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(54) **Manufacture of paper**

(57) Paper strengthened by starch, typically in
amounts of 3 to 15% dry weight, is made by flocculating
a cellulosic suspension using a polymeric retention aid
which can be dissolved cationic starch but is preferably
a synthetic polymer having IV above 4dl/g, shearing the
resultant flocculated suspension and reflocculating it by

adding bentonite or other microparticulate anionic ma-
terial, draining the flocculated or reflocculated suspen-
sion and drying the resultant wet sheet, wherein insolu-
ble particles of starch are added to the suspension as a
slurry of substantially freely dispersed particles in part
or all of the aqueous solution of the polymeric retention
aid.

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Description

[0001] This invention relates to the production of paper which is strengthened by starch.

[0002] It is standard practice to make paper on a paper-making machine by providing a cellulosic thin stock suspension, flocculating the suspension by adding a solution of polymeric retention aid and thereby forming a flocculated suspension, draining the flocculated suspension through a moving screen to form a wet sheet, and carrying the sheet through a heated drying zone and thereby forming a dry sheet. The retention aid can be dissolved cationic starch but is often a synthetic polymeric material. Although the use of polymer of rather low molecular weight can give some improvement in retention, the polymer is preferably of high or very high molecular weight, generally having intrinsic viscosity above 4dl/g.

[0003] A common alternative to this process involves shearing the flocculated suspension so as to degrade the flocs and then adding an aqueous suspension of micro-particulate anionic material and thereby reflocculating the suspension, and then draining the reflocculated suspension through the screen. Such processes using cationic starch and colloidal silica are described in U.S. 4,388,150 and processes using cationic synthetic polymer and bentonite are described in EP-A-235,893. Processes in which size is added after the flocculation with the cationic polymer are described in EP-A-499,448. Processes using other polymers and suspensions suitable for these are described in WO95/02088.

[0004] The cellulosic thin stock is often formed in part from recycled paper which may include soluble starch (cationic or anionic or non-ionic) and so the thin stock, and the final sheet, often includes soluble starch. For instance the dry sheet may contain as much as 1% starch derived from recycled paper. It is, however, often desired to add starch to the thin stock.

[0005] Thus, water soluble cationic starch may be added as part or all of the solution of polymeric retention aid (see for instance U.S. 4,388,150). The amount required for this purpose is usually not more than about 0.3% (dry weight starch based on the dry weight of paper).

[0006] It is often desired to add starch in order to strengthen the paper. For instance it is particularly desirable to include significant amounts of starch in fluting medium and liner board. These materials are usually substantially unfilled and increasing their strength makes them more suitable for use as packaging materials. It is also desirable to include significant amounts of starch in filled sheets as the inclusion of significant amounts of filler would otherwise tend to reduce the strength of the sheet.

[0007] In order to maximise strength, it is desirable to include starch in amounts of as much as 5 or 10% or even higher, but attempting to achieve this tends to make the process less efficient as regards energy consumption and/or rate of production, or can incur the risk of unacceptable increase in the chemical oxygen demand of the effluent from the process, because of increased starch in the effluent.

[0008] Various grades of starch are conveniently commercially available and include grades which are usually insoluble in the cellulosic suspension. They can be used either unmodified or chemically modified. Generally the starch is pre-solubilised at high temperature to render the starch soluble in the cellulosic suspension.

[0009] In this specification when we say a starch is insoluble we mean that it is insoluble in the cellulosic suspension and remains undissolved in the cellulosic suspension. When we say a starch is soluble we mean it is soluble in the cellulosic suspension.

[0010] Soluble cationic starch is reasonably substantive to the cellulosic fibres in amounts up to about 1 to 1.5% by weight of the starch, based on the dry weight of the paper. If the amount of cationic starch in the suspension is increased significantly above this, there may be little or no increase in the amount of starch which is retained in the paper and, instead, there is merely an increase in the amount of soluble cationic starch which is in the white water which drains through the screen. This is undesirable since it has to be removed before discharge as effluent, because of the high chemical oxygen demand that it may create in the effluent from the mill.

[0011] The soluble cationic starch can be made by chemical modification of starch or merely by cooking raw starch and adding a low molecular weight cationic polymer before, during or after the cooking. Suitable low molecular weight cationic polymers have intrinsic viscosity below 1dl/g. Examples of such systems are in CA 787,294 and U.S. 3,930,877.

[0012] In practice, when starch is being used as a strengthening aid it is usually necessary also to include a polymeric retention aid, and there have been various publications about adding combinations of materials. For instance in Tappi June 1976, 59, 6, pages 120 to 122 the performance of various dual polymer systems is examined, including the performance of a blend of soluble cationic starch and hydrolysed polyacrylamide. In CA 1,232,713 up to 1.5% soluble cationic starch is applied in combination with polyethylene oxide or cationic, non-ionic or anionic polyacrylamide retention aid having molecular weight above 1 million.

[0013] In Tappi Journal February 1984 pages 104 to 108 the effect of various blends of soluble cationic starch and polymers is examined and it is noted that cationic starches at 1% by weight improve drainage and retention but that at higher levels drainage is adversely affected.

[0014] It is stated that an ideal polymer for a board mill at low shear appears to be a cationic, low molecular weight, high charge density polymer, in particular polyethylene imine.

[0015] In normal commercial practice it is found that if the amount of cationic starch is increased above about 1 or 1.5% there is increased risk that the cationic starch will interfere with the effectiveness of the polymeric retention aid. As a result retention and drainage may deteriorate with the result that the machine has to operate more slowly or product quality deteriorates.

[0016] When it is desired to include a greater amount of starch than 1 to 1.5%, the usual technique involves applying an unmodified starch solution on a size press at the end of the paper-making machine, i.e., after partial or complete drying of the sheet. The application of a solution of starch at this point can result in high pick-up (for instance up to 7 or 10% is common). However it can result in the starch being concentrated more on the surface than in the centre of the sheet and it has the particular disadvantage that it necessitates redrying of the sheet, thus wasting heat energy and/or slowing down the process. It would therefore be desirable to be able to achieve these or higher levels of starch without providing unacceptable levels of soluble starch in the white water and without having to redry the sheet.

[0017] Another known method for providing significant loadings of starch in the paper involves applying a spray or a foam containing undissolved starch particles on to the wet sheet before it is carried through the driers, followed by cooking the starch during drying. This process also has the disadvantage of tending to produce a higher concentration of starch on the surface than in the centre of the sheet. However its particular disadvantage is that it is very difficult to achieve uniform application of the starch by spraying or foam application for prolonged periods because of the tendency of the starch composition to cause blockages in the spray or foam applicators.

[0018] Attempts to include cold-water insoluble particulate starch in the suspension before drainage have been proposed in the literature but have not achieved success.

[0019] For instance Fowler reviewed the general techniques of adding starch in Paper 1978 pages 74 and 93. He discussed the techniques mentioned above and also stated that if raw uncooked starch is added to the suspension followed by the addition of retention aid only minimal retention of starch can be achieved. He proposed that better retention is achieved if the starch is slurried with bentonite and added to the suspension prior to the retention aid, and he also proposed that retention can be increased further by including in the slurry a polymer having a charge opposite to the charge of the retention aid.

[0020] In U.S. 4,347,100 Brucato describes that mechanical and thermomechanical pulping processes can be improved by adding an anionic surfactant or an anionic polymer during the pulping process. He states that the addition of a cationic polymer causes reaction with the anionic polymer and the formation of a gum-like precipitate which contributes to strength, and he recommends the addition of cationic polymer in a stoichiometric amount based on the anionic polymer. He describes a titration technique for obtaining the desired stoichiometric amount. He also proposes that optimum strength can be achieved by including ungelatinised starch which is gelatinised during subsequent heat drying.

[0021] He states that the reaction of the cationic and anionic polymers to produce a gum-like precipitate carries the starch particles and retains the starch in the wood fibres. He says that the furnish is then supplied to the paper-making machine where it is formed into a sheet and heat dried. This suggests that the starch is being added to the pulp or to the thick stock. In all the examples the pulp had a consistency of 2.3% but Brucato suggests higher consistencies are desirable. The strengths are all measured on hand sheets. He gives no information about whether the process could be conducted on a paper making machine, nor how this could be done, nor the extent of retention of starch that can be achieved.

[0022] Brucato describes in U.S. 4,609,432 another method of obtaining strengthened paper, this time using two different cellulosic suspensions. 90 to 98% of the fibre weight is provided by a first cellulosic suspension, usually of refined fibres, and 2 to 10% of the fibre weight is provided by adding to this first suspension a second cellulosic suspension which contains a heat-sensitive bonding agent (such as uncooked starch) for bonding the fibres and a polymer for adhering the bonding agent to the fibres of the second suspension. For instance the second suspension can contain the second cellulosic fibres together with 20 to 200% uncooked dry starch and 0.01 to 0.1% cationic polymer. The cationic polymer is said to coat the starch particles and adhere them to the fibres of the second suspension. A typical process uses a first suspension containing 95% of the total fibres and a second suspension containing 5% of the fibres, 0.012% polyethylene imine and 20% starch. A hand sheet was formed from this and was then dried and it appears that the starch is activated during the drying. Again there is no indication about how to conduct the process on a machine nor about retention.

[0023] Brucato quotes the same list of cationic polymers in both patents, namely polyethylene imines (which are preferred in U.S. 4,609,432), polyamide polyamine resins, urea formaldehyde resins, melamine formaldehyde resins and polyacrylamides. It seems that Brucato wants to use low molecular weight polymers since all the classes of polymers he mentions except for the polyacrylamides inevitably have very low molecular weight and the polyacrylamide he exemplifies is Separan CP7, a trade mark of Dow Chemical Co., and we believe that this material also has a relatively low molecular weight, of about 1 million.

[0024] There is no suggestion in either of the Brucato patents that any additional retention aid should be used.

[0025] The stoichiometric reaction to form a precipitate in U.S. 4,347,100 will prevent the cationic polymer acting as

an effective retention aid. The total amount of polyethylene imine used in the examples of U.S. 4,609,432 may be sufficient to cause flocculation of the second suspension but will be much too low to cause flocculation of the combined suspension. For instance the highest dosage which is exemplified is around 0.002% based on total fibre weight.

[0026] The Brucato methods therefore require particular interaction between low molecular weight cationic polymer and other material within the suspension and do not result in the production of a flocculated or reflocculated suspension of the type that is attainable by the use of high molecular weight synthetic polymers or cationic starch optionally followed by anionic microparticulate material.

[0027] It is desirable to strengthen substantially unfilled sheets of paper (including paper board) that is to be used as packaging, but there is also a particular need to include starch as a strengthening aid in sheets which are highly filled, since the use of a large amount of filler tends to weaken the sheet. The filler can be preflocculated before addition to the cellulosic suspension. Although this has some advantages, it can cause particular weakening of the sheet. It is therefore known to include water-soluble starch in the preflocculated filler composition, but this causes difficulties in handling the flocculated suspension.

[0028] In GB 2,223,038 filler is included in a cellulosic suspension by adding a slurry of filler, insoluble starch particles and flocculating agent. Although many of the flocculating agents which are mentioned have very low molecular weight (for instance Magnafloc 1597 is a polyamine) some have a moderate molecular weight. Suspending agent such as a gum, a synthetic organic polymer, or a swelling clay (e.g., bentonite) can be included and preferably the suspending agent is chosen so as to reduce the net charge in the composition close to zero. For instance if a cationic flocculant is used then an anionic suspending agent is usually required. The amount of filler in the composition is preferably 30 to 40%, and the amounts of starch and flocculant (based on filler) are preferably 1 to 5% and 0.05 to 0.2% respectively, with the amount of starch in the final paper being said to be typically 0.05 to 1.5%. The resultant flocculated suspension will contain the starch particles trapped in the filler flocs, and it is added to the cellulosic suspension which is then drained and heated, with consequential cooking of the starch. In the examples, the amount of filler ranges from 7 to 24% and the amount of starch is 4% based on filler, i.e., about 0.3 to 1% based on paper.

[0029] Accordingly, none of these detailed methods provide any practical solution to the problem of providing a convenient technique which uses readily available starch and which does not result in undesirable contamination of effluent and which is capable of giving very high pick-up of starch in the paper and which does not involve the problems of size press application or spray or foam application on to the wet sheet.

[0030] So far as we are aware, the proposals of Fowler, Brucato and in GB 2,223,038 have not resulted in satisfactory processes for producing sheets containing a large amount of starch as a result of incorporating all the starch in the suspension before drainage. Accordingly, the problem remains that if large amounts of starch are to be incorporated then they have to be added to the wet sheet by spraying or foam or at the size press, and there remains an urgent need to find a way of incorporating starch in the thin stock so as to allow efficient and environmentally acceptable production of paper having a high starch content.

[0031] Support for our belief that such a process is not known arises from the fact that, subsequent to the priority date of this application, in Nordic Pulp and Paper Research Journal Number 4 1994 pages 237 to 241 it is stated that since starch has granular form with diameter of about 1 to 40µm the retention of the starch granules is very low when added directly to paper stock without dissolution or swelling in water. According to the proposals in this article it is possible to include high amounts of starch in laboratory handsheets by including in the cellulosic suspension starch having a particular flake form and which has been made by precipitation in mineral salts and processing the precipitate. It is commercially undesirable to have to undergo this particular process and it would be much more convenient to be able to obtain high starch levels in paper made on a conventional paper-making machine using conventional granular starches and without incurring significant effluent problems due to excessive drainage of starch through the screen.

[0032] Accordingly, the problem to be solved by this invention is the provision of a method in which it is possible to include starch in the thin stock in such a way that relatively large amounts of starch can be retained in the paper without interfering significantly with efficient production of the paper and without creating unacceptable effluent discharges.

[0033] In a first aspect of the invention, we make paper on a paper-making machine by a process comprising

providing a cellulosic thin stock suspension,

flocculating the suspension by adding an aqueous solution of polymeric retention aid selected from dissolved cationic starch and synthetic polymer having IV above 4dl/g and thereby forming a flocculated suspension, optionally shearing the flocculated suspension and reflocculating the sheared suspension by adding an aqueous suspension of micro-particulate anionic material and thereby forming a reflocculated suspension, draining the flocculated or re-flocculated suspension through a moving screen to form a wet sheet, and carrying the sheet through a heated drying zone and thereby forming a dry sheet, wherein insoluble particles of starch are added to the cellulosic suspension as a slurry of substantially freely dispersed particles in part or all of the aqueous solution of the polymeric retention aid or in part or all of the aqueous suspension of micro-particulate anionic material, and

the insoluble particles of starch are heated during the drying and release soluble starch into the sheet in the presence of moisture.

[0034] This first aspect of the invention can be conducted with or without the shearing and reflocculation with micro-particulate anionic material. If the reflocculation step is being used, then the particulate starch can be included in that suspension of microparticulate anionic material, optionally also with polymeric retention aid.

[0035] In order to promote good retention it is necessary that the particles of the starch should be able to interact with the surfaces of the cellulosic fibres and, if present, the anionic microparticulate material. It is therefore desirable for the starch particles to be added as a slurry of substantially independent particles so that the particles can interact with the fibres or microparticulate anionic material substantially independent of each other.

[0036] Best results are obtained in the invention when the process involves the described shearing and reflocculation stages.

[0037] A preferred, second, aspect of the invention is a process for making paper on a paper-making machine which comprises

providing a cellulosic thin stock suspension,
flocculating the suspension by adding an aqueous solution of polymeric retention aid selected from dissolved cationic starch and synthetic polymer having intrinsic viscosity at least 4dl/g and thereby forming a flocculated suspension,
shearing the flocculated suspension and reflocculating the sheared suspension by adding an aqueous suspension of micro-particulate anionic material and thereby forming a reflocculated suspension,
draining the reflocculated suspension through a moving screen to form a wet sheet, and
carrying the sheet through a heated drying zone and thereby forming a dry sheet,
wherein insoluble particles of starch are added to the cellulosic suspension as a slurry in part or all of the solution of polymeric retention aid, and the insoluble starch particles are heated during the drying to release soluble starch into the sheet in the presence of moisture.

[0038] In these preferred processes good retention of fibres, starch particles (and filler if present) is achieved by the reflocculation stage. The application of shear to the flocculated suspension containing the cellulosic fibres and the starch particles results in degradation of flocs in the flocculated suspension and redispersion of the previously flocculated material. As a result, any flocs of starch particles, or of fibres free of starch particles, tend to be broken up by the shearing.

[0039] The consequence of this is that a very uniform distribution of the individual starch particles is achieved in the reflocculated suspension, and thus in the drained sheet. As a result of this uniformity, the gelatinisation during the drying can be conducted more efficiently and the distribution of the starch within the sheet both before gelatinisation and after gelatinisation can be more uniform than if the process is conducted without the shearing and reflocculation.

[0040] Although it is preferred that the slurry of polymeric retention aid is added in a form wherein the starch particles are substantially freely dispersed in it, some flocculation of the starch slurry can be acceptable when the resultant flocculated cellulosic suspension is sheared and then reflocculated since this shearing will break up any initial flocs in the initial slurry. It is possible for the slurry to include some filler or fibres. Generally, in all processes of the invention, the slurry consists essentially only of the polymeric retention aid and the insoluble starch particles.

[0041] The paper that is produced can be filled, and an advantage of the invention is that papers having good strength can be obtained even when they contain high amounts of filler, for instance more than 20% by weight or more than 40% by weight and even up to 60% by weight based on the dry weight of the paper. Conventional fillers such as calcium carbonate or sulphate or talc or kaolin or other clays can be used.

[0042] Another very important feature of the invention is that it permits the production of unfilled paper, that is to say paper to which little or no deliberate addition of filler is made. This substantially unfilled paper generally has a filler content of not more than 15%, and usually not more than 10% by weight of the dry sheet. Usually any filler which is included originates from recycled paper which is used in forming the cellulosic suspension but if desired small amounts, for instance up to 5% or perhaps 10% by weight based on the dry weight of the suspension can be deliberately added to the suspension. The invention is therefore of particular value for the manufacture of fluting medium or liner board.

[0043] Accordingly, in a third aspect of the invention we make substantially unfilled fluting medium or liner board on a paper-making machine by a process comprising

providing a substantially unfilled cellulosic thin stock suspension,
adding an aqueous solution of polymeric retention aid selected from dissolved cationic starch and synthetic polymer having intrinsic viscosity at least 4dl/g,
draining the suspension through a moving screen to form a wet sheet, and

carrying the sheet through a heated drying zone and thereby forming a dry sheet, and wherein insoluble particles of starch are added to the suspension as a slurry of substantially freely dispersed particles in part or all of the aqueous solution of the retention aid, and wherein the insoluble particles of starch are heated during the drying and release soluble starch into the sheet in the presence of moisture.

[0044] In this aspect of the invention, the process can be performed by draining the flocculated suspension which results from the addition of the polymeric retention aid or by shearing that flocculated suspension and reflocculating it by the addition of an aqueous suspension of micro-particulate anionic material, and then draining the resultant reflocculated suspension.

[0045] A unique characteristic of the invention is that we can achieve a high starch content in the dry sheet as a consequence of the inclusion of the undissolved starch in the cellulosic suspension without causing pollution problems. Thus we can easily obtain a content of at least 2% or 3% and typically 5% and even up to 10 or 15% by weight starch in the dry sheet.

[0046] According to a fourth aspect of the invention, we make paper on a paper-making machine by a process comprising

providing a cellulosic suspension,
flocculating the suspension by adding an aqueous solution of polymeric retention aid selected from dissolved cationic starch and synthetic polymer having intrinsic viscosity at least 4dl/g and thereby forming a flocculated suspension,
optionally shearing the flocculated suspension and reflocculating the sheared suspension by adding an aqueous suspension of micro-particulate anionic material and thereby forming a reflocculated suspension,
draining the flocculated or reflocculated suspension through a moving screen to form a wet sheet, and
carrying the sheet through a heated drying zone and thereby forming a drying sheet,
wherein we include in the cellulosic suspension insoluble starch particles in an amount of above 3% by weight based on the dry weight of the suspension, and we retain insoluble starch particles in the wet sheet in an amount of at least 3% based on the dry weight of the sheet and heat the insoluble particles during the drying and thereby release soluble starch into the sheet in the presence of moisture.

[0047] Preferably we achieve high retention of the starch particles (e.g., above 80% or 90% or more), and any starch particles that do drain into the white water can be tolerated as they can be insoluble in the white water and so can be recycled and trapped on a subsequent pass through the machine. Alternatively they can be removed by filtration before discharge.

[0048] The preferred way of performing this fourth aspect of the invention is by including the starch as a slurry in part or all of the aqueous solution of polymeric retention aid or in part or all of the aqueous suspension of microparticulate anionic material. However other ways of including it can be used. For instance the particles may be sprayed or otherwise coated with a solution of the retention aid and added to the cellulosic suspension before or after adding the remainder of the retention aid.

[0049] When the process is conducted by draining the flocculated suspension, this suspension may have been formed in conventional manner (apart from the addition of starch). For instance it may have been made from a ground-wood, mechanical or thermomechanical pulp and the thin stock, or the thick stock from which it is formed, may have been treated with bentonite before the addition of the retention aid. In such processes, the retention aid is often substantially non-ionic, for instance being formed from 0 to 10 mole percent anionic and/or cationic monomers and 90 to 100 mole percent non-ionic monomers. However the invention, in this aspect, is not limited to the use of dirty pulps and includes the use of any suitable combination of pulp and high molecular weight retention aid (anionic, non-ionic or cationic) or dissolved cationic starch retention aid.

[0050] In these processes the retention aid and starch are usually added after the last point of high shear, e.g., in or immediately prior to the head box.

[0051] In the preferred processes of the invention, the flocculated suspension is subjected to shear so as to degrade the initial flocs and is then reflocculated, or subjected to super-coagulation, by the addition of anionic microparticulate material. The shearing can be achieved merely as a result of turbulent flow from the point at which retention aid is added to the point at which the microparticulate material is added, but often the shearing is applied by passage through a device such as a centriscreeen, fan pump or other deliberate shear mixing stage. The shearing results in reduction of the size of the flocs, for instance as described in EP-A-235,893.

[0052] The starch particles can then be added with the anionic microparticulate material. As a result of intimate admixture of the starch particles and this material, the starch particles appear to become entrapped within the super-coagulation that occurs upon the addition of the microparticulate material and as a result good retention of the starch

particles is obtained. When the starch is being added with the microparticulate material, the slurry of starch and microparticulate material is usually free of any other significant solid phase and usually consists essentially only of water, the microparticulate material, the starch and any dispersing agent or other additives necessarily associated with the microparticulate material. The ratio dry weight of starch to microparticulate material is generally in the range 5:1 to 100:1, often around 10:1 to 50:1, by weight.

[0053] Typically the starch particles are injected into a slurry of the microparticulate material, or the microparticulate material is injected into a slurry of the starch particles, just before addition to the cellulosic suspension, although if desired the materials may be premixed and the resultant slurry pumped from the mixing station towards the addition point. The addition point is usually in the headbox or at some other position after the last point of substantial shear since it is usually desirable that the reflocculated or supercoagulated structure should not be degraded excessively by subsequent shear prior to drainage.

[0054] It is usually preferred to introduce the starch particles as a slurry in part or all of the aqueous solution of retention aid. This allows for the retention aid to be absorbed or otherwise attached to the surfaces of the starch particles before the particles are mixed with the cellulosic suspension. As a result of using a high molecular weight retention aid or, less preferably, dissolved cationic starch the absorbed retention aid promotes bridging between the starch particles and the cellulosic fibres, and thus promotes retention.

[0055] The starch may be preslurried in the aqueous solution of retention aid but it is generally adequate to mix the insoluble starch (usually as an aqueous slurry) and the aqueous retention aid as they flow towards a point at which the retention aid is added to the cellulosic suspension. For instance the starch may be injected into the polymer stream at some point between the polymer make-up supply and the point where the solution is added to the cellulosic suspension. Often it is adequate to mix the starch particles into the solution just prior to the point at which the solution is added to the cellulosic suspension.

[0056] Frequently the starch is provided initially as a slurry of 10 to 40%, often around 20%, by weight starch in water and this slurry is added into the polymer solution in the amounts required to give the chosen dosage of polymer and starch. The dry weight ratio of starch:polymer is often in the range 50:1 to 500:1. Often the slurry contains from 1 to 50% (preferably 10 to 30%) by weight starch particles and 0.01 to 2% by weight polymer.

[0057] Although the slurry that is added to the cellulosic thin stock suspension can include other materials, it is generally preferred and convenient for the slurry to consist substantially only of the polymer and the starch and water. The amount of polymer is generally considerably above the amount which might, under relatively static conditions, have a significant flocculating effect on the starch particles. Thus, if the chosen amount of polymer is added gradually to an aqueous medium containing the chosen amount of starch with mild mixing, some flocculation may initially be visible to the naked eye but further addition of the polymer, accompanied by further mixing, will result in the starch particles becoming substantially freely dispersed in that they do not cling together as significant flocs. In practice the addition of the slurry of starch and polymer is normally accompanied by shear at the addition point and this will further promote the independent character of the particles. In view of the shearing that tends to occur during addition, and in view of the preferred shearing of the flocculated cellulosic suspension that follows the addition of the polymer and particles, some aggregation of the particles is acceptable. However trapping the starch particles in flocs of filler or fibre in the slurry is undesirable.

[0058] It is important that the polymer that is added is an effective retention aid for the cellulosic suspension in order that the polymer which is absorbed onto the starch particles will have adequate substantivity to the cellulosic fibres in the suspension. Selection of an appropriate retention aid that is substantive to the cellulosic suspension can be conducted in conventional manner. It can be anionic, non-ionic or cationic. Best results are usually obtained when the retention aid is cationic and so preferably the suspension is one onto which the selected cationic retention aid is substantive.

[0059] It is usually convenient and preferred for the starch to be added as a slurry with the entire retention aid that is to be used for flocculating the suspension, optionally prior to shearing and reflocculation, but if desired the slurry may be mixed with part only, for instance at least 5% and often at least 25% by weight, typically up to 50 or 75% by weight, of the total amount of retention aid. If retention aid is being added partly mixed with particulate starch and partly free of starch, different, high molecular weight, retention aids may be used for the two additions provided they are compatible, or the same material may be used for each addition.

[0060] Low molecular weight, coagulant-type polymer may be added at an earlier stage if required, in known manner but this is not considered as a retention aid in the context of the present invention.

[0061] Such coagulant polymers usually have intrinsic viscosity below 3dl/g and often below 1dl/g. They can have high cationic charge density, preferably above 4, and often above 5, meg/g. The low molecular weight polymer is preferably formed of recurring units of which at least 70%, and generally at least 90%, are cationic. Preferred polymers are homopolymers of diallyl dimethyl ammonium chloride and low molecular weight co-polymers of this with a minor amount (usually below 30% and preferably below 10%) acrylamide, low molecular weight homopolymers of dialkylaminoalkyl (meth) -acrylamide or -acrylate quaternary salt or acid addition salt and copolymers of these with small amounts

(generally below 30% and preferably below 10%) acrylamide, polyethylene imines, polyamines, epichlorhydrin diamine condensation products, dicyandiamide polymers and other conventional low molecular weight cationic coagulant polymers.

[0062] The retention aid with which the particulate starch is mixed prior to addition to the cellulosic suspension can be soluble cationic starch and thus the system can consist of insoluble starch particles (usually chemically unmodified insoluble starch particles) slurried in a solution of cationic starch. However it is generally preferred that the retention aid is a synthetic polymer.

[0063] The preferred retention aids for use in the invention are polymers which have intrinsic viscosity above 4dl/g and usually above 6dl/g, for instance 8-15dl/g or 8-20dl/g or higher.

[0064] In this specification, intrinsic viscosity is measured at 25°C in 1M sodium chloride buffered at pH7 using a suspended level viscosimeter.

[0065] Non-ionic retention aids that can be used include polyacrylamide or other polymer of water soluble ethylenically unsaturated monomer or monomer blend, and polyethylene oxide.

[0066] Suitable anionic retention aids are polymers of anionic ethylenically unsaturated sulphonic or carboxylic monomer such as acrylic acid (usually as a sodium or other water soluble salt) optionally copolymerised with non-ionic ethylenically unsaturated monomer such as acrylamide. Thus the anionic polymer may be formed from, for instance, 3 to 50 mole percent, often 3 to 20 mole percent anionic monomer such as sodium acrylate with the balance being acrylamide.

[0067] Amphoteric polymers containing both anionic and cationic monomer units, usually with acrylamide or other non-ionic monomer, can be used.

[0068] Cationic polymers are preferred.

[0069] The or each cationic high molecular weight polymer is usually a copolymer of ethylenically unsaturated cationic monomer, with the balance being other water soluble, generally non-ionic, ethylenically unsaturated monomer such as acrylamide. The amount of cationic monomer is usually at least 2 or 3 mole%. Generally it is not more than 20 mole% but it can be up to 50 mole % or more. The polymer can be wholly water soluble or it can be in the form of small particles of partially soluble cross-linked polymer as described in EP-A-202,780.

[0070] The or each high molecular weight cationic polymeric retention aid typically has a theoretical cationic charge density of not more than about 3meq/g, often not more than about 2meq/g. Generally it is at least about 0.1, or usually at least about 0.5, meq/g. In this specification, the theoretical cationic charge density is the charge density obtained by calculation from the monomeric composition which is intended to be used for forming the polymer.

[0071] Suitable cationic monomers include dialkyl aminoalkyl (meth) -acrylates and -acrylamides as acid addition or quaternary salts. The alkyl groups may each contain 1-4 carbon atoms and the aminoalkyl group may contain 1-8 carbon atoms. Particularly preferred are dialkylaminoethyl (meth) acrylates or acrylamides and dialkylamino-1,3-propyl (meth) acrylamides.

[0072] Although it is usually preferred for the retention aid to have intrinsic viscosity above 8dl/g, in some instances it can be desirable to use as the retention aid a copolymer of diallyl dimethyl ammonium chloride and acrylamide and which has intrinsic viscosity at least 4dl/g, even though it may not be practicable to manufacture such a polymer to the IV 8dl/g and higher values that are preferred for other polymers.

[0073] The total amount of polymeric retention aid is usually 0.01 to 1%, generally 0.02 to 0.1% (200 to 1,000 gram per tonne dry weight of suspension). When the process involves shearing and reflocculating with microparticulate material the amount of retention aid is generally in the range 0.01 to 0.06% or 0.1% but when the process is conducted merely with flocculation followed by drainage, i.e., without the shearing and reflocculation, the amount is usually in the range 0.04 to 0.15%, often 0.06 to 0.1%.

[0074] The amount depends, inter alia, on the choice of cellulosic thin stock. This may be formed from any convenient pulp or mixture of pulps. The thin stock typically has a cellulosic fibre content of 0.2 to 2.0%, usually 0.3 to 1.5% by weight.

[0075] The retention aid of IV above 4dl/g (or cationic starch) and the amount of it which is used in the process must be such as to give good retention of fibre fines and filler (if present). Selection of the retention aid and its amount can be conducted in conventional manner by performing the process in the absence of starch with different amounts of different retention aids so as to select an effective combination of retention aid and its amount for the particular cellulosic suspension that is being treated. Naturally this test should be conducted with the subsequent addition of microparticulate anionic material when the overall process involves the use of that material. When the initial cellulosic suspension includes anionic trash, it can be desirable to treat the suspension initially with a cationic coagulant and/or bentonite so as to reduce the amount of polymeric retention aid that is required.

[0076] The amount of retention aid will always be greater than the amount required to precipitate or interact with anionic soluble material in the cellulosic suspension. If the retention performance is plotted against dosage of polymer in a typical combination it will be seen that as the dosage increases retention will be poor and will increase only gradually at low values, but will then increase significantly over a relatively small dosage range, and will not then increase further

to any significant extent. The dosage at which retention improved markedly is an indication of the demand of that suspension for that retention aid and in the invention the total amount of that retention aid should be at or above the amount at which retention has increased significantly. Accordingly this amount is above the stoichiometric amount required to react with any anionic polymeric material in the cellulosic suspension and any pulp from which it is formed.

Generally the suspension is made without deliberate addition of anionic, polymeric materials.

[0077] By saying that the cellulosic suspension is flocculated we mean that it has the state which is typical of a cellulosic suspension which has been treated with an effective high molecular weight retention agent in an effective amount.

[0078] In preferred processes, the retention system is selected and optimised (using high IV polymer or dissolved cationic starch) for retention, drainage and drying properties in conventional manner, and the particulate starch is injected into the polymer solution with no substantial change in the optimum retention system.

[0079] The starch in the particles must remain substantially undissolved prior to the start of drainage of the suspension, since otherwise dissolved starch is likely to drain from the suspension. A simple way of determining whether or not the particles have remained substantially undissolved is to titrate the drainage water for dissolved starch. If the amount of dissolved starch in the drainage water is sufficiently low (after allowing for any dissolved starch introduced with the fibres from, for instance, recycled paper), this indicates that the particles have remained substantially undissolved. For instance preferably the amount of dissolved starch in the drainage water should represent less than 20%, preferably less than 10% and most preferably less than 5% of the amount of particulate starch in the suspension after discounting soluble starch originating elsewhere.

[0080] One way of providing that the particles remain substantially undissolved prior to drainage is to introduce the starch in ungelatinised, substantially water insoluble, form and to maintain the conditions in the suspension such that significant gelatinisation does not occur prior to the start of drainage. In such a process, it is necessary to gelatinise the starch during the draining and drying stages.

[0081] In conventional processes, draining is completed at temperatures above ambient, and drying is conducted with the application of heat. By appropriate choice of the draining and drying conditions and of the grade of ungelatinised starch, it is possible to achieve appropriate gelatinisation during the drying stage, while the sheet is still moist. It can be desirable to apply deliberate heating to the wet sheet, even before final drainage is completed, so as to pre-warm it before entry to the drying stages. For instance the wet sheet may be passed under a steam hood or heater such as a Devroniser (trade mark), and this can facilitate full gelatinisation and dissolution of the starch.

[0082] The act of shearing the flocculated suspension prior to reflocculation will necessarily tend to break up any flocs or aggregates of starch particles, and so this preferred process will tend to result in the starch particles being more uniformly distributed as mono-particles through the sheet. As a result, more thorough gelatinisation of these particles will occur than when clusters of particles are present in the sheet, and this is an important advantage of the preferred processes of the invention which involve shearing and reflocculation of the flocculated suspension.

[0083] The starch particles need to gelatinise while there is still some moisture in the sheet in order to allow gelatinisation to proceed satisfactorily and in order to allow the particles to spread in the sheet so as to tend to provide a film within the sheet, in contrast to mere spot bonds. As a result of the starch gelatinising in the presence of moisture, it will tend to migrate between the fibres so as to obtain more uniform distribution of the starch on and around and between the paper fibres. The amount of moisture that should remain in the sheet when the starch is dissolving can be quite low, and only needs to be sufficient to allow migration of the gelatinised starch sufficient to give adequate distribution of the starch through the sheet.

[0084] To facilitate attainment of rapid gelatinisation, it may be desirable to use a starch that has naturally a low temperature gelatinisation or that has been modified to reduce its temperature of gelatinisation, provided it remains substantially undissolved prior to drainage.

[0085] Usually the starch is an uncooked, raw starch such as raw maize, potato, corn, wheat or tapioca starch.

[0086] Pregelatinised or precooked (and therefore soluble) starch can be included as insoluble particles. Thus, instead of relying on the insolubility of ungelatinised starch particles and the subsequent cooking occurring during the process, the dissolution of precooked starch in the particles of the suspension can be prevented by protecting the starch with a water impermeable shell or matrix that disintegrates during the subsequent draining or drying. Any material which provides sufficient water impermeability to prevent significant dissolution of the starch prior to draining can be used provided the shell or matrix will disintegrate to release the starch during draining and/or drying.

[0087] The shell or matrix does not have to provide long term water-impermeability. For instance a slow dissolving shell or matrix may be sufficient to protect the starch since even if the shell disintegrates partially within the headbox there may still be inadequate time for the enclosed starch particle to dissolve in the headbox.

[0088] The shell or matrix may be a thermoplastic material having a melting point such as to prevent premature disintegration of the shell or matrix. For instance the normal temperature of the suspension leading to the headbox is typically in the range 40-50°C and the ambient temperature around the drainage screen is typically in the same range. If the particles are provided with a coating or matrix which has a melting temperature at about or above the temperature

of the headbox, substantially no melting will occur until the headbox and most of the melting and substantially all the dissolution of the starch will not occur until most of the draining has been completed. Suitable thermoplastic materials that can be used include hydrocarbon waxes.

[0089] Instead of using a thermoplastic shell or matrix, a pH sensitive shell or matrix may be used. For instance the cooked starch may be encapsulated or otherwise protected by polymer that is water insoluble and non-swellable at the pH of the starch dispersion which is provided to the mill, and this dispersion is added to the headbox which is at a pH at which the polymer swells or dissolves. For instance the protective polymer can be a copolymer of water soluble and water insoluble ethylenically unsaturated monomers such as methacrylic acid or other water soluble monomer and ethyl acrylate or other water insoluble monomer. The manufacture of pH sensitive polymers of this general type by oil-in-water emulsion polymerisation is well known.

[0090] Methods of incorporating an active ingredient within particles of a protective matrix or within a shell are well known and can be used in the invention. For instance the mixture of the starch and protective material may be spray dried or a coacervate coating may be formed around starch particles.

[0091] The amount of starch that is included in the sheet will normally be at least 0.05% and usually at least 0.2% dry weight. The greatest advantages of the process are achieved when the amount is above 2 or 3%, for instance 5%, 10% or even up to 12 or 15% by weight. However an advantage of the process of the invention is that the process can be operated either at high starch loadings or low starch loadings merely by altering the amount of starch, without making any significant changes in the remainder of the process.

[0092] The size of the particles is generally at least 90% by weight below 100 μ m, preferably below 50 μ m, often 5 to 50 μ m. The starch particles may have a size of at least 90% by weight up to 10 μ m, generally 5-10 μ m. The starch is preferably granular, so that all three dimensions may be broadly similar.

[0093] The anionic microparticulate or colloidal material (when used) is preferably bentonite, that is to say an inorganic swelling clay, for instance as described in EP-A-235,893. However it can be colloidal silica (such as described in U.S. 4,643,801), polysilicate microgel (such as described in EP-A-359,552), polysilicic acid microgel as described in EP-A-348,366, or aluminum modified versions of any of these. Instead of using inorganic anionic colloidal material, organic material can be used. Thus it is possible to use an anionic organic polymeric emulsion. The emulsified polymer particles may be insoluble due to being formed of a copolymer of, for instance, a water soluble anionic polymer and one or more insoluble monomers such as ethyl acrylate, but preferably the polymeric emulsion is a crosslinked micro-emulsion of water soluble monomeric material. The particle size of the colloidal material is generally below 2 μ m, preferably below 1 μ m and most preferably below 0.1 μ m.

[0094] The amount of colloidal material (dry weight based on the dry weight of the cellulosic suspension) is generally at least 0.03% and usually at least 0.1%. It can be up to, for instance 2% but is generally below 1%. The choice and the amount of the anionic colloidal material should be such as to cause what is frequently referred to as "super coagulation".

[0095] The anionic microparticulate or colloidal material is preferably added to the suspension after the last point of high shear, for instance at the headbox, and the suspension can then be drained in conventional manner.

[0096] Initial selection of suitable materials can be made on the basis of trials with conventional laboratory apparatus such as a Britt jar and a hand sheet technique, but commercial operation of the process is conducted on a paper-making machine wherein the cellulosic thin stock is provided in conventional manner, generally by dilution of thick stock with white water, and is fed towards a headbox through suitable apparatus such as a fan pump and centriscreeen, and is discharged from the headbox onto a moving screen.

[0097] This screen may travel at conventional screen speeds which are normally in excess of 100 metres per minute and typically are in the range 700 to 1500 metres per minute.

[0098] The machine will include a drying zone in conventional manner but an advantage of the invention is that it is not necessary for the machine to be equipped with a size press or with any other means of applying starch to the wet sheet or to the dried sheet.

[0099] If desired, however, further starch can be applied to the wet sheet or the dried sheet in conventional manner.

[0100] The following are examples.

Example 1

[0101] A mill trial was carried out on a Fourdrinier machine producing fluting medium at 600m/min from 100% waste furnish. A cationic polymer of acrylamide with 10% mole cationic acrylate, IV 12dl/g, was added to the thin stock before the centriscreeen at a dose level of 800g/tonne. A 20% slurry of raw starch was added to the polymer line just prior to the addition of the polymer to the thin stock, in sufficient quantities to provide 5% starch on dry weight of paper. Bentonite was added to the thin stock after the centriscreeen and just before the head box, at a dose level of 0.5%.

[0102] Analysis of starch retained in the sheet showed that over 95% of the added starch was retained in the sheet. The heating during the drying stages of the machine caused the starch to be gelatinised during the drying.

Example 2

[0103] Liner board having a weight of about 140 grams per square metre was made on a Fourdrinier machine in a process using as retention aid an aqueous solution of a polymer of acrylamide with 10 mol % dimethylaminoethyl acrylate quaternary salt [DMAEAq], having IV 12dl/g, at a dosage of 850g/tonne in the top ply and 790g/tonne in the bottom ply, added before the centriscreen and bentonite at a dosage of 5kg/t in both the top and bottom ply added after the centriscreen. The suspension included recycled paper and it was found that the starch content in the sheet, with no deliberate addition of starch, fluctuated between about 0.9 and 1.2%.

[0104] Particulate raw potato starch was then injected as a slurry into the polymer feed line at a dosage of 1.42% based on the dry weight of the suspension. When steady state conditions had been re-established, the amount of starch in the sheet was 2.49%, indicating substantially complete retention of the particulate starch.

[0105] When the amount of particulate starch in the suspension was increased to 3.11%, the amount in the sheet was raised to 4.34%, and when the amount in the suspension was raised to 3.50%, the amount in the sheet was raised to 4.55%, again indicating substantially complete retention.

[0106] The burst strength was increased by about 35% and the CMT value by about 20%.

Example 3

[0107] In order to conduct preliminary screening of suitable combinations of materials, a waste furnish was prepared from 60% newsprint, 30% cardboard and 10% magazine and was pulped in a laboratory disintegrator for 20 minutes and then diluted to form a 0.5% thin stock suspension at 25°C. It was left to condition for 24 hours. It had pH 7.5 to 7.7.

[0108] 500mls of thin stock was placed in a Britt Dynamic Drainage jar fitted with a machine wire with the stirrer set at 1500rpm. The required amount of a 20% starch slurry was mixed with the required amount of a 0.5% solution of polymer and added to the drainage jar. After stirring for 60 seconds at 1500rpm the stirrer was slowed to 800rpm and the required amount of bentonite slurry was added. After 10 seconds mixing, the backwater was collected for 30 seconds.

[0109] The collected backwater was cooked at 100°C for 30 minutes, the volume re-adjusted to the original volume and the sample centrifuged to remove fibres. Acidified potassium iodide/iodine reagent was added and the blue starch/iodine complex was assessed optically and compared to a calibration graph to give an indication of the starch content of the water. Due to the particular analytical techniques used the values are more indicative of relative values than absolute values, but increasing the value indicates increased retention.

[0110] In a first series of tests, polymer (acrylamide with 10 mol % dimethylaminoethyl acrylate quaternary salt, IV 12dl/g) was added at 750 grams per tonne fibre, bentonite at 2,000 grams per tonne fibre and starch 80kg per ton fibre (8%). The following results were obtained.

Addition Point	Starch Retention
Starch No Polymer No Bentonite	74
Starch before Polymer	81.4
Starch with Polymer	96.5
Starch after Polymer	82.6
Starch with Bentonite	93.1

[0111] These results indicate that best results are obtained when starch is mixed with the polymer (followed by the bentonite). Useful retention is also obtained when the polymer is added separately and the starch is subsequently added with the bentonite. Addition of the starch by itself, before or after the polymer, gives poor results.

Example 4

[0112] A process broadly as in Example 3 was repeated comparing the retention (measured as in Example 3) at 4%, 6% and 8% starch when there is no polymer and bentonite (control) or when the starch is added with 750g/t polymer followed by 2,000g/t bentonite.

Starch Addition	Retention System	Starch Retention
4%	No	57.9
4%	Yes	99.4

(continued)

Starch Addition	Retention System	Starch Retention
6%	No	63.1
6%	Yes	83.7
8%	No	71.2
8%	Yes	90.5

[0113] The amount of starch added based on the volume of the suspension at the 4%, 6% and 8% amounts based on the weight of fibre was 200, 300 and 400ppm respectively.

Example 5

[0114] A process broadly as described in Example 3 was used except that in the three tests conducted using polymer in the absence of anionic microparticulate material the starch was added with the polymer solution to the drainage jar with the stirrer set at 800rpm and after 10 seconds mixing the backwater was collected for 30 seconds. Starch retention was measured as in Example 3.

[0115] The results were as follows:

Product	Dosage	Starch
		Retention
Polyethylene imine	1,000g/t	72.6
Polyamine epichlorhydrin	1,000g/t	78.3
10 mol % DMAEAq/90 mol % acrylamide copolymer IV 12	750g/t	92.5
10 mol % DMAEAq/90 mol % acrylamide IV 12 followed by polysilicic acid	750g/t plus 500g/t	91.7

[0116] These results clearly demonstrate the greatly improved retention that is attainable using high IV cationic polymer compared to low molecular weight cationic polymers. They also show that good results can be obtained using polysilicic acid as the anionic microparticulate material but direct comparison between the two tests with the cationic polyacrylamide is not wholly reliable because of the different conditions used for the tests.

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 polymeric retention aid selected from dissolved cationic starch and synthetic polymer having IV above 4dl/g and thereby forming a flocculated suspension,
 shearing the flocculated suspension and reflocculating the sheared suspension by adding an aqueous suspension of micro-particulate anionic material and thereby forming a reflocculated suspension,
 draining the flocculated or re-flocculated suspension through a moving screen to form a wet sheet, and
 carrying the sheet through a heated drying zone and thereby forming a dry sheet,
 wherein insoluble particles of starch are added to the cellulosic suspension as a slurry of substantially freely dispersed particles in part or all of the aqueous solution of the polymeric retention aid, and
 the insoluble particles of starch are heated during the drying and release soluble starch into the sheet in the presence of moisture.

2. A process according to claims 1 in which the anionic microparticulate material is selected from inorganic swelling clays, colloidal silica, polysilicate microgels, polysilicic acid microgels and aluminium modified colloidal silica, aluminium modified polysilicate microgel and aluminium modified polysilicic acid microgel.

3. A process according to claim 1 or claim 2 in which the paper is a filled paper.

4. A process according to claim 1 or claim 2 in which the paper is substantially unfilled paper.

5. A process according to any preceding claim in which the starch in the particles is ungelatinised such that substantially no dissolution of starch into the suspension occurs prior to drainage, and the starch is gelatinised during the draining and/or drying.

6. A process according to any preceding claim in which the retention aid is a synthetic polymeric material having intrinsic viscosity at least 4dl/g.

7. A process according to any preceding claim in which the retention aid is a synthetic polymeric material having intrinsic viscosity at least 8dl/g.

8. A process according to any preceding claim in which the polymeric retention aid is cationic.

9. A process according to any preceding claim in which the insoluble particles of starch are added as a slurry in a solution of substantially all the polymeric retention aid.

10. A process according to any of claims 1 to 3 or any of claims 5 to 9 in which the sheet contains 20 to 60% by weight filler.

11. A process according to claim 1 or claim 2 or any of claims 4 to 9 in which the sheet is a substantially unfilled sheet which is fluting medium or liner board.

12. A process according to any preceding claim in which the amount of starch in the sheet is from 2 to 15%.