrative only and should not be construed to limit our invention unduly.

### 35 Example 1

The polymerization of poly(vinyl acetate-co-N-vinyl formamide) (VAc-NVF) was conducted by formation of a surfactant of NVF-co-VAc in the premix solution which

stabilized the emulsion/suspension for the polymerization of the desired poly(vinyl acetate-co-N-vinyl formamide).

5 The initial charge for the premix solution was 330 grams deionized water, 20 grams NVF (from Air Products and Chemicals), 15 grams VAc (from Hoechst-Celanese), and 1.0 grams tert-butyl peroxyneodecanoate (Triganox™ 23, from Noury Chemicals). The delay feed was 340 grams distilled VAc and 27 grams NVF.

10

The initial charge was loaded in a jacketed 5-liter resin kettle equipped with mechanical stirrer, condenser, nitrogen inlet, thermal couple and dropping funnel. Under stirring and blanketing with a weak flow of nitrogen, the mixture was heated via a circulating bath to 60°C, and the temperature was maintained for 30 minutes. The delay feed was added then within one hour through the dropping funnel. During the addition of delay feed, the solution became increasingly cloudy and heat of polymerization raised the temperature to 66-68°C, at which point the reflux started. The polymerization was continued for two more hours to yield a latex with 51% solids and a viscosity of 22,000 centipoises (mPa.s). The residual monomer as determined by bromate/bromide titration was 1.6 percent.

25

After filtration the wet cake of copolymer was suspended in 500 cm<sup>3</sup> methanol. A solution of 45 cm<sup>3</sup> of concentrated HCl (36-38%) in 100 cm<sup>3</sup> methanol was added to the suspension which was heated to reflux for one hour. Drying in vacuum at 30°C yielded about 180 grams of slightly yellow material in powder form, which readily dissolved in water. The product was an amine-functional poly(vinyl alcohol), PVOH/VAm•HCl having about 12 mole% VAm•HCl.

35

Examples 2-10

Virgin Southern pine unbleached pulp was obtained from  
Herty (Canadian Freeness  $\approx$  475). Handsheets were prepared  
5 and tested as follows:

Preparation of Laboratory Handsheets:

The protocol for preparation of laboratory handsheets  
10 was based on a procedure derived from TAPPI 205.  
Sufficient moist pulp to contain 24g of pulp on a dry basis  
was soaked in about 1800 cm<sup>3</sup> of tap water for at least three  
hours. The slurry was then transferred to a British  
Standard pulp disintegrator, any wet end additives (such as  
15 alum, anionic starch, and amine functional poly(vinyl  
alcohol)) to be utilized were added; the final volume was  
made up to 2000 cm<sup>3</sup>, and the mixture was stirred for 50,000  
revolutions. After mixing, the contents were transferred  
to a 10 liter plastic bucket and diluted to a final volume  
20 of 7.2 liters (approximately 0.33% consistency using a  
procedure subsequently described). The pH was adjusted to  
the desired value using 0.1M sulfuric acid or 0.1M sodium  
hydroxide. The slurry was stirred for 30 minutes at low  
speed using a laboratory mixer.

25  
Twelve to sixteen 400 cm<sup>3</sup> aliquots were dipped from the  
bucket and transferred to 600 cm<sup>3</sup> beakers. Pulp slurries  
are difficult to pour while at the same time maintaining a  
uniform fiber concentration, so the following technique was  
30 used for obtaining aliquots with fairly uniform fiber  
concentrations. The pulp slurry was stirred with a large  
spatula, a 400 cm<sup>3</sup> beaker was immersed below the surface and  
stirring was stopped. The beaker was withdrawn directly  
from the bucket, full to the brim, and the entire contents  
35 transferred to the 600 cm<sup>3</sup> beaker. The British Standard  
handsheet machine was used to make handsheets from each

beaker of slurry as described in TAPPI Method 205. After pressing as described, the sheets were conditioned overnight in a constant temperature/humidity chamber operated at 23°C and 50% relative humidity (R.H.). The handsheets were removed from the mirror surface drying plates, allowed to equilibrate for 15-30 minutes at room temperature (R.T.), weighed and stored in polyethylene Ziplock™ bags until testing.

10      Determination of Pulp Consistency:

The procedure utilized for the determination of pulp consistency was similar to TAPPI Method 240. Whatman #1 filter paper pads were oven dried for 15 minutes at 105°C, equilibrated for 5 minutes at R.T. and weighed to determine dry basis weight. About 2 grams of moist pulp was accurately weighed into a 600 cm<sup>3</sup> beaker and slurried with 300 cm<sup>3</sup> of water. The slurry was transferred to a small Waring Blendor and stirred for 30 seconds on low speed. The dispersed slurry was filtered using one of the pre-weighed filter papers and the moist pad was dried for 15 minutes at 105°C on an Emerson speed dryer. The dried pad was equilibrated for 5 minutes at R.T. and weighed. The amount of dry pulp in the original sample was thus determined.

For each new container or pulp sample used for handsheet preparation, three samples were taken from various locations in the sample and the consistency was determined as described above. The average consistency so determined was used in all subsequent handsheet preparations using that material.

35      Testing of Laboratory Handsheets:

The basic evaluation method used in these Examples was



the tensile breaking strength of paper strips as measured using an Instron machine (see TAPPI Method 495). Ten 0.5 inch (13 mm) wide strips were cut from the set of handsheets being evaluated using a paper strip cutter  
5 designed for this purpose. Five strips from each set were tested in dry mode to determine the tensile strength in units of lb/in (kN/m) of width. The other five strips were soaked in tap water for 30 minutes, lightly blotted with a paper towel and then immediately tested using the same  
10 procedure, thus yielding the wet tensile strength. Independent tests showed 30 minutes soaking time was sufficient to completely saturate the paper. Some tests involved different water soak times as noted in the Examples.

15

Two sets of conditioning were employed: (a) room temperature for 7 days, and (b) room temperature for 7 days plus 1 hour at 100°C. Handsheets were prepared using no additives (Control Example 2) and with the polymer of  
20 Example 1, alkyl ketene dimer (AKD) or both, as shown in Table 1 which also gives wet and dry tensile index values determined as described above.

The AKD used was Hercon™ 70 (Hercules). It is a  
25 water based system believed to also contain some cationic starch for stabilizing the water dispersion (emulsion).

Table 1						
Example	AKD	PVOH/VAm•HCl	Dry Tensile Index		Wet Tensile Index	
			(a)	(b)	(a)	(b)
	wt%	wt%	lb/in (kg/cm)		lb/in (kg/cm)	
2	0	0	61.0	64.4	1.5	2.1
			10.68	11.28	0.26	0.37
3	0	0.5	67.1	72.9	6.2	7.4
			11.75	12.77	1.09	1.30
5	0.5	0	55.5	60.8	3.2	4.4
			9.72	10.65	0.56	0.77
4	0.20	0.30	66.5	70.6	7.9	9.4
			11.65	12.36	1.38	1.65
6	0.40	0.10	67.0	66.4	5.5	7.2
			11.73	11.63	0.96	1.26
7	0.25	0.25	65.0	74.9	7.7	9.5
			11.39	13.12	1.35	1.66
8	0.20	0.30	62.6	66.6	6.8	9.1
			10.96	11.66	1.19	1.59
9	0.15	0.35	68.6	71.0	8.3	9.3
			12.01	12.43	1.45	1.63
10	0.10	0.40	73.2	69.2	7.7	8.9
			12.82	12.12	1.35	1.56

(a) Conditioned 7 days at room temperature

(b) Conditioned 7 days at room temperature plus 1 hour at 100°C

The results noted in Table 1 are illustrated in the figure showing the synergistic behavior graphically. These results show wet strength values for paper containing both the AKD and the PVOH/VAm•HCl that are significantly higher than their additive effects which would be expected from the use of either material alone. In the figure, plots (a) and (a') represent the actual and expected values (respectively) for the wet tensile index of samples conditioned at room temperature for 7 days. Plots (b) and (b') show the actual and expected values, respectively, for the wet tensile index of samples conditioned at room temperature for 7 days and at 100°C for 1 hour.

The properties (wet and dry) of samples from these handsheets are listed in Table 2.

Table 2								
Test Conditioning	Example 2		Example 3		Example 4		Example 5	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
	R.T.	1 hr @100 °C	R.T.	1 hr @100 °C	R.T.	1 hr @100 °C	R.T.	1 hr @100 °C
Grammage, g/m <sup>2</sup>	155.6	155.6	153.2	153.2	158.2	158.2	155.0	155.0
Basis Wt lb/ft <sup>2</sup>	31.9	31.9	31.4	31.4	32.4	32.4	31.7	31.7
Basis Wt kg/m <sup>2</sup>	156	156	153.5	153.5	158	158	155	155
Dry Tensile, lb/in	54.2	57.2	58.7	63.8	60.1	63.8	49.1	53.8
Dry Tensile, kN/m	9.49	10.02	10.28	11.17	10.53	11.17	8.6	9.4
Wet Tensile, lb/in	1.3	1.9	5.4	6.5	7.1	8.5	2.8	3.9
Wet Tensile, kN/m	0.23	0.33	0.95	1.14	1.24	1.49	0.5	0.7
Dry Tensile Index, Nm/g	61.0	64.4	67.1	72.9	66.5	70.6	55.5	60.8
Wet Tensile Index, Nm/g	1.5	2.1	6.2	7.4	7.9	9.4	3.2	4.4
Wet/Dry (%)	2.4%	3.3%	9.2%	10.2%	11.8%	13.3%	5.7%	7.2%
Breaking Length (m)	6101	6437	6708	7291	6654	7064	5546	6077

The PVOH/VAm•HCl was dissolved in water and added to the pulp slurry in the pulp disintegrator prior to handsheet preparation. When used together, the PVOH/VAm•HCl and AKD were predissolved in water prior to addition to the pulp slurry in the pulp disintegrator. The AKD was available as an emulsion and the dry weight was determined to establish the percent  
5 used. When used alone, the AKD was diluted in water prior to addition to the pulp slurry in the pulp disintegrator.

Example 11

10 Samples of Examples 2, 3, 5 and 7 were tested using the standard Mullen Burst test. Tests were run dry and wet. The dry test involved 5 samples each, dried and conditioned at 50% R.H. and room temperature prior to testing. In the wet burst  
15 test, two conditions were employed. An instantaneous wetting time (immersion for approximately 2 seconds) and a 5-minute immersion in water were the chosen conditions followed by blotting on adsorbent paper to remove excess water. The burst tests were then immediately run. The data are listed in  
Table 3. The combination of AKD and PVOH/VAm•HCl yields better  
20 wet burst strength than AKD or PVOH/VAm•HCl alone at the same total additive level.

Table 3					
			Mullen Burst Strength psi (kPa)		
Example	AKD wt%	PVOH/VAm•HCl wt%	Dry	Wet <sup>1</sup>	Wet <sup>2</sup>
2	0	0	104 (715)	3 (20)	-
3	0	0.5	127 (875)	17 (115)	18 (125)
5	0.5	0	101 (695)	72 (495)	11 (75)
7	0.25	0.25	102 (705)	90 (620)	26 (180)

<sup>1</sup> Instantaneous

<sup>2</sup> (5 min.immersion)

#### Examples 12-19

A sample of wet pulp (Canadian Freeness  $\approx$  700) (unbleached) was obtained from James River. Handsheets were prepared and tested according to the procedure used in Examples 2-10, except for the polymer and size additives which are given in Table 4 as weight percent based on dry pulp weight. The polymer was PVOH/VAm•HCl of Example 1 and the sizing agents were alkenyl succinic anhydrides (ASA), namely, dodecenyl succinic anhydride (DDSA), octenyl succinic anhydride (OSA), or n-octadecenyl succinic anhydride (n-ODSA). The DDSA and n-ODSA were obtained from Humphrey Chemical Company, and the OSA was obtained from Milliken Chemical Company. Table 4 also lists the wet and dry tensile index values.

Table 4								
Example	12	13	14	15	16	17	18	19
PVOH/VAm•HCl (wt%)	0	0.5	0.25	0	0.25	0	0.25	0
DDSA (wt%)	-	-	0.25	0.5	-	-	-	-
OSA (wt%)	-	-	-	-	0.25	0.5	-	-
n-ODSA (wt%)	-	-	-	-	-	-	0.25	0.5
Dry Tensile Index (Nm/g) <sup>(a)</sup>	43	65.4	62.3	42.9	59.1	41.3	65.6	46.8
Dry Tensile Index (Nm/g) <sup>(b)</sup>	46	76.1	57.9	45.4	65.0	41.8	61.9	49.3
Wet Tensile Index (Nm/g) <sup>(a)</sup>	1.1	8.2	4.7	1.1	4.7	1.0	6.0	1.1
Wet Tensile Index (Nm/g) <sup>(b)</sup>	1.5	8.3	5.6	1.5	5.8	1.4	6.4	2.7

<sup>(a)</sup> Conditioned 7 days at room temperature.

<sup>(b)</sup> Conditioned 7 days at room temperature and 1 hour at 100°C.

The comparison of wet tensile index and dry tensile index for the ASA-PVOH/VAm•HCl mixtures versus the expected result assuming additivity is given in Table 5. The additive expectation was calculated from the average of the ASA and the PVOH/VAm•HCl unblended control samples. In all cases, the wet tensile index was equal to or higher than the additive calculation, thus exhibiting synergistic behavior as also noted with AKD-PVOH/VAm•HCl blends, although not as pronounced. In most cases, the dry tensile index generally exhibited higher values for the mixture as compared to the additive calculation.

Table 5				
	Wet Tensile Index (Nm/g)		Dry Tensile Index (Nm/g)	
	(a)	(b)	(a)	(b)
Example 14	4.7	5.6	62.3	57.9
DDSA + PVOH/VAm•HCl				
Additive Expectation	4.65	4.9	54.2	60.8
Example 16	4.7	5.8	59.1	65.0
OSA + PVOH/VAm•HCl				
Additive Expectation	4.6	4.85	53.4	59.0
Example 18	6.0	6.4	65.6	61.9
n-ODSA + PVOH/VAm•HCl				
Additive Expectation	4.65	5.5	56.1	62.7

(a) Conditioned 7 days at room temperature.

(b) Conditioned 7 days at room temperature and 1 hour at 100°C.

#### Examples 21-24

Using the procedure described in the foregoing Examples, handsheets were prepared from bleached kraft pulp obtained from The State University of New York using as additives the PVOH/VAm•HCl polymer of Example 1 and AKD (Hercon™). Wet and dry tensile tests were run on conditioned samples and the results are shown in Table 6.



Table 6						
Example	AKD	PVOH/VAm•HCl	Dry Tensile Index		Wet Tensile Index	
	wt%	wt%	(Nm/g)		(Nm/g)	
			(a)	(b)	(a)	(b)
21	0	0	0.80	0.80	33.7	33.2
22	0.5	0	2.2	2.6	30.3	31.2
23	0	0.5	1.22	1.22	33.6	34.6
24	0.25	0.25	3.8	3.8	33.4	35.0

(a) Conditioned 7 days at room temperature

(b) Conditioned 7 days at room temperature plus 1 hour at 100°C

Although the bleached pulp paper demonstrated little or no improvement in dry tensile from the additive combination, there was clearly a synergistic behavior between the AKD and the PVOH/VAm•HCl in wet tensile enhancement. The polymer alone gave marginal wet tensile improvement to the bleached pulp, in contrast to the more significant increases observed for unbleached pulp, as shown by Examples 2 and 3. Yet, when combined with AKD, the results for unbleached pulp were markedly better than what could have been expected from the additive effects of AKD and polymer alone in this product.

#### Examples 25-30

(Comparative)

Evaluations of wet and dry tensile properties were made on several unbleached pulp (James River Pine) handsheets made with AKD (Hercon™)-cationic starch blends

as are commonly used in the paper industry. Preparation, conditioning and testing procedures were as noted for the prior Examples. Results are given in Table 7.

5

10

15

Table 7							
Example	AKD	Cationic Starch		Wet Tensile Index		Dry Tensile Index	
	wt%	Type	wt%	(Nm/g)		(Nm/g)	
				(a)	(b)	(a)	(b)
25	0	--	0	1.1	1.1	43.0	46.0
26	0.5	--	0	1.9	2.6	42.4	47.0
27	-	Apollo 600	0.5	1.2	1.6	46.5	43.5
28	0.25	Apollo 600	0.25	1.1	1.8	46.3	47.4
29	-	Astro X-101	0.5	1.0	1.7	42.6	45.5
30	0.25	Astro X-101	0.25	1.3	2.0	42.7	45.2

Conditioning: (a) 7 days at R.T., (b) 7 days at R.T. and 1 hour at 100°C.

20

25

The data of Table 7 show that there is no synergy between AKD and cationic starch with respect to tensile enhancement. Use of AKD alone at 0.5 wt. percent did appear to improve wet tensile over the control (Example 25) and use of intermediate levels of AKD (0.25 wt. percent) provided values which were proportionate or below. No consistent trend was noted for dry tensile values.

30

Examples 31-32

(Comparative)

Poly(vinyl alcohol), PVOH, was used with AKD (Hercon™)  
5 instead of cationic starch as shown in Examples 27-30. The  
PVOH was Vinol™ 205 from Air Products and Chemicals, Inc.

10

Example	AKD	PVOH	Wet Tensile Index		Dry Tensile Index	
	wt%	wt%	(a)	(b)	(a)	(b)
25	0	0	1.1	1.5	43.0	46.0
26	0.5	0	1.9	2.6	42.4	47.0
31	0	0.5	1.0	1.3	41.6	45.6
32	0.25	0.25	1.0	1.5	43.5	42.8

15

(a) Conditioned 7 days at room temperature

(b) Conditioned 7 days at room temperature plus 1 hour at 100°C

20

PVOH demonstrated no tensile improvements alone or  
with AKD.

Example 33

25

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Water sorption tests were run on handsheets made from  
James River Pine Pulp and from Herty unbleached Pulp  
modified with AKD (Hercon™) and PVOH/VAm•HCl alone and  
together in various proportions with total add-on at 0.5  
wt. percent. Results with the polymer alone showed water  
sorption to be only slightly lower than the control with  
saturation observed almost immediately upon immersion. AKD  
modification showed much lower sorption which increased  
with time. This reduced water sorption effect was also  
noted for the AKD-PVOH/VAm•HCl blend with most of the  
reduced sorption benefit achieved at 0.1 wt. percent AKD

(0.4 wt.% polymer) and essentially full benefit at the 0.2, 0.3 and 0.4 weight percent AKD levels (0.3, 0.2 and 0.1 wt. percent polymer, correspondingly). From this study it appears that AKD when used with PVOH/VAm•HCl continues to serve as a sizing agent in addition to enhancing synergistically, in cooperation with the polymer, the wet tensile strength of the paper.

Example 34

Additional primary amine containing poly(vinyl alcohols) are useful in this invention. The reaction of poly (vinyl alcohol) with 4-aminobutyraldehyde dimethyl acetal (ABAA)  $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}(\text{OMe})_2$  allows for a another facile route for primary amine incorporation. A sample of Airvol™ 325LA poly(vinyl alcohol) was reacted with 10 mole% ABAA in a water solution (see synthesis Example 35). The resultant product was evaluated as per the established testing protocol noted for the other examples. Using the James River pulp (Canadian Freeness  $\approx$  700), the wet and dry tensile index values are shown for the addition of 0.5% PVOH/ABAA, 0.5% AKD, 0.25% PVOH/ABAA/0.25% AKD. The results demonstrate the blend yields higher values than additive expectations.

Table 8				
	1 week @ RT		1 week @ RT + 1 hour @ 100°C	
	Dry Tensile Index	Wet Tensile Index	Dry Tensile Index	Wet Tensile Index
Sample Description	Nm/g	Nm/g	Nm/g	Nm/g
Control	46.5	1.1	51.0	2.4
+0.5% AKD (Hercon™ 70)	48.2	1.6	46.2	2.8
+0.5% PVOH/ABAA	83.0	7.7	68.9	9.3
+0.25% PVOH/ABAA 0.25% AKD	54.9	6.4	65.1	7.3
Additive Expectation for Wet Tensile Index	-	4.65	-	6.05

### Synthesis Example 35

Poly(vinyl alcohol) (Airvol™ 325LA, 20.00 g, 0.454 mole) was dissolved in water (100 cm<sup>3</sup>) at 80°C under  
 5 nitrogen. After dissolution, concentrated hydrochloric acid (6.53 g, 0.0681 mole) and 4-aminobutyraldehyde dimethyl acetal (6.05 g, 0.0454 mole) were added to the reaction along with additional water (30 cm<sup>3</sup>). The reaction  
 10 was then continued at 80°C under nitrogen for 4.5 h. The reaction was not neutralized. The water was removed on a rotary evaporator, and the product was dried further in a vacuum oven (50°C/1 torr (130Pa)) to give 27.68 g of product.

Other advantages and features of our invention will be apparent to those skilled in the art from the foregoing disclosure without departing from the scope of the invention.

CLAIMS:

1. A method of improving the wet-strength of  
cellulosic paper which comprises adding to the paper during  
5 the papermaking process an amine-functional poly(vinyl  
alcohol) and a cellulose reactive size selected from 4 or 5  
membered cyclic ester or anhydride having one or more alkyl  
or alkenyl substituents each of which contains at least  
4 carbon atoms and having a total of at least 8 carbon  
10 atoms in said substituent(s).

2. A method as claimed in Claim 1, wherein said  
copolymer and size are added to the paper pulp slurry.

15 3. A method as claimed in Claim 1, wherein said  
copolymer and size are added to the paper sheet.

4. A method as claimed in any one of the preceding  
claims, wherein said copolymer is a poly(vinyl alcohol/  
20 vinyl amine) wet-strength resin.

5. A method as claimed in Claim 4, wherein said  
copolymer is a hydrolyzed copolymer of vinyl acetate and a  
vinyl amide.

25 6. A method as claimed in Claim 5, wherein said  
copolymer is a hydrolyzed copolymer of vinyl acetate and N-  
vinyl formamide or N-vinyl acetamide.

30 7. A method as claimed in Claim 6, wherein said  
copolymer is a hydrolyzed copolymer of vinyl acetate and 1  
to 25 mole percent, based upon incorporated monomer, of N-  
vinyl formamide.

35 8. A method as claimed in any one of Claims 5 to 7,  
wherein said copolymer before hydrolysis contains 5 to 20

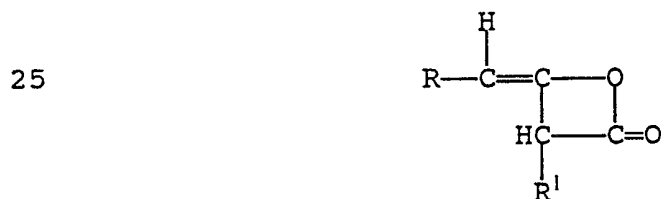
mole percent of incorporated vinyl amide.

9. A method as claimed in any one of Claims 1 to 3,  
wherein said copolymer is a reaction product of a  
5 poly(vinyl alcohol) homo- or co-polymer with an  
aminoaldehyde or aminoacetal.

10. A method as claimed in Claim 9, wherein said  
copolymer is the reaction product of 4-aminobutyraldehyde  
10 dimethyl acetal and a poly(vinyl alcohol) homo- or  
copolymer.

11. A method as claimed in any one of the preceding  
claims, wherein said size is selected from 4 or 5 membered  
15 cyclic ester or anhydride having one or more alkyl or  
alkenyl substituents each of which contains at least  
8 carbon atoms.

12. A method as claimed in any one of the preceding  
20 claims, wherein said size is an alkyl ketene dimer having  
the structural formula:



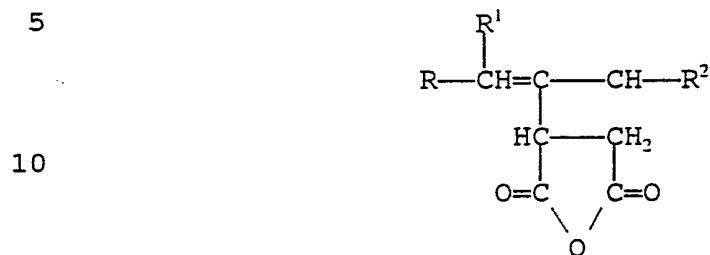
wherein R and R<sup>1</sup> are independently straight or  
branched chain alkyl or alkenyl groups containing 4 to 20  
carbon atoms.

35 13. A method as claimed in Claim 12, wherein R and R<sup>1</sup>  
are identical.

14. A method as claimed in Claim 12, wherein the size  
comprises an equilibratable mixture of vinyl β-lactones and  
40 2,4-substituted cyclobutane-1,3-diones.



15. A method as claimed in any one of Claims 1 to 11, wherein said size is an alkenyl succinic anhydride having the structural formula:



15 wherein each R, R<sup>1</sup> and R<sup>2</sup> are independently H, CH<sub>3</sub> or C<sub>2</sub>-C<sub>18</sub> alkyl and R + R<sup>1</sup> + R<sup>2</sup> have 5-30 carbon atoms.

16. A method as claimed in Claim 15, wherein the size is selected from dodecenyl succinic anhydride, octenyl succinic anhydride, and n-octadecenyl succinic anhydride.

17. A method as claimed in any one of the preceding claims, wherein each of said resin and said size is added in amounts of 0.05 to 4.0 weight percent based upon dry paper pulp.

18. A method as claimed in Claim 1, and substantially as herein before described in any one of Examples 4 to 10, 14, 16, 18, 24, 33 and 34.

19. The use of an amine-functional poly(vinyl alcohol) and a cellulose reactive size selected from 4 or 5 membered cyclic ester or anhydride having one or more alkyl or alkenyl substituents each of which contains at least 4 carbon atoms to improve the wet-strength of cellulosic paper.

20. A use as claimed in Claim 19, wherein the said copolymer and/or size is as defined in any one of Claims 2 to 17.

21. A cellulosic paper product having improved wet-  
strength containing products formed by addition to the  
paper during manufacture thereof of a combination of an  
amine-functional poly(vinyl alcohol) resin and a cellulose  
5 reactive size which is a 4 or 5 membered cyclic ester or  
anhydride having one or more alkyl or alkenyl substituents  
each of which contains at least 4 carbon atoms.

22. A product as claimed in Claim 21, wherein said  
10 copolymer and/or size is as defined in any one of Claims 2  
to 17.

23. A cellulosic paper product having improved wet-  
strength when prepared by a method as claimed in any one of  
15 Claims 1 to 17.

24. A product as claimed in Claim 21 and  
substantially as herein before described in any one of  
Examples 4 to 10, 14, 16, 18, 24, 33 and 34.  
20

**Patents Act 1977**  
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**Relevant Technical fields**

(i) UK CI (Edition L ) D1R (RDG, RDH, RDL, REZ, RFA, RFZ)

(ii) Int CI (Edition 5 ) D21H

**Search Examiner**

ALEX LITTLEJOHN

**Databases (see over)**

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI

**Date of Search**

5 AUGUST 1993

Documents considered relevant following a search in respect of claims

1-24

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
Y	EP 0348127 A2 (EXXON) - see especially page 1 lines 9-12	1-7, 11-16 19-23
Y	EP 0337310 A1 (AIR PRODUCTS) - see whole document	1-5, 11-16 19-23
Y	US 4774285 (PFOHL) - see whole document	1-7, 11-16 19-23

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