PAPER AND PAPERBOARD PRODUCTION PROCESS AND CORRESPONDING NOVEL RETENTION AND DRAINAGE AIDS, AND PAPERS AND PAPERBOARDS THEREBY OBTAINED

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ABSTRACT

The invention relates to an improved paper production process, according to which a branched polymer prepared in reverse phase emulsion is used as the main retention aid, and then bentonite is used as the secondary retention aid (a dual type system). The two additions are separated by a stage for shearing the fibrous suspension (or mass).

A distinctly improved retention of the fines is obtained, and also a distinct improvement in drainage. Moreover, the bentonite content in the white water is reduced.
Figure 1  
Turbidité eaux blanches = f(polymères)  
Exemple 1

![Graph showing turbidity levels in white waters as a function of polymers with 8 trials labeled from 0 to 8. Each trial has different turbidity levels measured in NTU (Nephelometric Turbidity Units).](image)
Figure 2
Turbidité des eaux blanches=f(polymères + bentonite)

Exemple 1

<table>
<thead>
<tr>
<th>ESSAIS</th>
<th>Turbidité (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4000</td>
</tr>
<tr>
<td>1</td>
<td>3500</td>
</tr>
<tr>
<td>10</td>
<td>3000</td>
</tr>
<tr>
<td>11</td>
<td>2500</td>
</tr>
<tr>
<td>12</td>
<td>2000</td>
</tr>
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<td>13</td>
<td>1500</td>
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<td>14</td>
<td>1000</td>
</tr>
<tr>
<td>15</td>
<td>500</td>
</tr>
<tr>
<td>16</td>
<td>0</td>
</tr>
</tbody>
</table>

Turbidité X
Turbidité R1
Turbidité R2
Figure 3

Rétention totale = f(polymères)

Exemple 1

% Rét X
% Rét R2

% rétention totale

ESSAIS

0 1 2 3 4 5 6 7 8

71.2 70.1 62.2 64 72.5 83.8 86.3 92.35 87.8

95 90 85 80 75 70 65 60 55 50
Figure 4

Rétention totale = f(polymères + bentonite)

Exemple 1
Figure 6

Répartition de charges=f(polymeres + bentonite)
Figure 7

Turbidité eaux blanches 30' = f(polymères)

Exemple 1
Figure 8
Turbidité des eaux blanches 30 = f (polymères + bentonite)
Figure 14  
Rétention totale = f(polymères + bentonite)  

Exemple 2

<table>
<thead>
<tr>
<th>ESSAIS</th>
<th>% Rét X</th>
<th>% Rét R2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>71.2</td>
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<td>5</td>
<td>81.1</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>92.1</td>
<td>91.9</td>
</tr>
<tr>
<td>7</td>
<td>95.9</td>
<td>96</td>
</tr>
<tr>
<td>8</td>
<td>82.4</td>
<td>72</td>
</tr>
</tbody>
</table>

% rétention totale
Figure 16  Rétention de charges=f(polymères + bentonite)  Exemple 2

<table>
<thead>
<tr>
<th>Essais</th>
<th>Rét. cendres X</th>
<th>Rét. cendres R2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>55</td>
<td>57.9</td>
</tr>
<tr>
<td>6</td>
<td>83.4</td>
<td>88.5</td>
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<tr>
<td>7</td>
<td>95.7</td>
<td>98.1</td>
</tr>
<tr>
<td>8</td>
<td>56.1</td>
<td>53.6</td>
</tr>
</tbody>
</table>
Figure 17: Turbidité eaux blanches $30' = f(\text{polymères})$

Exemple 2

- Turbidité $30' \times$
- Turbidité $30' \times R2$

ESSAIS

Turbidité (NTU)
Figure 18 Turbidité des eaux blanches 30'=(polymères + bentonite) Exemple 2
Figure 19

CSF (ml) = f(polymères)

Exemple 2

<table>
<thead>
<tr>
<th>ESSAIS</th>
<th>CSF (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>365</td>
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<tr>
<td>1</td>
<td>396</td>
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<tr>
<td>2</td>
<td>410</td>
</tr>
<tr>
<td>3</td>
<td>410</td>
</tr>
<tr>
<td>4</td>
<td>390</td>
</tr>
</tbody>
</table>
Figure 20

CSF (ml) = f(polymères + bentonite)

Exemple 2

<table>
<thead>
<tr>
<th>Essais</th>
<th>CSF (ml)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
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<td>5</td>
<td>390</td>
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<tr>
<td>7</td>
<td>449</td>
</tr>
<tr>
<td>8</td>
<td>394</td>
</tr>
</tbody>
</table>
PAPER AND PAPERBOARD PRODUCTION PROCESS AND CORRESPONDING NOVEL RETENTION AND DRAINAGE AIDS, AND PAPERS AND PAPERBOARDS THUS OBTAINED

[0001] The present invention relates to the technical field of paper production and the polymers used in this field.

[0002] The invention relates to a process for producing a paper or paperboard with improved retention and other properties.

[0003] During the production of paper, paperboard, or the like, it is well known to introduce into the pulp retention aids whose function is to retain a maximum of fines and fillers in the sheet. The beneficial effects that result from the utilization of a retention aid are essentially:

[0004] increased production and reduction of production costs; energy savings, more reliable operation of the machine, higher yield in terms of fibers, fines, fillers and anionic finishing products, lower acidity in the circuit linked to a decrease in the use of aluminum sulfate, and hence a reduction in corrosion problems;

[0005] an improvement in quality: better formation and better look-through, an improvement in the moisture content, the opacity, the gloss, and the absorptive capacity of the sheet, and a reduction in the porosity of the paper.

[0006] Long ago, it was proposed that bentonite be added to the pulp, possibly together with other mineral products such as aluminum sulfates or even synthetic polymers, notably polyethylene imine (see for example the documents DE-A-2 262 906 and U.S. Pat. No. 2,368,635).

[0007] In the document U.S. Pat. No. 3,052,595, it was proposed to associate the bentonite with a polyaCRYlamide of an essentially linear nature. This process met with competition from systems that were easier to use yet performed just as well. Moreover, even with the current linear polyaCRYlamides, the retention capacity is still insufficient.

[0008] In the document EP-A-0 017 353, it was proposed, for the retention of low-filler pulps (less than 5% fillers), to associate the bentonite with a nonionic to slightly anionic linear copolyacrylamide. This process has not been very widely used, since these polymers perform relatively poorly in terms of retention, especially that of pulps containing fillers, no doubt as a result of insufficient synergy between these copolymers and bentonite, which does not have much of a tendency to reaggregate.

[0009] In the document EP-A-0 235 893, it was proposed to use essentially linear cationic polyaCRYlamides having molecular weights of greater than one million, of thirty million and higher. This results in the attainment of a retention effect that is satisfactory, but is still deemed inadequate in the papermaking application; since the use of bentonite causes problems during the subsequent treatment of the effluents issuing from the machine, users select this system only if there are significant advantages.

[0010] In the notes presented at the lecture given in Seattle on Oct. 11-13, 1989, published under the title “Supercoagulation in the control of wet end chemistry by synthetic polymer and activated bentonite,” R. Kajasvirta described the mechanism of supercoagulation of activated bentonite in the presence of a cationic polyaCRYlamide, without specifying its exact nature. This process has the same drawbacks as above.

[0011] Lastly, European Patent 0 574 335 produced an important improvement by proposing the use branched polymers (particularly polyaCRYlamides) in powder form.

[0012] The invention eliminates the drawbacks mentioned above.

[0013] Its object is to obtain an improved process of the type in question, which is comprised of adding to the suspension or fibrous mass or paper pulp to be flocculated, as the main retention aid, an agent consisting of or comprising a branched polyaCRYamide which is characterized in that it has been prepared in reverse phase or water-in-oil emulsion, and bentonite as the second retention aid (a so-called “dual” system of the type also known as “micro-particle”).

[0014] The phrase “exists in reverse phase emulsion” or similar expressions related to the polymer used (i.e., injected or introduced into the pulp to be flocculated) according to the invention, will be understood by one skilled in the art to designate the reverse phase water-in-oil emulsion that is dissolved in water before its injection or its introduction into the mass or pulp to be flocculated (this dissolution in water results in what is known as the “reversal” of the initial reverse phase water-in-oil emulsion; these processes are well known to one skilled in the art).

[0015] The additions of the polymer and the bentonite are separated by a shearing stage, for example at the level of the mixing pump known as a “fan pump.” In this field, the reader is referred to the specification of U.S. Pat. No. 4,753,710, as well as to a vast body of prior art related to the addition point of the retention aid relative to the shearing stages existing in the machine, including U.S. Pat. No. 3,052,595; Unbehendt, TAPPI Vol. 59, No. 10, October, 1976; Luner, 1984 Papermakers Conference or TAPPI, April, 1984, pp. 95-99; Sharpe, Mercer & Co., Inc., Rabway, N.J., USA, around 1980, Chapter 5, “Polyelectrolyte Retention Aids”; Britt, TAPPI Vol. 56, October 1973, p. 46 ff.; and Waechter, TAPPI, March, 1983, p. 137; or even U.S. Pat. No. 4,388,150 (Eka Nobel).

[0016] The reader is also referred to U.S. Pat. No. 4,753,710 for all of the generalities related to paper production, the usual additives used, and similar details.

[0017] It is possible to replace the bentonite, as the secondary retention aid, with a kaolin, as described in the Applicant’s French patent application 95 13051, this kaolin preferably being pretreated with a polyelectrolyte. One skillful in the art can refer to this French patent application 95 13051.

[0018] This process makes it possible to obtain a distinctly improved retention of fines and fillers without a reverse effect. An additional characteristic of this improvement is that the drainage properties are improved.

[0019] The branched polyaCRYlamide (or more generally the branched (co)polymer) is introduced into the suspension, in a distinctly preferred way, in the form of a reverse phase water-in-oil emulsion at a rate of 0.03 to one per mill (0.03 to 1% w/w) or 30 to 1,000 g/t by weight of active material.
(polymer) relative to the dry weight of the fibrous suspension, preferably 0.15 to 0.5 per mill, or 150 to 500 g/t. [0020] In a way that is known to one skilled in the art, the reverse phase emulsion polymer is diluted in water and inverted (solubilized) by this dilution before its introduction, as described above.

[0021] This selection of the reverse phase emulsion form makes it possible, in the papermaking application for the retention of fillers and fines, to reach a level of performance unequalled up to now. Moreover, the utilization of branched polymers makes it possible to obtain a better retention of the bentonite in the sheet, as described in the above-mentioned European patent 0 574 335, and thus to limit its negative effects on the subsequent treatment of the effluents issuing from the machine. Furthermore, the choice of this branched polyacrylamide increases the fixation capacity of the bentonite in the sheet, consequently resulting in a synergy, and hence a recoagulation, which reduces the bentonite content in the white water.

[0022] It is understood that it is essential according to the invention that the polymer be prepared by means of a reverse phase oil-in-water emulsion polymerization. However, this polymer can then be used (i.e., injected or introduced into the mass or pulp to be flocculated) either in the form—preferably—of this reverse phase emulsion after its dissolution in water, or in the form of a powder obtained by drying (especially drying by means of “spray drying”) the reverse phase emulsion from the polymerization, and then redissolving this powder in water, for example at a concentration on the order of 5 g of active polymer/liter, the solution thus obtained then being injected into the pulp at substantially the same polymer dosages.

[0023] Advantageously, in practice, the branched (co)polyacrylamide is a cationic copolymer of acrylamide and of an unsaturated cationic ethylenic monomer, chosen from the group comprising dimethylaminoethyl acrylate (ADAME), dimethylaminoethyl methacrylate (MADAME), quaternized or sulfated by different acids and quaternizing agents, benzyl chloride, methyl chloride, alkyl or aryl chloride, dimethyl sulfate, dialkyl(dimethyl)ammonium chloride (DADMAC), acrylamidopropyltrimethylammonium chloride (APTAC), and methacrylamidopropyltrimethylammonium chloride (MAPTAC).

[0024] In a known way, this copolymer is prepared by a branching agent constituted by a compound having at least two reagent groups chosen from the group comprising the double bonds, aldehyde bonds, or epoxy bonds. These compounds are well known and are described, for example, in the document EP-A-0 374 458 (see also the Applicant's document FR-A-2 589 145).

[0025] As is known, a “branched” polymer is a polymer that has in the chain branches, groups or branchings globally disposed in one plane and not in the three directions, unlike a “cross-linked” polymer; branched polymers of this type, of high molecular weight, are well known as flocculating agents. These branched polyacrylamides are distinguished from the cross-linked polyacrylamides by the fact that in the latter, the groups are disposed three dimensionally so as to lead to practically insoluble products of infinite molecular weight.

[0026] The branching can be carried out preferably during (or possibly after) the polymerization, for example by reaction of two soluble polymers having counter-ions, or by reaction on formaldehyde or a polyvalent metal compound. Often, the branching is carried out during the polymerization by the addition of a branching agent, and this method is clearly preferred according to the invention. These processes for polymerization with branching are well known.

[0027] The branching agents that can be incorporated comprise ionic branching agents such as polyvalent metal salts, formaldehyde, glyoxal, or even, preferably, covalent cross linkers that will copolymerize with the monomers, preferably monomers with diethylenic unsaturation (like the family of diacrylate esters such as the diacrylates of polyethylene glycol PEG) or polyethylene unsaturation, of the type classically used for the cross-linking of water-soluble polymers, and particularly methylenebisacrylamide (MBA), or any of the other known acrylic branching agents.

[0028] These agents are often identical to the cross linkers, but cross-linking can be avoided when desiring to obtain a polymer that is branched but not cross-linked, by optimizing polymerization conditions such as the concentration of the polymerization, type and quantity of transfer agent, temperature, type and quality of initiators, and the like.

[0029] In practice, the branching agent is methylenebisacrylamide (MBA), introduced at a rate of five to two hundred (5 to 200) moles per million moles of monomers, preferably 5 to 50.

[0030] Advantageously, the quantity of branched polyacrylamide introduced into the suspension to be flocculated is between thirty and one thousand grams of active polymer/ton of dry pulp (30 and 1,000 g/t), or between 0.03 per mill and one per mill, preferably 150 to 500 g/t, it was observed that if the quantity is lower than 0.03% o (0.03 per mill), no significant retention is obtained; likewise, if this quantity exceeds 1% o (1 per mill), no proportional improvement is observed; however, unlike the linear cationic polycrylamides, as described in the documents EP-A-0 017 353 and EP 0 235 893 mentioned in the preamble, there is no observed reverse dispersion effect by recirculation of the closed circuits of the excess polymer not retained in the sheet. Preferably, the quantity of branched polyacrylamide introduced is between 0.15 and 0.5 per mill (0.15 and 0.5% o) of the quantity of dry pulp, or between 150 g/t and 500 g/t.

[0031] As stated above, it is important that the branched polymer be prepared in reverse phase (water-in-oil) emulsion form in order to achieve the improvement of the invention. Emulsions of this type and the process for preparing them are well known to one skilled in the art.

[0032] This approach was condemned in the above-mentioned European patent 0 574 335, in which it was indicated that if a branched polymer is used in emulsion, the indispensable presence of surfactants in these emulsions promotes the formation of foams during the production of the paper and the appearance of disparities in the physical properties of the finished paper (modification of the absorbency in the places where part of the oil phase of the emulsion is retained in the sheet).

[0033] Therefore, it was not obvious to consider a fortiori the reverse phase water-in-oil emulsions whose oil content is clearly high.
[0034] The invention was even more difficult to achieve in that it was important to stay within the field of branched polymers and not to cross over to the field of cross-linked polymers. It is known that technically, especially on an industrial production scale, the borderline between the two areas is very easily crossed, in a way that is, moreover, irreversible. Since the branched area is very limited, the difficulty of developing the invention is considerable, and the Applicant deserves credit for undertaking to use of this technology in the field of paper production, which poses particular problems and has strict quality requirements.

[0035] The risk of failure, which may explain the fact that this technology had not been used, was even greater in that cross-linked emulsions are not known to provide any particular advantage in paper.

[0036] In comparison with the linear polymers, the branched polymers in powder form of the above-mentioned European patent 0 574 335 had already made substantial progress relative to the properties and the paper production process. The improvement was on the order of 20 to 40% depending on the properties.

[0037] With the present branched emulsions, an improvement on the order of 50 to 60% is obtained, which would not have been foreseeable since, on the contrary, it was known that the cross-linked products did not work.

[0038] According to the invention, in a preferred but non-limiting way, a "moderately branched" polymer is used, for example with 10 ppm of branching agent relative to the active material.

[0039] As already indicated above, the polymer can be used either in the form of its synthetic reverse-phase emulsion, dissolved or "inverted" in water, or in the form of the solution in water of the powder obtained by drying said synthetic emulsion, particularly by means of spray-drying. Spray-drying is a process that is also known to one skilled in the art. The reader is referred to the tests below in order to verify that the results are comparable.

[0040] Bentonite, also known as "smectic swelling clay," from the montmorillonite family, is well known and there is no need to describe it in detail here; these compounds, formed of microcrystallites, comprise surface sites having a high cation exchange capacity capable of retaining water (see for example the document U.S. Pat. No. 4,305,781, which corresponds to the document EP-A-0 017 353 mentioned above, and FR-A-2 283 102).

[0041] Preferably, a semisodic bentonite is used, which is introduced just upstream from the headbox, at a rate of 0.1 to 0.5 percent (0.1 to 0.5%) of the dry weight of the fibrous suspension.

[0042] As a filler, it is possible to use kaolins, GCC or ground CaCO₃, precipitated CaCO₃ or PCC, and the like.

[0043] The branched polymer in reverse phase emulsion according to the invention is injected or introduced prior to a shearing stage into the paper pulp (or fibrous mass to be flocculated), which is more or less diluted according to the experience of one skilled in the art, and generally into the diluted paper pulp or "thick stock," i.e. a pulp diluted to about 0.7 to 1.5% solid matter such as cellulose fibers, possible fillers, and the various additives commonly used in papermaking.

[0044] According to a variant of the invention with fractionated introduction, some of the branched polymer in emulsion according to the invention is introduced at the level of the stage for preparing the "thick stock" with about 5% or more solid matter, or even at the level of the preparation of the thick stock before a shearing stage.

[0045] The following examples illustrate the invention without limiting its scope.

EXAMPLE 1

[0046] Production of a Branched Polymer in the Form of a Reverse Phase Water-in-Oil Emulsion

[0047] In a reactor A, the constituents of the organic phase of the emulsion to be synthesized are mixed at the ambient temperature.

[0048] a) Organic Phase

[0049] 252 g of Exxsol D100

[0050] 18 g of Span 80

[0051] 4 g of Hypermer 2296

[0052] b) In a Beaker B, the Aqueous Phase of the Emulsion to be Produced is Prepared by Mixing:

[0053] 385 g of acrylamide at 50%

[0054] 73 g of ethyl acrylate trimethyl ammonium chloride 80%

[0055] 268 g of water

[0056] 0.5 g of methylenebisacrylamide at 0.25%

[0057] 0.75 ml of sodium bromate at 50 g l⁻¹

[0058] 20 ppm of sodium hypophosphite relative to the active material

[0059] 0.29 ml of Versenex at 200 g l⁻¹

[0060] The contents of B are mixed into A under agitation. After the mixing of the phases, the emulsion is sheared in the mixer for 1 minute in order to create the reverse phase emulsion. The emulsion is then degassed by means of a nitrogen bubbling; then after 20 minutes the gradual addition of the metabisulfite causes the initiation followed by the polymerization.

[0061] Once the reaction is finished, a "burn out" (treatment with the metabisulfite) is carried out in order to reduce the free monomer content.

[0062] The emulsion is then incorporated with its inverting surfactant in order to subsequently release the polymer in the aqueous phase. It is necessary to introduce 2 to 2.4% ethoxylated alcohol. The standard Brookfield viscosity of said polymer is 4.36 cps (viscosity measured at 0.1% in a 1 M NaCl solution at 25° C. at sixty rpm).
In accordance with a variation of the MBA content from 5 to 20 ppm, the results in terms of UL viscosity are the following:

<table>
<thead>
<tr>
<th>Test</th>
<th>MBA ppm</th>
<th>NaH₂PO₄ ppm (*)</th>
<th>UL Viscosity</th>
<th>IR (1) (%)</th>
<th>IVR (2) (%)</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>R 52</td>
<td>5</td>
<td>20</td>
<td>4.36</td>
<td>12.8</td>
<td>0</td>
<td>Branched</td>
</tr>
<tr>
<td>R 102</td>
<td>10</td>
<td>20</td>
<td>3.74</td>
<td>28.9</td>
<td>0</td>
<td>Branched</td>
</tr>
<tr>
<td>SD 102</td>
<td>10</td>
<td>20</td>
<td>3.70</td>
<td>26</td>
<td>0</td>
<td>Branched</td>
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<tr>
<td>X 104</td>
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<td>2.31</td>
<td>45</td>
<td>50</td>
<td>Cross-linked</td>
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<td>X 204</td>
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<td>2.51</td>
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<td>Linear</td>
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<tr>
<td>EM 140 LH</td>
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<td>40</td>
<td>3.16</td>
<td>0</td>
<td>&lt;0</td>
<td>Linear</td>
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<tr>
<td>EM 140 BD</td>
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<td>0</td>
<td>1.85</td>
<td>80</td>
<td>100</td>
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<td>FO 4198</td>
<td>5</td>
<td>20</td>
<td>3.2</td>
<td>5</td>
<td>&lt;0</td>
<td>Branched</td>
</tr>
</tbody>
</table>

FO 4198: a branched powder containing 20 ppm transfer agent and 5 ppm branching agent.

(*) sodium hypophosphate, transfer agent

(1): ionic regain in %

(2): intrinsic viscosity regain in %

EM140 CT: a standard emulsion of very high molecular weight containing no branching agent.

EM140 L: a standard emulsion of high molecular weight containing no branching agent.

EM140 LH: an emulsion of average molecular weight containing no branching agent.

EM140 BD: a cross-linked emulsion containing no transfer agent and 5 ppm cross linker.

SD102: the emulsion R 102 dried by spray-drying, and the powder obtained dissolved in water to 5 g of active polymer/liter.

It is noted that the linear products do not develop any ionic regain IR, and their intrinsic viscosity IV decreases under the effect of an intense shearing (two of the IV values are negative); the branched products in emulsion develop an ionic regain IR, but no IV (values <=0); the cross-linked products develop a high ionic regain and a very high IV regain.

Definitions of the ionic regains and intrinsic viscosity regains:

Ionic regain IR = (X - Y) / 100

Y: ionicity after shearing in meq/g.

Intrinsic viscosity regain IVR = (V1 - V2) / V2 x 100

with V1: intrinsic viscosity after shearing in dL/g

V2: intrinsic viscosity before shearing in dL/g

The pulp used is diluted to a consistency of 1.5%. A sample of 2.24 dry g of pulp, or 149 g of pulp at 150%, is taken, then diluted to 0.4% with clear water.

The 560 ml volume is introduced into the plexiglass cylinder of the automated sheet former, and the sequence is begun.

Some of the emulsions cited above will be the subjects of a study of effectiveness in retention and drainage in an automated sheet former at the Center for Paper Technology.

Procedure for testing the emulsions

Pulp used:

20% mechanical pulp
20% natural calcium carbonate.

Sizing in a neutral medium with 2% of an alkyl ketene dimer emulsion.

The following operations are then carried out:

Measurement of the turbidity of the water under the wire.

Dilution of a beaker of thick stock for a new sheet with the reclaimed water under the wire.
[0071] drying of the so-called 1st pass sheet.

[0072] start of a new sequence for producing the so-called 2nd pass sheet.

[0073] After 3 passes, the products to be tested are changed.

[0074] The following analyses are then performed:

[0075] measurement of the matter in suspension in the water under the wire (TAPPI standard: T 656 cm/83)

[0076] measurement of the ash in the sheets (TAPPI standard: T 211 om-93)

[0077] measurement of turbidity 30' after the fibers are deposited in order to learn the state of the ionic medium.

[0078] measurement of the degree of drainability of the pulp with a Canadian Standard Freeness (CSF; TAPPI standard T 227 om-94).

Notes for Tables (I) and (II) below:

| X | so-called first-pass measurement |
| R1 | so-called second pass-measurement (1st recycling) |
| R2 | so-called third pass measurement (2nd recycling) |
| Ash % | weight of ash retained (= filler retention) in the sheet / weight of the sheet.

[0079] Comments on the Results: see Tables (I) and (II) Below Relative to Example 1, and FIGS. 1 through 10, Which Represent the Corresponding Histograms

[0080] The cross-linked polymers have no advantage as to the flocculation and the retention of fillers and fines in spite of the high rate of shear applied during the process to the fibrous mass (and not applied to the polymer itself), in this case 1,500 rpm, which is characteristic of this type of microparticulate retention system. They show a poor capture of fillers and colloidal matter, since no reduction in turbidity is observed.

[0081] The combination with bentonite does not significantly improve the effectiveness in terms of retention and only slightly improves the effectiveness in terms of drainage.

[0082] As for the linear polymer, its behavior follows the tendency to improve the retention of fillers and fines.

[0083] The combination according to the invention of a branched polymer in reverse phase emulsion and bentonite provides a net gain in filler retention and in total retention, and is revealed to be superior to the known linear polymer/bentonite system.

[0084] The coagulation capacity is better for a branched polymer in emulsion, which translates into an excellent reduction in the turbidity at 30' (30 min.).

[0085] The R 52 test and the R 102 test show that the invention makes it possible to obtain branched products having UL viscosities higher than those accessible through gel polymerization as described in European patent 0 574 335. Any attempt to reach such highly advantageous UL viscosity values using a gel polymerization process with drying into a powder would result in a product that was totally insoluble and therefore totally unusable in the industry.

[0086] The SD 102 test shows that the polymer used in the form of a solution in water of the powder obtained by drying the reverse phase emulsion from the synthesis of the polymer behaves like the polymer used in the form of the solution in water of said synthetic reverse phase emulsion. In particular, no degradation of the polymer is observed during the stage for drying by means of spray-drying.

[0087] It is useful to compare the R 52 test to the FO 4198 test (powder), since the polymers have the same chemistry, hence the same cationicity, and the same % of MBA, while the R52 of the invention is far superior to the powder in terms of drainage and retention (96.3 as compared to 87.6); compare also the turbidity in NTU after 30 minutes, 32 as compared to 75 NTU units.

[0088] Such UL viscosity values specifically result in substantially improved drainage.

[0089] The invention also relates to a novel retention aid for the production of a sheet of paper, paperboard or the like, which is comprised of a branched acryllic (co)polymer as described above, in reverse phase emulsion, which is characterized in that its UL viscosity is >3, >3.5 or >4. Said agent can be used either in emulsion, inverted in water, or in a solution of the powder obtained by drying the emulsion, as described above.

EXAMPLE 2

[0090] Production of a Branched Acrylamidopolypropyltrimethylammonium Chloride (AP TAC) Based Polymer in the Form of a Reverse Phase Oil-in-Water Emulsion:

[0091] In a reactor A, the constituents of the organic phase of the emulsion to be synthesized are mixed at the ambient temperature.

[0092] a) Organic Phase

[0093] 252 g of Exxsol D100

[0094] 18 g of Span 80

[0095] 4 g of Hypermer 2296

[0096] b) In a Beaker B, the Phase of the Emulsion to be Produced is Prepared by Mixing:

[0097] 378 g of acrylamide at 50%

[0098] 102.2 g of acrylamidopolypropyltrimethylammonium chloride (60%)

[0099] 245.7 g of water

[0100] 0.5 g of methylenebisacrylamide at 0.25%

[0101] 0.75 ml of sodium bromate at 50 g/l

[0102] 20 ppm of sodium hypophosphate relative to the active material

[0103] 0.29 ml of Versenex at 200 g/l

[0104] The contents of B are mixed into A under agitation. After the mixing of the phases, the emulsion is sheared in the mixer for 1 minute in order to create the reverse-phase emulsion. The emulsion is then degassed by means of a
nitrogen bubbling; then after 20 minutes, the gradual addition of the metabisulfite causes the initiation followed by the polymerization.

[0105] Once the reaction is finished, a “burn out” is carried out in order to reduce the free monomer content.

[0106] The emulsion is then incorporated with its inverting surfactant in order to subsequently free the polymer in the aqueous phase.

<table>
<thead>
<tr>
<th>Table of Example 2:</th>
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<tbody>
<tr>
<td>Test</td>
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</tr>
<tr>
<td>M 52</td>
</tr>
<tr>
<td>M 102</td>
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<tr>
<td>XM 104</td>
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<td>XM 204</td>
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<tr>
<td>EK 190</td>
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<td>EK 190</td>
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EK 190: a standard emulsion of a copolymer of acrylamide and acrylamide-epichlorohydrin trimethylammonium chloride, linear.

[0107] Procedure for Testing the Emulsions

[0108] (identical to that of Example 1)

[0109] Comments on the Results: see Table (III) Below Relative to Example 2, and FIGS. 11 Through 20, Which Represent the Corresponding Histograms

[0110] The results invite the same comments as those of Example 1 and confirm the great advantage of the present invention.

[0111] The invention also relates to the novel retention aids described above, characterized in that they consist of, or comprise, at least one branched (co)polymer of the type described, prepared in reverse phase emulsion, intended to cooperate with a secondary retention aid after an intermediate stage for shearing the paper pulp, as well as to the processes for producing sheets of paper, paperboard or the like using the agents according to the invention or the process according to the invention, and the sheets of paper, paperboard and the like thus obtained.

[0112] Said agent can be used either in emulsion inverted in water, or in a solution of the powder obtained by drying the emulsion, as described above.

1. Process for producing a sheet of paper, paperboard or the like having improved retention and drainage properties, of the type which uses a dual system of an acrylic polymer and bentonite or a possibly treated kaolin as the primary and secondary retention aids, respectively, the introductions of which are separated by a stage for shearing the suspension or fibrous mass or paper pulp, characterized in that said polymer is a branched acrylic (co)polymer prepared in the form of a reverse phase water-in-oil emulsion, used either in emulsion inverted in water, or in a solution of the powder obtained by drying the emulsion.

2. Process according to claim 1, characterized in that the branched acrylic (co)polymer prepared in reverse phase emulsion is introduced into the paper pulp at a concentration of 0.03 to one per mill (0.03 to 1% o) by weight, or 30 to 1,000 g/t, of the dry weight of the fibrous suspension of paper pulp, preferably 0.15 to 0.5 per mill (0.15 to 0.5% o), or 150 to 500 g/t.

3. Process according to claim 1 or 2, characterized in that the branched acrylic (co)polymer prepared in reverse phase emulsion is a cationic copolymer of acrylamide and of an unsaturated cationic ethylenic monomer chosen from the group comprising dimethylaminoethyl acrylate (ADAME), dimethylaminoethyl methacrylate (MADAME), quaternized or salfified by different acids and quaternizing agents, benzyl chloride, methyl chloride, alkyl or aryl chlorides, dimethyl sulfate, dialkyl(dimethyl)ammonium chloride (DAMAC), acrylamidopropyltrimethylammonium chloride (APMac), and methacrylamidopropyltrimethylammonium chloride (MAPMac).

4. Process according to any of claims 1 through 3, characterized in that the branched acrylic (co)polymer in reverse phase emulsion is branched by means of a branching agent constituted by a polyfunctional compound having at least two reagent groups chosen from the group comprising the double bonds, the aldehyde bonds or the epoxy bonds.

5. Process according to any of claims 1 through 4, characterized in that the branched acrylic (co)polymer in reverse phase emulsion is branched by means of a branching agent constituted by methylenebisacrylamide (MBA).

6. Process according to claim 5, characterized in that the MBA is introduced at a concentration of 5 to 200 molar per million molar units of monomers.

7. Process according to claim 5 or 6, characterized in that the bentonite is a semiindicated bentonite, used at a rate of 0.1 to 0.5 per cent (0.1 to 0.5%) of the dry weight of the fibrous suspension.

8. Process according to claim 5, 6 or 7, characterized in that the pulp used, which contains the filler, is diluted, after which the polymer is added as the main retention aid a shearing stage is carried out, for example in the mixing pulp or “fan pump,” then the bentonite is added as the secondary retention aid.

9. Process according to claim 8, characterized in that the quantity of branched polyacrylamide (or more generally of branched acrylic (co)polymer), introduced either in reverse phase water-in-oil emulsion inverted in water, or in a solution of the powder obtained by drying the emulsion, is between 0.03 and 1% o, or between thirty and one thousand grams per ton (30 and 1,000 g/t) of dry pulp.

10. Process according to claim 8 or 9, characterized in that the quantity of branched polyacrylamide (or more generally of branched acrylic (co)polymer), introduced either in reverse phase water-in-oil emulsion inverted in water, or in a solution of the powder obtained by drying the emulsion, is between 0.15 and 0.5% o (or between 150 and 500 g/t).

11. Process according to claim 8, 9 of 10, characterized in that the bentonite is replaced by kaolin, possibly pretreated with an electrolyte, as the secondary retention aid.

12. Process according to any of claims 1 through 11, characterized in that the branched polymer prepared in reverse phase emulsion is injected or introduced (either in emulsion inverted in water, or in a solution of the powder obtained by drying the emulsion), before a shearing stage, into the paper pulp (or fibrous mass to be flocculated), which is more or less diluted according to the experience of one skilled in the art, and generally into the diluted paper pulp or “thin stock,” i.e. a pulp diluted to about 0.7-1.5% solid.
matter such as cellulose fibers, possible fillers, and the various additives common in papermaking.

13. Process according to any of claims 1 through 12, characterized in that some of the branched polymer in emulsion is introduced at the level of the stage for preparing the "thick stock" with about 5% or more solid matter, or even at the level of the preparation of the thick stock before a shearing stage.

14. Novel retention aid for the production of a sheet of paper, paperboard or the like, characterized in that it comprises a branched polyacrylamide (or more generally a branched acrylic (co)polymer) in reverse phase (or oil-in-water) emulsion (either in reverse phase emulsion dissolved or "inverted" in water, or in a solution of the powder obtained by drying the reverse phase emulsion, especially by means of spray-drying).

15. Novel retention aid for the production of a sheet of paper, paperboard or the like according to claim 14, characterized in that the branching agent is a branching agent constituted by a polyfunctional compound having at least two reagent groups chosen from the group comprising the double bonds, the aldehyde bonds or the epoxy bonds, particularly methylenebisacrylamide (MBA).

16. Novel retention aid for the production of a sheet of paper, paperboard or the like according to claim 15, characterized in that the branching agent is introduced at a rate of five to two hundred (5 to 200) moles per million moles of monomers, preferably 5 to 50.

17. Novel retention aid for the production of a sheet of paper, paperboard or the like according to claim 14, 15 or 16, characterized in that the branched polyacrylamide is a cationic copolymer of acrylamide and of an unsaturated cationic ethylenic monomer, chosen from the group comprising dimethylaminoethyl acrylate (ADAME), dimethylaminoethyl methacrylate (MADAME), quaternized or sialified by different acids and quaternizing agents, benzyl chloride, methyl chloride, alkyl or aryl chlorides, dimethyl sulfate, diallyldimethylammonium chloride (DADMAC), acrylamidopropyltrimethylammonium chloride (APTAC), and methacrylamidopropyltrimethylammonium chloride (MAPTAC).

18. Novel retention aid for the production of a sheet of paper, paperboard or the like according to any of claims 14 through 17, characterized in that its UL viscosity is >3.

19. Novel retention aid for the production of a sheet of paper, paperboard or the like according to any of claims 14 through 18, characterized in that its UL viscosity is >3.5.

20. Novel retention aid for the production of a sheet of paper, paperboard or the like according to any of claims 14 through 19, characterized in that it is obtained with the use of a process according to any of claims 1 through 14.

21. Novel retention aid for the production of a sheet of paper, paperboard or the like according to any of claims 14 through 20, characterized in that it is "moderately branched," for example with 10 ppm of branching agent relative to the active material.

22. Sheet of paper, paperboard or the like, characterized in that it is obtained with the use of a retention aid according to any of claims 14 through 21.

23. Sheet of paper, paperboard or the like, characterized in that it is obtained with the use of a process according to any of claims 1 through 13.

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