

Manufacture of Paper

This invention relates to the production of paper which is strengthened by starch. Various processes for making paper, and for making paper strengthened by starch, are described in, for instance, WO95/33096, which is incorporated herein by reference.

Processes which are currently of particular interest in paper making comprise providing a cellulosic thin stock suspension, flocculating this suspension, shearing the flocculated suspension, reflocculating the sheared suspension by adding an aqueous reflocculating composition, draining the suspension through a wire to form a wet sheet, and drying the sheet. The flocculation is generally caused by the use of a natural or synthetic polymeric retention aid and the reflocculation is generally caused by the use of an aqueous suspension of bentonite or other anionic microparticulate material.

It is known to include starch in the final sheet so as to improve the strength. One conventional treatment comprises applying a solution of substantially fully cooked starch to the sheet before final drying. It is also known to apply partially or wholly uncooked starch in this position and to cook it during the drying. It is also known to include substantially uncooked starch in the aqueous suspension before drainage, for instance as a result of being added with the polymeric retention aid or with the aqueous reflocculating composition. The substantially uncooked starch may have been slightly cooked so as to facilitate its final cooking, but most or all of the cooking is conducted during the drying stage thereby converting the substantially uncooked starch to substantially fully cooked starch in the final sheet.

In the invention, substantially fully cooked starch is added to the suspension after the suspension has been flocculated, and preferably after the flocculated suspension has been sheared. Preferably the aqueous reflocculating composition comprises the substantially fully cooked starch.

The aqueous reflocculating composition preferably comprises an aqueous dispersion of anionic microparticulate material. The substantially fully cooked starch may be precooked to its substantially fully cooked state and then the cooked starch and the anionic microparticulate material may be blended to form the final dispersion containing both. For instance the starch may be cooked and then mixed with an

aqueous dispersion of the microparticulate material.

Preferably, however, the reflocculating composition is made by mixing substantially uncooked starch with an aqueous dispersion of the microparticulate material and cooking the starch in that dispersion. If necessary or desirable, the resultant dispersion may then be diluted with water. It seems that cooking the starch in the presence of the microparticulate material generates a particularly desirable structure within the reflocculating composition.

Preferred anionic particulate materials are swelling clays such as silica, colloidal silicic acid and colloidal silicas, polysilicate and polysilicic acid microgels and aluminium modified versions of these, and organic microparticles, for instance all as described in WO95/33096.

Another reflocculating composition that can be used is an aqueous solution of a polymer which is generally counterionic to the polymeric retention aid which was used for causing the initial flocculation of the cellulosic thin stock suspension, and in particular it can be a material as described in WO98/29604.

The starch must be fully cooked prior to drainage, and preferably prior to addition to the aqueous cellulosic thin stock suspension, by which we mean that the starch granules must have burst and become substantially fully gelatinised. Naturally it is usually necessary to maintain the starch under some degree of agitation during cooking, as is conventional.

Preferably substantially no uncooked starch is included in the suspension which is drained, and thus it is not necessary to rely on cooking of the starch during drying of the sheet.

The starches which can be used can be any of the conventional starches such as cationic, anionic or amphoteric starches and can be derived from, for instance, corn, wheat, potato or tapioca or may be recovered starch.

In another embodiment of the invention, the aqueous reflocculating composition can contain, as its essential component, merely cooked starch which is sufficiently counterionic to the sheared cellulosic flocs for it to act as a reflocculating composition. In practice the cooked starch which best meets this requirement is usually amphoteric cooked starch.

Accordingly, the invention also provides a novel paper making process in which the reflocculation of the sheared suspension is achieved merely by adding cooked amphoteric or other suitable starch, without the customary anionic microparticulate material. Such processes give satisfactory retention and drainage properties despite the absence of the microparticulate material.

All the processes of the invention give improved strength, for instance as indicated by the burst strength.

The amount of starch which is to be added will be selected having regard to the degree of strength that is required and having regard to the other components in the suspension. Generally it is at least 0.5 and usually at least 1% by weight and can be as much as 10 or 15% by weight, based on the dry weight of the cellulosic thin stock.

The polymeric retention aid which is used can be cationic starch but is generally a synthetic polymer. The synthetic polymer can comprise a combination of low and high molecular weight polymers, as is known, but generally the final polymeric retention aid which is added is a synthetic polymer having intrinsic viscosity at least 4dl/g. The synthetic polymer can be non-ionic, anionic or cationic, but is usually cationic. Preferably the retention aid is a synthetic cationic polymer of intrinsic viscosity of at least 4dl/g. Typically the cationic polymers may be copolymers of acrylamide with for instance diallyl dimethyl ammonium chloride or dialkylaminoalkyl (meth) -acrylate or -acrylamide polymers (usually as acid addition or quaternary ammonium salt). Suitable materials are described in, for instance WO95/33096 and in the documents to which it refers.

Similarly, reference should be made to those documents for a description of suitable cellulosic materials and process steps.

The process can be used to generate any weight of paper, including paper board, and so may be low weight or high weight. The invention is of particular value in relatively low weight materials since it is in these materials that it can be difficult to achieve adequate cooking of uncooked starch during the drying stage. Thus, for instance, the invention is of particular value in the production of sheets of below 150 grams per square metre, but it can also be applied to higher weight sheets and boards.

Chelating agent may be incorporated in the reflocculating composition and/or in the aqueous phase in which the starch is to be cooked, if the water is hard.

The following examples illustrate the invention.

Example 1

110 grams per square metre hand sheet was prepared by flocculating cellulosic thin stock with higher molecular weight water soluble cationic polymer derived from acrylamide and cationic monomer in conventional manner followed by shearing followed by the addition of an aqueous reflocculating composition.

The burst strength (in KPA) depended on the reflocculating composition.

In one series of experiments, the reflocculating composition consisted of an aqueous dispersion of bentonite alone or with anionic potato starch. The burst strength when the bentonite was used alone was 299KPA. The burst strength when the anionic potato starch was cooked in the bentonite dispersion was 352 and the burst strength when the anionic starch was cooked and added after the shearing but before the bentonite was 322.

Example 2

Example 1 was repeated and varying the reflocculating composition. When bentonite was added alone the burst strength was 169. The burst strength when precooked anionic starch was included in the bentonite dispersion was 281. The burst strength when the anionic starch was cooked in the bentonite was 350. The burst strength when the anionic starch was precooked and added after the shearing, but in the absence of any bentonite during the process, was 308.

When amphoteric starch was included and cooked in the bentonite, the burst strength was 271. When amphoteric starch was cooked and added after the shearing stage but without the addition of bentonite then or subsequently good retention was obtained and the burst strength was 379. In this series of experiments the amount of starch was 7% based on fibre.

Example 3

Free drainage test was carried out on a packaging grade paper furnish derived from waste using a copolymer of acrylamide with dimethylaminoethyl acrylate, methyl chloride quaternary ammonium salt of intrinsic viscosity in excess of 12dl/g as the retention aid and either bentonite or cooked starch as the reflocculating composition. For each dose the free drainage was measured in seconds for 100ml, 200ml and

300ml drained respectively and shown in Table 1.

Table 1

Treatment	Dose (ppm)	Seconds for 100ml	Seconds for 200ml	Seconds for 300ml
Retention Aid	300	5	28	78
Bentonite	3000			
Retention Aid	500	5	23	66
Bentonite	3000			
Retention Aid	500	3	15	42
Cooked Starch	30000			
Retention Aid	500	3	15	37
Cooked Starch	40000			
Retention Aid	500	2.5	12	31
Cooked Starch	60000			

As can be seen the tests using cooked starch in place of bentonite gave faster free drainage.

Example 4

Britt dynamic retention tests were carried out on a packaging grade paper furnish derived from waste using a copolymer of acrylamide with dimethylaminoethyl acrylate, methyl chloride quaternary ammonium salt of intrinsic viscosity in excess of 12dl/g as the retention aid and either bentonite or cooked starch as the reflocculating composition. The solids content in the water drained and the retention were measured for each test and shown in Table 2.

Table 2

Treatment	Dose (ppm)	Back water solids %	Retention %
Retention Aid	500	0.240	79.6
Bentonite	3000		
Retention Aid	500	0.198	83.8
Cooked Starch	40000		

As can be seen from the results the test with cooked starch shows improved retention.

Example 5

Example 3 was repeated except using a newsprint stock derived from 70% deinked waste and 30% mechanical pulp. The results are shown in table 3.

Table 3

Treatment	Dose (ppm)	Seconds for 100ml	Seconds for 200ml	Seconds for 300ml
Retention Aid	1000	11	45	—
Bentonite	3000			
Retention Aid	1000	5	23	60
Cooked Starch	40000			

The test using cooked starch showed improved drainage times.

Example 6

Example 4 was repeated except using a newsprint stock derived from 70% deinked waste and 30% mechanical pulp. The results are shown in table 4.

Table 4

Treatment	Dose (ppm)	Back water solids %	Retention %
Retention Aid	1000	0.38	68.6
Bentonite	3000		
Retention Aid	1000	0.27	77.7
Cooked Starch	40000		

Higher retention was achieved using cooked starch in place of bentonite.

Example 7

The process of Example 1 was repeated using a 0.7% brown millstock and using 750 grams per tonne of a copolymer of acrylamide with dimethylaminoethyl acrylate, methyl chloride quaternary ammonium salt of intrinsic viscosity in excess of 12dl/g as the retention aid. Five series of experiments were conducted using as the sole reflocculating composition an anionic cooked starch, three types of amphoteric cooked starch and an unmodified cooked potato starch at various doses. The burst strength of the paper sheets formed were measured and the results are shown in Table 5.

Table 5

Cooked Starch Reflocculating Composition	Corrected Burst Strengths (Kpa) for various starch dosages (Kg/tonne)				
	5	10	20	30	40
anionic Aniofax AP25	228.6	256.8	260.41	280.6	279.5
amphoteric CATO 245	259.2	284.1	273.9	308.4	316.0
amphoteric CATO 247	255.0	253.9	263.0	289.3	320.5
amphoteric CATO 255	257.8	266.7	294.7	314.4	346.7
Unmodified Potato Starch	239.7	243.8	260.6	269.1	271.2

As a comparison the process was repeated using bentonite in place of cooked starch. The burst strengths are shown in Table 6.

Table 6

	Corrected Burst Strengths (Kpa) for various starch dosages (Kg/tonne)				
	0.5	1	2	3	4
bentonite	207	210	208	205	200

As can be seen the burst strength of the paper was greatly improved when using cooked starch as the reflocculating composition.



CLAIMS

1. A process for making paper on a paper-making machine comprising
providing a cellulosic thin stock suspension,
flocculating the suspension by adding an aqueous solution of a polymeric retention aid selected from natural and synthetic polymer and thereby forming a flocculated suspension,
shearing the flocculated suspension,
reflocculating the sheared suspension by adding an aqueous reflocculating suspension,
draining the reflocculated suspension through a wire to form a sheet, and
drying the sheet,
characterised in that substantially fully cooked starch is added to the suspension after the shearing and before the draining.
2. A process according to claim 1 in which the substantially fully cooked starch is added in the aqueous reflocculating composition.
3. A process according to either preceding claim in which the aqueous reflocculating composition comprises an aqueous dispersion of anionic microparticulate material.
4. A process according to claim 3 in which the aqueous reflocculating composition comprises an aqueous dispersion of a swelling clay, colloidal silica, polysilic acid or polysilicate microgel or aluminium modified silicates.
5. A process according to claim 3 or claim 4 comprising the step of making the reflocculated composition by a process comprising mixing substantially uncooked starch with an aqueous dispersion of the microparticulate material and cooking the starch in that dispersion.
6. A process according to claim 2 in which the starch is amphoteric.
7. A process according to claim 6 in which the aqueous reflocculating composition is substantially free of anionic microparticulate material or synthetic polymeric retention aid.
8. A process according to any one of claims 1 to 7 in which the retention aid is selected from cationic starch and synthetic polymer.

9. A process according to any one of claims 1 to 8 in which the retention aid is a synthetic cationic polymer of intrinsic viscosity of at least 4dl/g.

