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⑤④ **Production of paper.**

⑤⑦ Internally sized paper is made by incorporating cationic retention aid into a cellulosic suspension to form flocs, breaking these down to microflocs, aggregating them by bentonite or other anionic polymeric material, draining the suspension and drying the resultant sheet, and the size is incorporated in the suspension as a non-ionic or anionic emulsion after the addition of the cationic retention aid.

This invention relates to the production of sized cellulosic sheet materials. These sheet materials are referred to below as paper but they can be of a wide range of weights and so include not only materials having the weight of traditional papers but also materials that can be referred to as paper board.

Paper is made by providing a cellulosic suspension, draining this suspension to form a sheet and drying the sheet. The paper can be sized either by surface sizing or by internal sizing. Surface sizing is generally conducted by applying the size to the sheet after partial or full drying and so is wasteful of energy and also tends to concentrate the size on the surface. Internal sizing is effected by including the size in the suspension prior to drainage.

Various hydrophobic materials are known for internal sizing and each of them is generally formulated as an aqueous emulsion prior to addition to the cellulosic suspension. Suitable sizes are rosin sizes, including fortified rosin sizes, and reactive sizes, for instance ketene dimer sizes and anhydride sizes.

The sizes generally tend naturally to be non-ionic or anionic. Traditional thinking dictates that there should be the maximum opportunity for the size to be absorbed on to all the particles that eventually go into the paper sheet and so conventional processes involve adding the emulsion at an early stage in the paper-making process, thereby giving sufficient time for the size to be absorbed on to the particles (i.e., cellulosic fibres and any filler particles) prior to drainage. Typically therefore the size is added at a sufficiently early stage that the sized suspension is subjected to considerable agitation or shear, for instance by passage through a centriscreen, fan pump or other apparatus that results in the application of shear, before drainage.

Since the solid components of the cellulosic suspension are naturally also often anionic it is known to be desirable to add various materials to precipitate the size on to the fibres or in some other way to make the size more substantive to the fibres. For instance rosin size and fortified rosin size is usually supplied as an anionic emulsion and is applied simultaneously with alum which precipitates the emulsion particles on to the cellulosic fibres.

When adding a reactive size, the conventional practice is to add it in the form of a cationic emulsion, i.e., an emulsion of the non-ionic or anionic size which contains a cationic material in an amount sufficient to render the emulsion particles cationic. For instance commercial ketene dimer sizes are usually supplied as cationic emulsions.

A variety of cationic additives are known for incorporation with the reactive size so as to form a cationic emulsion. The cationic additive can have a low or very low molecular weight. For instance one class of cationic additives that are known for use with ketene dimer sizes consists of dicyandiamide polymers. These are formaldehyde condensation products that are incorporated while they have a low molecular weight (generally well below 1000) and are water soluble. They render the ketene dimer particles substantive to the cellulosic fibres and subsequently they act as cure promoters for the ketene dimer to accelerate curing of it on to the paper, and during this process they polymerise and become higher molecular weight and insoluble.

Instead of adding the cationic additive to the size, it is also known to incorporate the cationic additive in the cellulosic suspension and then to add the size. For example EP-A-174911, 175647, 176479 and 227600 all mention the possibility of adding the cationic material and the size in any order, and JP-A-54096104 and JP-A-54068405 both describe adding cationic polymer to cellulosic suspension and then adding anionic sizing agent. In such processes, it is to be expected that the sized suspension, to which a cationic polymer had previously been added, would be subjected to considerable agitation and shear (as in conventional processes) before the drainage.

Cationic polymers that can be used include water soluble cationic starches and, especially, water soluble, medium or high molecular weight, synthetic cationic polymers. Typically they have a molecular weight of above 500,000, and often much higher. These materials are also used in the paper industry as retention aids, but for this purpose conventional thinking has dictated that they should be added immediately prior to drainage, after the last point of high shear. This is because it is well known in the literature that retention is adversely affected if a suspension is subjected to agitation or other shear after the application of the polymeric retention aid and before drainage. Accordingly, when these cationic retention aids are used to increase the substantivity to the size of the solid components of the suspension in otherwise conventional paper-making processes, their incorporation will have little or no effect on retention. As a result, it is in practice necessary to add further retention aid at the end of the process so as to achieve adequate retention values.

Thus the conventional process would necessitate the use of a cationic polymer or other retention aid at an early stage in the process followed by sizing, the application of shear and then the addition of a conventional cationic retention addition immediately prior to drainage. Even when subsequent retention aid is added, the retention values may be rather poor and in particular a significant amount of cellulosic fibres and, if present, filler particles that are coated with size are liable to drain through the sheet into the white water. Thus the perceived advantage of adding the size sufficiently early to allow adsorption on to all the solid particles in fact incurs a disadvantage, namely that a substantial amount of size is lost due to inadequate retention of these fine par-

5 ticles. A related, and very serious, problem arises when the suspension contains substantial amounts of filler. Many fillers for cellulosic suspensions are hydrophobic and so there is little or no need to coat them with size. However the cationic pretreatment will tend to render these particles (as well as the paper fibres) cationic and so will promote the deposition of the size on to the filler particles. The surface area of the filler particles can be very large and so a large amount of size can be absorbed unnecessarily on to filler. The size that is thereby carried into the sheet by the filler tends to be unnecessary, and the size that is thereby lost as a result of poor retention of the filler is completely wasted.

10 A further related problem exists when, as is common, the filler content of the suspension varies during a prolonged production run. This variation can be caused by deliberate alteration in the amount of filler. Frequently, however, the variation occurs spontaneously because part or all of the suspension is formed from waste paper, and this inevitably is liable to have a variable filler content. Thus, during a process, the amount of filler is liable to fluctuate significantly and, accordingly, the amount of size that is absorbed unnecessarily on to the filler is liable to fluctuate. As a result, it is difficult, and often impossible, to obtain a sheet having uniform sizing properties, since there may either be excess size on the sheet or insufficient size, depending upon how much is wasted on to filler particles.

15 Ketene dimer sizing compositions have the advantage that they can be supplied to the mill as a relatively stable cationic aqueous emulsion that is ready for use, but they have two main disadvantages. One is that, although the emulsion is relatively stable, it does undergo some hydrolysis on storage with the result that properties are liable to deteriorate if the emulsion is stored for too long, for instance for several weeks. Another disadvantage is that the ketene dimer tends to cure rather slowly and so may need to be accompanied by a cure promoter, as discussed above.

20 Anhydride sizes have the advantage that they cure more readily but they have some disadvantages, primarily due to the high reactivity of the anhydride size. Because it reacts quickly with water, the emulsion must normally be prepared at the mill. However, even when it is prepared at the point of use, hydrolysis is liable to occur sufficient to generate anionic carboxyl groups. The hydrolysis can tend to destabilise the emulsion. An important problem that arises from the hydrolysis is that the carboxyl groups can react with cationic polymer present in the emulsion to cause the formation of sticky complexes and these can cause picking at the press and runnability problems on the machine, which are well known problems of anhydride sizing. Although runnability problems can occur with other anionic or potentially anionic sizes it is well accepted that these problems are particularly serious with anhydride sizes. It seems that their tendency towards the formation of sticky complexes with cationic polymer is greater than is the tendency with other anionic sizes.

30 Conventional sizing processes therefore have a rather high consumption of size and either suffer from inadequate curing (unless cure promoters are added) or give rise to runnability problems on the machine, depending on the choice of size. In particular, the sizes that are commercially preferred for many reasons (the anhydride sizes) tend to cause runnability problems and this severely limits their applicability. A further problem is that the efficiency of the sizing can be difficult to maintain because of variable size demand due to variations in the filler.

40 As mentioned, in order to improve retention in a paper-making process it is conventional to add the retention aid after the last point of high shear. However some processes are known in which cationic retention aid is added to the suspension to cause flocculation of the suspension, the flocs are subsequently or substantially simultaneously broken down into cationically charged microflocs without substantial resuspension of the fibres, the cationically charged microflocs are aggregated by addition of a material such as bentonite or colloidal silicic acid, and the aggregated suspension is dried to form a sheet. Such processes are described in, for instance, U.S. 4,388,150, U.S. 4,753,710 and EP 235893.

45 It is also known to use such processes for making sized paper and in particular examples in EP 235893 show incorporating size in the cellulosic suspension in conventional manner and then adding cationic polymeric retention aid and then shearing and then adding bentonite. It is also stated that the size and the cationic polymeric retention aid can be provided in a single anhydrous composition, with the result that the size and the retention aid would be added to the suspension simultaneously. Addition from a single composition restricts the flexibility of the process. Processes such as EP 235893 have also been performed by adding conventional cationic size emulsion substantially immediately after the retention aid. This again incurs the disadvantage of, for instance, having to formulate the size with a cationic additive. In particular, there is no suggestion here as to how to solve the well established runnability problems that arise when ASA sizes are used.

50 It would be desirable to be able to improve the efficiency of sizing processes while avoiding the the problems of sticky deposition and runnability traditionally associated with anhydride sizes, and it would be desirable to be able to produce sized paper in a process that gives good retention, dewatering and formation properties.

55 In one aspect of the invention, internally sized paper is made by a process comprising flocculating a suspension of cellulosic fibres by addition of a cationic retention aid, breaking the flocs down to form cationically

charged microflocs without substantial resuspension of fibres, adding a non-ionic or anionic emulsion of anhydride size to the suspension after flocculating the suspension and generally after forming the microflocs, aggregating the microflocs by addition of a solution or suspension of anionic compound to form an aggregated suspension containing the size, draining the aggregated suspension to form a sheet and drying the sheet.

5 The size must be added after the suspension has been flocculated and preferably it is added after the flocs have been broken down to microflocs without substantial resuspension of fibres. Accordingly, in contrast to conventional sizing operations, the size is deposited on to the flocculated material rather than on to the individual fibres and filler particles (if present). Accordingly, there is less tendency than in conventional sizing processes for size to be wasted by being adsorbed on to filler particles that are not retained in the sheet, and the process is less susceptible than conventional sizing processes to variations due to changes in the amount or type of filler.

10 An important advantage compared to other processes in which cationic polymer is added to the suspension before the size arises because much of the filler is trapped in the microflocs thereby greatly reducing the surface area of filler that is exposed to the size, and greatly improved retention further reduces the size demand. For instance the surface area exposed to the size in the invention typically can be, for instance, only one tenth of the surface area exposed when the fibres and filler have not previously been flocculated into microflocs or larger flocs and so the invention allows the attainment of good sizing with smaller amounts of size than would previously have been required.

15 A further advantage is that the formation of sticky complexes and runnability problems are minimised in the invention partly because it is not necessary to include cationic material in the emulsion and partly because of the reduced recycling in the white water of sized filler and fibre particles.

Although these advantages are particularly significant for anhydride sizing, in other aspects of the invention the process can be conducted using other sizes instead of the anhydride size. These other sizes can be sizes such as rosin but they are preferably reactive sizes such as ketene dimer sizes and any of the others mentioned above.

20 Often the size, in all aspects of the invention, is added after the last point of high shear (e.g., fan pump or centriscreeen) that will break the flocs down to microflocs and the anionic compound is usually also added after the last point of high shear. The size can be added after the aggregation provided there is sufficient mixing to distribute the size throughout the aggregated structure, and this will generally involve breaking the aggregated structure down to smaller aggregates prior to drainage. This can be acceptable. It is generally more convenient, however, to add the size either during aggregation or prior to aggregation. If it is being added during aggregation the size and the anionic compound can be added as a single composition, but prolonged contact between the size and the anionic compound may be undesirable (for instance if that compound can interact with the size) in which event it is desirable either to mix the components immediately prior to addition to the suspension or to add them separately but close to one another.

25 The cationic retention aid can consist of or include cationic starch, but preferably comprises synthetic cationic water soluble polymer having molecular weight above 500,000. This synthetic material may be the only retention aid that is used or, as mentioned, it may be used in combination with cationic starch or other materials. The suspension may include dry strength resins and/or relatively low molecular weight cationic materials added for the purpose of improving strength properties or other purposes, for instance as described in U.S. 4,913,775 the entire disclosure of which is herein incorporated by reference.

30 The cationic retention aid can be of relatively high molecular weight (for instance intrinsic viscosity IV above 4dl/g) in which event it can be desirable to add also to the suspension, generally immediately before the addition of the size, a lower molecular weight synthetic cationic water soluble polymer, for instance having a molecular weight of IV 3dl/g or less, typically molecular weight 50,000 to 2 million. For instance polydimethyldiallyl ammonium chloride (or copolymer with acrylamide) or other low molecular weight cationic material can be added.

Intrinsic viscosity measurements mentioned in this specification are obtained using a Suspended Level Viscometer in a buffered IN sodium chloride solution at 25°C.

35 The cationic retention aid is preferably one of the materials described in EP 235893 or U.S. 4,913,775 or U.S. 4,753,710 and reference should be made to those documents for a full description of suitable materials.

40 The addition of the retention aid causes flocculation and the flocculated suspension is subjected to sufficient agitation to break the flocs down to microflocs. Provided the amount of retention aid is sufficiently high, the microflocs are cationically charged and that the breaking down of the flocs to the microflocs does not cause substantial resuspension of fibres (and filler if present) into the suspension. The amount of cationic retention aid that is required to achieve the formation of these stable microflocs will depend on the nature of the polymer, the nature of the suspension and whether or not any other cationic polymer has been added to the suspension. Thus, when other cationic material is present in the suspension, for instance cationic starch or a relatively low

molecular weight synthetic cationic polymer serving as, for instance, a dry strength resin, the amount of the defined cationic retention aid can be less than would be required if the suspension is substantially free of other cationic materials. For instance if other cationic materials, such as low molecular weight polymers, are present it may be possible for the amount of cationic retention aid to be as low as 0.005% or, more usually, 0.01% (dry weight polymer based on dry weight suspension), i.e., usually at least 100 grams dry polymer per ton dry weight paper. Usually however the amount of cationic retention aid is at least 0.03% and often up to around 0.1 or even 0.3%. The amount will generally be more than is required in conventional processes where the retention aid is added at the headbox, so as to ensure that the fibres and any filler are sufficiently cationic to be substantive to the size, even after any possible shearing of the flocs created by the retention aid, e.g., as in U.S. 4,753,710.

The agitation necessary to break the flocs down to the stable microflocs can follow merely from turbulence along ducting in the paper-making machine or can follow from the application of a deliberate shear stage, such as a fan pump or a centriscreeen.

The cationic polymer retention aid is preferably a polymer as described in EP 235893, U.S. 4,753,710 or U.S. 4,913,775, and generally has a molecular weight above 1 million and often above 5 million, for instance in the range 10 to 30 million or more. Expressed as intrinsic viscosity, its value is generally above 4dl/g and often above 7dl/g, often in the range 10 to 12dl/g although higher values can be used. If the cationic retention aid is of relatively low molecular weight (for instance below IV 4 or below 1 or 2 million) it may be necessary to restrict the amount of shear that is applied to the system after the addition of the retention aid since excessive shear will then have an increased tendency to result in rather poor retention unless other process steps are added. However good results can be obtained upon application of shear if the retention aid has very high molecular weight and is fully soluble in water, for instance when the retention aid is a linear synthetic cationic polymer having intrinsic viscosity above 8, and often above 12dl/g.

When cationic starch is to be used as the retention aid, suitable materials are as described in U.S. 4,388,150.

The microflocs are subsequently aggregated by the addition of anionic compound capable of causing such aggregation. This compound can be a water soluble anionic polymer and thus can be an anionic polymeric retention aid, for instance having molecular weight above 1 million. Synthetic anionic retention aids, for the final addition, include anionic acrylic polymers such as anionic copolymers of acrylamide with (meth) acrylic acid or other ethylenically unsaturated carboxylic acid, and having intrinsic viscosity typically above 10, often above 15 and frequently above 20dl/g.

Preferably, however, the anionic compound is an inorganic material, and in particular it is preferably colloidal silicic acid as described in U.S. 4,388,150 or WO86/05826 or, most preferably, bentonite. The bentonite can be any suitable anionic swelling clay, that is to say a smectite for instance as described in EP 235893 or U.S. 4,753,710 and so can be any swelling clay having a significant smectite or montmorillonite structure such as Wyoming bentonite or Fullers Earth, or hectorite or sepielite or attapulgite.

The amount of anionic compound will be selected so as to give the desired aggregation and will depend on, inter alia, the amount of cationic polymer that was used. Suitable amounts can easily be found by routine experimentation and are generally in the range 0.01 to 0.5%. In particular, when a bentonite is being added, the amount is usually at least 0.01%, and most usually at least 0.03%, and can be as described in U.S. 4,753,710, e.g., up to 0.5%. Generally it is in the range about 0.05% to 0.3%.

Instead of or in addition to adding bentonite or water soluble anionic polymer before, with or after adding the size, highly branched or swellable anionic polymers, e.g., reverse phase emulsion polymers of cross linked acrylic acid acrylamide copolymers, can be used.

An advantage of the process is that it is not necessary or desirable to add cationic retention aid after the size, and yet good retention, dewatering, formation and drying can be obtained.

The cellulosic suspension can be any suspension suitable for making sized paper. It can include recycled paper. It can be unfilled or filled and so may contain any of the conventional fillers. The invention is of particular value when the suspension contains at least 10% inorganic filler (dry weight), for instance up to 50%.

The preparation of the suspension and the details of the paper-making process (including the drainage and drying steps) may all be conventional except as described herein. The paper can be any sized paper, including paper board.

The size can be an unreactive size such as a rosin size or fortified rosin size. This can be added in combination with alum but it can alternatively be added in the absence of alum, reliance being placed instead on the cationic polymer in the suspension to precipitate the rosin on to the fibres.

Preferably however the size is a reactive size such as any of those mentioned above. Preferably it is a nonionic or anionic emulsion of ketene dimer or anhydride size (for instance alkenyl succinic anhydride size). This may be formed using non-ionic or anionic oil-in-water emulsifying agent and water in conventional manner,

except for the omission of the cationic agent which has previously normally been included. For instance if the size previously included a cationic starch, in the invention it could include oxidised starch instead, and anionic emulsifying or dispersing agents such as sodium polyacrylate of molecular weight below 10,000 or naphthalene formaldehyde sulphonate condensates can be used. Generally, however, a low molecular weight emulsifier, generally an anionic or non-ionic emulsifier or mixture thereof, is used.

The preferred compositions for the invention are substantially non-ionic and include a non-ionic emulsifier.

If the size is a ketene dimer size, a cure promotor can if desired be included in the suspension before, during or after the addition of the size.

The invention is of particular value when the size is an anionic or potentially anionic size, that is to say a material that is liable to undergo hydrolysis during the emulsification or use of the size so as to render it anionic, and thus prone, in conventional processes, to causing problems due to stickiness and difficulties in runnability. The invention is of particular value when the size is an anhydride size, especially when it is an alkenyl succinic anhydride (ASA) size, since the invention provides a way of overcoming the runnability problems associated with such sizes and giving fast sizing and good retention without the need to make other additions to the process to try to achieve these objectives.

One preferred process comprises using cationic starch as part or all of the retention aid and colloidal silicic acid as the anionic compound, but in general the preferred processes comprise the use of cationic synthetic polymer as part or all of the retention aid and bentonite as the anionic compound. The preferred size is an ASA size provided as a non-ionic or anionic emulsion.

The cationic retention aid can be included in the thick stock and/or in the recycled white water but it is often added to the thin stock, for instance at the fan pump. The anionic size is usually added at some later stage in the process, generally at the inlet to the final centriscreeen or at a subsequent stage. For instance it can be added with the bentonite or other anionic compound.

Since it is not necessary to pre-mix the size with cationic retention aid, it is possible to emulsify the size direct into the suspension of bentonite or other anionic compound or direct into some other flowing aqueous stream by which the size is added to the cellulosic stock, provided the size is mixed with the aqueous diluent in the presence of appropriate non-ionic or anionic emulsifier.

In a particularly preferred process of the type commercialised as Hydrocol (trade mark) and described in U.S. 4,753,710 a high molecular weight water soluble synthetic cationic polymer is mixed into the suspension (optionally after incorporating a lower molecular weight cationic polymer such as polyethylene imine or a dry strength resin), the suspension is then passed through one or more shear pumps and/or centriscreeens and is then fed to the headbox. A dispersion of bentonite is fed towards the headbox or some other position after the last point of high shear and anionic or non-ionic emulsion of anhydride size (or other size) is injected into the bentonite dispersion as that dispersion flows towards the point of addition to the cellulosic suspension, or else is injected direct into the cellulosic suspension simultaneously with the bentonite.

The amount of size that is added can be conventional or, because of its more efficient utilisation, can be less than conventional. For instance it is typically added in amounts of from 1 to 20kg/t, preferably 2 to 6kg/t.

The process of the invention results in a considerable saving in the amount of size that is required and in much greater uniformity of sizing, especially when the cellulosic suspension contains inorganic filler and, in particular, when it contains recycled materials of variable quality. The retention aid acts as a flocculating agent for the filler and fibres and addition of the size to the suspension after flocculation (even though the flocs may have been broken down to microflocs by shearing as in U.S. 4,753,710) leads towards much more efficient utilisation of the size. Accordingly, it is highly desirable that the size is added to the cellulosic suspension when this is in a flocculated or microfloculated state, rather than in its initial unflocculated state.

The following are some examples.

Example 1

A papermaking stock consisting of 50% bleached softwood chemical pulp, 40% bleached hardwood chemical pulp and 10% calcium carbonate filler was beaten at a consistency of 2% to 45°SR. The prepared thick stock was diluted to 0.5% consistency prior to treatment. Into this fibre suspension a cationic polyacrylamide solution was added at 0.05% aqueous solution 0.5kg/tonne dry polymer/dry paper. The polymer was a copolymer of 76 weight percent acrylamide with 24 weight percent methyl chloride quaternised dimethylaminoethyl acrylate having IV 10dl/g. This addition caused flocculation and the suspension was subjected to thorough mixing by turbulence to break the flocs down to microflocs.

A non-ionically emulsified alkenyl succinic anhydride size was added as a 5% aqueous emulsion at various dose levels. The size emulsion was prepared by adding a mixture of 95% by weight of a conventional alkenyl succinic anhydride and 5% by weight of a non-ionic oil in water emulsifier, into water with a silverson mixture.

The mixture was stirred vigorously for 1 minute to produce a 5% active alkenyl succinic anhydride emulsion.

A 0.5% aqueous slurry of prehydrated bentonite was prepared and was then added at a dose level of 2kg/t dry bentonite/dry paper.

In the laboratory sheet making machine, handsheets were prepared from the treated pulp described above. The sheets were pressed and dried in a standard manner, and the degree of sizing determined by a 1 minute Cobb test.

The same process was repeated using, instead of the bleached softwood, a waste furnish consisting of 75% newsprint, 18% manilla and 9% cardboard beaten to 45°SR. The results were as follows:

Dose Level kg/t	Chemical Pulp Cobb gm.m ⁻²	Waste Furnish Cobb gm.m ⁻²
1	86.7	58.4
2	23.6	17.9
3	18.2	14.4
4	19.3	15.4
6	16.5	11.1

In each of the tests, excellent retention values were obtained and the low Cobb values obtainable at relatively low dosages of size indicate the effectiveness of the sizing.

Example 2

The process of Example 1 was repeated except that the polymer was a copolymer of 58:42 weight percent of the same monomers as in Example 1, the polymer had an IV of 7dl/g, the polymer was added at a dose of 1kg/t, the cellulosic suspension was a fine paper furnish, and the emulsion was premixed with the bentonite slurry. The following results were obtained:

Dose Level kg/t	Cobb gm.m ⁻² Value
2	19.6
4	20.0
10	19.8

Again, good retention was observed.

Example 3 (Comparative)

A papermaking stock consisting of 50% bleached softwood chemical pulp, 40% bleached hardwood chemical pulp and 10% calcium carbonate filler was beaten at a consistency of 2% to 45°SR.

A range of anionic sizes were evaluated for their ability to bring about sizing on the stock without further chemical addition. Standard handsheets were prepared as described in Example 1. The sizes used were:

- i. Alkenyl succinic anhydride (95% w/w) pre-mixed with an anionic phosphate ester (5% w/w) emulsifier, at size dosages of 0.15 and 0.175% active ASA.
- ii. Alkenyl succinic anhydride (66% w/w) pre-mixed with an anionic liquid dispersion polymer (26.5% w/w) and an anionic phosphate ester (7.5% w/w) at the same size dosages. The anionic liquid dispersion polymer

used was a copolymer of 70 mole % acrylamide and 30 mole % sodium polyacrylate.

iii. A commercially available rosin emulsion (Bewoid Super 40) at dosages of 2.0 and 2.5% as received.

iv. A distearyl alkyl ketene dimer emulsion prepared using naphthalene sulphonic acid (3% dry/dry on A.K.D.). The final emulsion contained 5% active A.K.D. and was applied at dosages of 1.5 and 3.0% as received.

In every instance, the Cobb test showed the paper was "waterleaf", i.e., it was substantially unsized.

Example 4

The process of Example 3 was repeated except that a copolymer of about 20 mole percent methyl chloride quaternised dimethylaminoethyl acrylate with about 80 mole percent acrylamide and having intrinsic viscosity about 8dl/g was added at 1kg/t dry/dry to the suspension as a 0.5% active solution in water and the suspension was then agitated before adding the size. After adding the size, pre-hydrated bentonite was added as a 0.5% aqueous slurry at a dose level of 2kg/t dry on dry. The results are shown below:

Cationic Copolymer Dose Level	Sizing Agent	Size Dose Level	Bentonite Dose Level	Cobb Value (gm.m ⁻²)
1 kg/t	(i)	0.15%	2 kg/t	46.9
1 kg/t		0.175%	2 kg/t	27.4
1 kg/t	(ii)	0.15%	2 kg/t	26.9
1 kg/t		0.175%	2 kg/t	25.3
1 kg/t	(iii)	2.0%	2 kg/t	Waterleaf
1 kg/t		2.5%	2 kg/t	105.5
1 kg/t	(iii)*	2.0%	2 kg/t	26.2
1 kg/t		2.5%	2 kg/t	22.4
1 kg/t	(iv)	1.5%	2 kg/t	21.2
1 kg/t		3.0%	2 kg/t	17.4

*with aluminium sulphate

In this table, the dose level is as explained in Example 3.

These results again show that satisfactory sizing can be achieved in the invention. In all the processes high retention values and rapid dewatering was obtained.

Claims

1. A process of making internally sized paper by adding a non-ionic or anionic emulsion of size to a cellulosic suspension in the presence of cationic polymer that renders the size substantive to the solids in the suspension, draining the suspension to form a sheet and drying the sheet, characterised in that the process comprises flocculating the suspension by adding water soluble cationic retention aid to the suspension, breaking the flocs down to cationically charged microflocs without substantial resuspension of fibres, adding the non-ionic or anionic size emulsion to the suspension after the flocculation, adding a solution or dispersion of anionic compound to form an aggregated suspension containing the size, and draining the aggregated suspension to form the sheet.
2. A process of making internally sized paper comprising flocculating a suspension of cellulosic fibres by addi-

tion of cationic retention aid, breaking the flocs down to form cationically charged microflocs without substantial resuspension of fibres, aggregating the microflocs by addition of a solution or dispersion of anionic compound, draining the aggregated suspension to form a sheet and drying the sheet, wherein size is present in the aggregated suspension, characterised in that the size is added in the form of a non-ionic or anionic emulsion in water to the suspension after flocculating the suspension by the addition of the cationic retention aid.

- 5 3. A process according to claim 1 or claim 2 in which the size is an anhydride size.
- 10 4. A process according to claim 1 or claim 2 in which the size is an alkenyl succinic anhydride size.
- 5 15 6. A process according to any preceding claim in which the anionic compound is selected from organic polymeric material, bentonite and colloidal silicic acid.
- 15 6. A process according to any preceding claim in which the cationic retention aid comprises material selected from cationic starch and synthetic cationic polymers having molecular weight above 500,000 and the anionic compound is selected from bentonite and colloidal silicic acid.
- 20 7. A process according to any preceding claim in which the cationic retention aid comprises cationic synthetic polymer having molecular weight above 500,000 added in an amount of 0.01 to 0.3% dry on dry and the anionic compound comprises bentonite added in an amount of from 0.01 to 0.5% by weight dry on dry.
- 25 8. A process according to claim 7 in which the cationic retention aid comprises a cationic polyacrylamide having intrinsic viscosity above 4dl/g.
- 25 9. A process according to any preceding claim in which the suspension is a filled suspension containing at least 10% by weight inorganic filler.
- 30 10. A process according to any preceding claim in which all the cationic retention aid used in the process is present in the suspension before the size is added.
- 30 11. A process according to any preceding claim in which the size is added after the flocs have been broken down by agitation to the microflocs.
- 35 12. A process according to any preceding claim in which the anionic compound and the size are both added after the last point of high shear.
- 35 13. A process according to claim 12 in which the size and the anionic compound are added together or separately but close to one another.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 92 30 1137

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 050 316 (PAPETERIES DE GASCOGNE) * claims 1-14 * -----	1	D21H17/16 D21H17/68 D21H17/29 D21H17/44 D21H23/76 D21H17/69
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			D21H D21D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 25 MAY 1992	Examiner FOUQUIER J.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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