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# (54) A process for the production of paper.

(57) A method for the production of paper by forming and dewatering a suspension of cellulose containing fibres on a wire. The forming and dewatering takes place in the presence of an anionic, inorganic colloid, an aluminate and a cationic synthetic polymer. The process gives improved dewatering and improved retention of fines and optional fillers.

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## Description

### A process for the production of paper

The present invention relates to a process for the production of paper utilizing an improved retention- and dewatering system. More particularly the invention relates to the use of a combination of a cationic synthetic polymer, an anionic inorganic colloid and aluminate as retention- and dewatering system in papermaking.

It is previously known to use combinations of cationic retention agents and inorganic colloids as retention-and dewatering agents in the production of paper. The European patent application 0218674 discloses the use of polyacrylamide in combination with anionic silica sols as binders and retention agents. It is assumed that the colloidal particles of the sols with their strong charges produce a cross-linking of the polymeric retention agents and that very good retention and dewatering effect is obtained through this. From the British patent 2015614 it is further known to use polymeric cationic retention agents in combination with polyaluminum compounds. It is further known from the US patent 4,643,801 to use a combination of a cationic starch, an anionic silica sol and an anionic high molecular weight polymer, particularly an anionic polyacrylamide, as a binder in papermaking. The three component system according to the US patent can be used with additional aluminum compounds, such as alum, sodium aluminate or polyhydroxyaluminum chloride.

According to the present invention it has been found that the retention- and dewatering effect in papermaking is improved if an aluminate is used in combination with cationic, synthetic polymer and an anionic inorganic colloid. As the dewatering effect is increased the speed of the papermachine can be increased and, further, less water will have to be dried off in the drying section of the paper machine.

The present invention thus relates to a process for the production of paper by forming and dewatering a suspension of cellulose containing fibres, and optionally fillers, on a wire whereby the forming and dewatering takes place in the presence of an anionic inorganic colloid, an aluminate and a cationic synthetic polymer.

The three components can be added to the fibre stock in arbitrary order. The best effect is obtained if the aluminate is added to the stock first, followed by addition of cationic synthetic polymer and then the anionic inorganic colloid. A considerable improvement, in comparison with known technique, is obtained also when the anionic inorganic colloid is first added to the stock and the cationic polymer and the aluminate are added subsequently, in any order. Separate addition of the three respective components is preferred although it is possible to pre-mix two of the components before the addition.

As cationic synthetic polymers for use according to the present invention such cationic, organic nitrogen containing polymers which are conventionally used as retention agents and/or wet strength agents in papermaking are suitable. Particularly suitable are cationic polyacrylamides, polyethyleneimines, polyamine resins and polyamidoamine resins etc. Polyamine resins and polyamidoamine resins are suitably used in their epichlorohydrine modified form. Other cationic synthetic polymers which can also be used are the cationic melamine-formaldehyde and urea-formaldehyde wet strength resins. The amount of the cationic synthetic polymer should suitably be within the range of from 0.01 to 3 per cent by weight, preferably within the range of from 0.03 to 2 per cent by weight, based on dry fibres and optional fillers.

The anionic inorganic colloids which are used are per se previously known for use in papermaking. As examples of such colloids can be mentioned montmorillonite, bentonite, titanyl sulphate sols, silica sols, aluminum modified silica sols or aluminum silicate sols. The terms colloid and colloidal indicate very small particles. The particles of the anionic substances should suitably have a specific surface area above 50 m$^2$/g, more suitably above 100 m$^2$/g, and preferably within the range of 50 to 1000 m$^2$/g. Silica based colloids are the preferred anionic inor ganic colloid.

Particularly suitable silica based colloids are the silica sols with colloidal particles as disclosed in the European patent 41056, which is hereby incorporated by reference in this application, and the aluminum containing silica sols which are disclosed in the European patent application 0218674, which likewise is incorporated by reference. The colloidal silica in the sols should preferably have a specific surface area of 50 to 1000 m$^2$/g and more preferably of about 100 to 1000 m$^2$/g, and the best results have been obtained when the specific surface area has been about 300 to 700 m$^2$/g. It has been found that the colloidal silica particles should suitably have a particle size below 20 nm and preferably from about 10 down to about 1 nm (a colloidal silica particle having a specific surface area of about 550 m$^2$/g corresponds to an average particle size of about 5 nm). Good results are obtained with the mentioned silica sols in the form of an alkali stabilized sol which contains about 2 to 60 per cent by weight of $SiO_2$, preferably from about 4 to 30 per cent by weight of $SiO_2$. The silica sol can be stabilized with alkali in a molar ratio of $SiO_2$:$M_2O$ of from 10:1 to 300:1, preferably 15:1 to 100:1 (M is an ion from the group Na, K, Li and $NH_4$). As mentioned above good results are obtained using colloidal particles which have at least a surface layer of aluminum silicate or aluminum modified silica sol, so that the surface groups of the particles contain silicon and aluminum atoms in a ratio of from 9.5:0.5 to 7.5:2.5 and the given surfaces and particle sizes also apply to these sols. Silica sols which fulfil the above given specifications are available commercially, eg from Eka Nobel AB.

The amount of anionic colloid which is added to the stock should suitably be within the range of from 0.005 to 2 per cent by weight, preferably from 0.01 to 0.4 per cent by weight, based on dry cellulose fibres and optional fillers. The concentration of the colloid, preferably colloidal silica, in the sol added to the stock is not critical. From a practical point of view it is suitable that the sols at the addition to the stock have a concentration of from 0.05 to 5.0 per cent by weight.

Aluminate refers to alkali aluminate which per se is well-known for use in paper production, particularly for hydrophobing with rosin. Sodium aluminate ($Na_2Al_2O_4$) is preferably used, but potassium aluminate can of course also be used even if is less advantageous from an economical point of view. The amount of aluminate can vary within wide limits. The addition of aluminate to the stock is suitably made in the form of aqueous solutions and the concentration in the solutions is not critical but is adjusted with regard to practical considerations. According to the invention it has been found that already very small amounts of aluminate, with regard to the amount of anionic inorganic colloid, give considerable improvements in the dewatering effect. An improvement is obtained already at a weight ratio aluminate, calculated as $Al_2O_3$, to inorganic colloid of 0.01:1. The upper limit is not critical. However, no improvements worth mentioning are obtained when the ratio of aluminate to inorganic colloid exceeds 3:1. The ratio is suitably within the range of from 0.02:1 to 1.5:1 and preferably from 0.05:1 to 0.7:1. The given ratios all relate to weight ratio between aluminate, calculated as $Al_2O_3$, and the inorganic colloid.

The improved retention- and dewatering effect with the system of the invention is obtained over a broad pH range for the stock. The pH can be within the range from about 4 to about 10. The pH is suitably above 5 and preferably within the range of from 6 to 9. If the desired pH is not reached by the addition of the aluminate solution, which in itself is alkaline, the pH of the stock can be adjusted for example by addition of sodium hydroxide. If alkaline buffering fillers are used, for example chalk, a suitable pH is normally reached without adjustments. Other fillers than chalk can of course also be used, but then care has to be taken so that the pH of the stock is kept within the above given limits.

At paper production according to the invention mineral fillers of conventional types can be used, for example kaolin, titanium dioxide, gypsum, chalk and talcum. The term "mineral filler" is herein used to include, in addition to these fillers, also wollastonite and glass fibres and also mineral low density fillers, such as expanded perlite. The mineral filler is usually added in the form of an aqueous slurry in conventional concentrations used for such fillers. The filler can optionally be treated before the addition to the stock with components of the dewatering- and retention- system of the invention, for example by treatment with the cationic synthetic polymer and the aluminate or the inorganic colloid, whereafter the remaining component is added to the stock.

The three-component system of the invention can be used at production of paper from different types of stocks of cellulose containing fibres. The stocks should suitably contain at least 50 per cent by weight of cellulose containing fibres. The three-component system can for example be used for stocks of fibres from chemical pulp, such as sulphate and sulphite pulp, thermomechanical pulp, refiner pulp and groundwood pulp from as well hardwood as softwood. It can of course also be used for stocks from recycled fibres. The terms paper and papermaking, which are used herein do of course not only include paper and its production, but also other cellulose fibre containing sheet or web form products, such as pulp sheet, board and cardboard and their production.

The process according the invention can be carried out in per se known manner and with other additions to the fibre stock, such as sizing agents etc.

The invention is further illustrated in the following examples wherein parts and per cent relate to parts by weight and per cent by weight unless otherwise stated.

Example 1

In the following tests the dewatering effect was investigated by means of a "Canadian Freeness Tester", which is the usual method for characterizing the dewatering capability according to SCA-C 21:65.

The stock was based on bleached birch/pine sulphate pulp (60:40) and contained 30 per cent by weight of chalk. The pH of the stock was 8.5 and CSF was 300 ml.

In the table amounts for the chemical additions refer to ton dry stock system (fibres+fillers). The anionic colloid was an alkali stabilized silica sol with a specific surface area of 500 $m^2/g$. The cationic synthetic polymer was a cationic polyacrylamide of medium cationicity sold by Allied Colloids under the name Percol 292. The sodium aluminate was added in the form of a 0.025% aqueous solution and the given amounts of aluminate are expressed as kg $Al_2O_3$. The additions of chemicals were made to 1 l diluted stock (about 0.3%) with intervals of 15 seconds under agitation in the order aluminate, cationic polymer, inorganic colloid. The flocked stock was transferred to the freeness apparatus and measurements were made 15 seconds after the last addition. The water which is collected is a measurement of the dewatering effect and is expressed in ml Canadian Standard Freeness (CSF). The water obtained in the tests using the three components was very clear and this shows that a good retention of the fines material to the flocks had also been obtained.

| Test No. | $Al_2O_3$ kg/t | Cationic polymer kg/t | Anionic Colloid kg/t | CSF ml |
|---|---|---|---|---|
| 1 | - | - | - | 300 |
| 2 | - | 0.3 | - | 370 |
| 3 | - | 0.6 | - | 385 |
| 4 | - | 0.9 | - | 390 |
| 5 | 0.15 | - | - | 290 |
| 6 | 0.15 | 0.3 | - | 350 |
| 7 | - | - | 1.0 | 295 |
| 8 | 0.15 | - | 1.0 | 290 |
| 9 | - | 0.3 | 0.5 | 420 |
| 10 | - | 0.3 | 1.0 | 430 |
| 11 | - | 0.3 | 1.5 | 440 |
| 12 | 0.075 | 0.3 | 0.5 | 495 |
| 13 | 0.15 | 0.3 | 1.0 | 520 |
| 14 | 0.225 | 0.3 | 1.5 | 515 |

| Test No. | $Al_2O_3$ kg/t | Cationic polymer kg/t | Anionic Colloid kg/t | CSF ml |
|---|---|---|---|---|
| 15 | - | 0.6 | 0.5 | 425 |
| 16 | - | 0.6 | 1.0 | 490 |
| 17 | - | 0.6 | 1.5 | 510 |
| 18 | 0.075 | 0.6 | 0.5 | 495 |
| 19 | 0.15 | 0.6 | 1.0 | 570 |
| 20 | 0.225 | 0.6 | 1.5 | 585 |

As evident also use of very small amounts of aluminate gives a considerably improved dewatering effect for the system of cationic polymer and anionic colloid. The corresponding effect of the aluminate is not obtained if it is used in combination with only cationic polymer or only anionic colloid.

Example 2

This example corresponded entirely to example 1 with the only difference that other cationic synthetic polymers were used. These were A) an epichlorohydrine modified polyamidoamine resin sold by Hercules Inc. under the name Kymene 557 H and B) a modified polyamine resin sold by Hercules Inc. under the name Delfloc-50.

| Test No. | $Al_2O_3$ kg/t | Cat. Polymer type;kg/t | Anionic Colloid kg/t | CSF ml |
|---|---|---|---|---|
| 1 | - | - | - | 300 |
| 2 | - | A; 0.6 | - | 305 |
| 3 | - | A; 1.2 | - | 315 |
| 4 | - | A; 2.4 | - | 315 |
| 5 | - | A; 1.2 | 0.5 | 325 |
| 6 | - | A; 1.2 | 1.0 | 330 |
| 7 | - | A; 1.2 | 1.5 | 310 |
| 8 | 0.075 | A; 1.2 | 0.5 | 360 |
| 9 | 0.15 | A; 1.2 | 1.0 | 390 |
| 10 | 0.225 | A; 1.2 | 1.5 | 410 |
| 11 | 0.30 | A; 1.2 | 2.0 | 395 |
| 12 | - | B; 1.2 | - | 290 |
| 13 | - | B; 1.2 | 1.5 | 280 |
| 14 | 0.225 | B; 1.2 | 1.5 | 335 |

Example 3

In this example a groundwood stock was used which did not contain any fillers. To the stock 0.5 g/l of $Na_2SO_4.10H_2O$ had been added to give an ion strength corresponding to the one under large scale conditions. The cationic polymer was the same polyacrylamide as in Example 1. The anionic colloid was an aluminum modified, 15% alkali stabilized, silica sol where the surface of the colloidal particles had been modified with 9% aluminum atoms and the surface area of the particles was 500 $m^2/g$. The order of addition was sodium aluminate, cationic polymer followed by anionic colloid. Tests were made both with a stock pH of 6 and a stock pH of 7.5 whereby the pH had been adjusted with diluted $H_2SO_4$ and diluted NaOH respectively.

| Test No | $Al_2O_3$ kg/t | Cationic polymer kg/t | Anionic colloid kg/t | CSF ml |
|---|---|---|---|---|
| pH 6.0 | | | | |
| 1 | - | - | - | 120 |
| 2 | - | 0.3 | - | 190 |
| 3 | - | 0.6 | - | 220 |
| 4 | - | 0.9 | - | 245 |
| 5 | - | 1.2 | - | 250 |
| 6 | - | 0.6 | 0.5 | 275 |
| 7 | - | 0.6 | 1.0 | 305 |
| 8 | - | 0.6 | 1.5 | 300 |
| 9 | 0.075 | 0.6 | 0.5 | 325 |
| 10 | 0.15 | 0.6 | 1.0 | 345 |
| 11 | 0.225 | 0.6 | 1.5 | 350 |
| pH 7.5 | | | | |
| 12 | - | 0.6 | - | 220 |
| 13 | - | 0.6 | 0.5 | 245 |
| 14 | - | 0.6 | 1.0 | 270 |
| 15 | - | 0.6 | 1.5 | 275 |
| 16 | 0.075 | 0.6 | 0.5 | 295 |
| 17 | 0.15 | 0.6 | 1.0 | 325 |
| 18 | 0.225 | 0.6 | 1.5 | 340 |
| 19 | - | 0.9 | 1.5 | 310 |
| 20 | 0.225 | 0.9 | 1.5 | 370 |

Example 4

In these tests a groundwood stock with addition of 0.5 g/1 of $Na_2SO_4.10H_2O$ was used as in Example 3. The pH of the stock was 6.5 and the added chemicals were sodium aluminate, a cationic polyethylene imine sold by BASF under the name Polymin SK and an anionic colloid which was a bentonite colloid having a specific surface area of from about 400 to 800 m$^2$/g in water.

| Test No. | $Al_2O_3$ kg/t | Cationic polymer kg/t | Anionic colloid kg/t | CSF ml |
|---|---|---|---|---|
| 1 | - | - | - | 120 |
| 2 | - | 0.3 | - | 175 |
| 3 | - | 0.6 | - | 230 |
| 4 | - | 0.9 | - | 300 |
| 5 | - | 1.2 | - | 310 |
| 6 | - | 0.6 | 0.5 | 260 |
| 7 | - | 0.6 | 1.0 | 280 |
| 8 | - | 0.9 | 1.0 | 340 |
| 9 | 0.075 | 0.6 | 0.5 | 295 |
| 10 | 0.15 | 0.6 | 1.0 | 335 |
| 11 | 0.15 | 0.9 | 1.0 | 390 |

## Claims

1. A process for the production of paper by forming and dewatering a suspension of cellulose containing fibres on a wire, characterized in that the forming and dewatering takes place in the presence of an anionic inorganic colloid, an aluminate and a cationic synthetic polymer.

2. A process according to claim 1, characterized in that the anionic colloid is a silica based colloid.

3. A process according to claim 1 or 2, characterized in that the colloid is a silica sol, a silica sol with particles having at least a surface layer of aluminum silicate or an aluminum modified silica sol.

4. A process according to claim 1, 2 or 3, characterized in that the particles of the colloid have a specific surface area within the range of from 50 to 1000 m$^2$/g.

5. A process according to claim 3, characterized in that the particle size of the colloid is 20 nm at the most.

6. A process according to claim 1, characterized in that the cationic synthetic polymer is a cationic polyacrylamide, polyethyleneimine, polyamine or polyamidoamine.

7. A process according to any of the preceding claims, characterized in that the aluminate is added to the fibre suspension before the anionic inorganic colloid and the cationic synthetic polymer.

8. A process according to any of claims 1, 2, 3, 4 or 5, characterized in that the amount of anionic inorganic colloid is within the range of from 0.005 to 2 per cent by weight, based on dry fibres and optional fillers.

9. A process according to claim 1 or 6, characterized in that the amount of cationic synthetic polymer is within the range of from 0.01 to 3 per cent by weight, based on dry fibres and optional fillers.

10. A process according to claim 1, characterized in that the weight ratio of aluminate, calculated as $Al_2O_3$, to anionic inorganic colloid is within the range of from 0.01:1 to 3:1.