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(54) **Title:** METHOD FOR PITCH CONTROL DURING BLEACHING

(57) **Abstract:** The invention relates to a method for pitch control and/or removal during bleaching of cellulosic fibres. Cellulosic fibres are obtained from a pulping process and formed into an aqueous cellulosic fibre suspension, and bleaching of the cellulosic fibre suspension is performed in a bleaching process comprising at least one acidic stage, where pH of the cellulosic fibre suspension is <6. A pitch control agent is added to the cellulosic fibre suspension before the acidic stage, wherein the pitch control agent comprises at least one cationic polymer comprising cationic functional groups which are hydrolysed at pH 9.0

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METHOD FOR PITCH CONTROL DURING BLEACHING

The present invention relates to a method for pitch control and/or pitch removal during bleaching of cellulosic fibres in a pulp manufacturing process according to the preambles of enclosed claims.

Cellulosic fibres obtained from a chemical pulping process are bleached in a bleaching process, where residual lignin is removed from the fibres in order to increase their brightness. Bleaching is a stage-wise process, where various bleaching chemicals are usually used at different successive stages to break lignin into smaller structures. Breakdown structures of lignin are water soluble, especially at pH >7, and they are removed from the fibres, as well as from the bleaching process, in alkaline extraction stages located after or between the bleaching stages.

During bleaching, pitch and other pitch-like substances, resins and extractives present in pulp are also liberated from the fibres. It has been observed that if the pitch and pitch-like substances are not bound to a pitch control agent in the acidic bleaching stages, they easily form agglomerates, which can deposit on process equipment, block process filters and/or create spots in the final fibrous web. The pitch and pitch-like substances are nowadays preferably effectively removed from the bleaching process at the alkaline extraction stage together with lignin.

Talc is commonly used as a pitch control agent to reduce tackiness of pitch and pitch-like substances. Talc is added to the bleaching process, where it interacts with the liberated pitch and pitch-like substances and reduces their tendency to form agglomerates. At the alkaline extraction stage pitch and pitch-like substances, which are soluble at alkaline pH, such as fatty acids, are freed from talc and removed with process water together with lignin. Talc itself remains in the pulp manufacturing process with the fibres. Pitch and pitch-like substances, which are not soluble in alkaline pH, such as sterols and betulinol, may also remain in the pulp manufacturing process, staying at least partly bound with talc particles during the alkaline extraction stage. These non-alkaline soluble neutral pitch and pitch-like

substances may still cause deposit problems later in the pulp manufacturing process or degrade the quality of the obtained cellulose.

However, recently there has been an increasing interest and desire to reduce the use of talc in industrial processes, as some talc varieties may contain asbestos, which is a problem in view of occupational safety. Furthermore, some industries which use bleached cellulose fibres as their raw material, such as manufacturers of carboxymethylated cellulose, prefer pulps which do not contain additional inorganic material, such as talc. Consequently, there is an emerging need for new alternative pitch control agents.

The object of the present invention is to minimize or even eliminate the disadvantages existing in the prior art.

One object of the present invention is to provide a method for effectively controlling pitch and pitch-like substances during a bleaching of cellulosic fibres.

One object of the present invention is to provide an effective alternative for talc in the bleaching process of cellulosic fibres.

Yet another object of the present invention is to provide a method with which pitch and pitch-like substances are effectively removed from cellulosic fibre suspension during the bleaching process.

These objects are attained with the invention having the characteristics presented below in the characterising part of the independent claim.

Some preferred embodiments of the invention are presented in the dependent claims.

The embodiments mentioned in this text relate, where applicable, to all aspects of the invention, even if this is not always separately mentioned.

In a typical method according to the present invention for pitch control and/or pitch removal during bleaching of cellulosic fibres,

- cellulosic fibres are obtained from a pulping process and formed into an aqueous cellulosic fibre suspension,
- bleaching of the cellulosic fibre suspension is performed in a bleaching process comprising at least one acidic stage, where pH of the cellulosic fibre suspension is <6, and
- a pitch control agent is added to the cellulosic fibre suspension before the acidic stage, wherein the pitch control agent comprises at least one cationic polymer, and wherein the cationic polymer comprises cationic functional groups which are hydrolysed at pH 9 or higher.

Typical use of cationic polymer comprising cationic functional groups which are hydrolysed at pH 9 or higher according to the present invention is as pitch control agent in bleaching process of cellulosic fibres for controlled removal of pitch and pitch-like substances.

Now it has been surprisingly found out that talc can be replaced as a pitch control agent by a cationic polymer, which comprises cationic functional groups which are hydrolysed at pH 9 or higher. Cationic groups of the polymer are able to interact with pitch and pitch-like substances at least as effectively as talc at acidic pH and then release pitch and pitch-like substances during the subsequent alkaline extraction stage, thus preventing the agglomeration of pitch and pitch like substances in the pulp manufacturing process. When the polymer comprises cationic groups that are hydrolysed during the alkaline extraction stage, the hydrolysed groups release the pitch and pitch-like substances to the aqueous phase in the alkaline extraction stage, whereby the pitch and pitch-like substance can be effectively removed with the aqueous phase from the pulp manufacturing process. In this manner the achieved pitch control effect may be significantly improved, even when compared to talc. The polymer amounts needed for effective pitch removal are also much lower than the talc amounts needed for the same effect. Furthermore, use of a cationic polymer as pitch control agent reduces the content of inorganic material in the obtained bleached pulp, which make the pulp more suitable for a variety of different

purposes, such as manufacture of carboxymethyl cellulose. Furthermore, the possibility to reduce or eliminate inorganic material, such as talc, in the obtained bleached pulp may reduce dusting problems in paper or board products for which the obtained bleached pulp is used.

Polymers, which are suitable for use in the present invention, comprises cationic functional groups which are hydrolysed at pH 9 or higher, i.e. the polymer comprises cationic groups which are hydrolysed in a pH range from pH 9 to pH 14, preferably from pH 9 to pH 11.

In the present context, the pitch control denotes actions which inhibit or at least minimize the formation of agglomerates, deposits and the like, as well as formation of defects, such as visual dark spots, in the final bleached pulp, which are caused by pitch and/or pith-like substances by removing them effectively during the alkaline extraction stage(s) of the bleaching.

The present invention provides thus a method for control and/or removal pitch and pitch-like substances during bleaching of cellulosic fibre suspension. Pitch and pitch-like substances, in the context of the present invention, comprise a mixture of various resins and extractives, such as fatty acids, resin acids, steryl esters, sterols, triglycerides, etc., which are liberated from hardwood and/or softwood fibres during bleaching process. The present invention is effective for removal of fatty acids, resin acids, steryl esters, sterols and/or betulinol. The present invention is especially effective for removal of neutral pitch and pitch-like substances, which are not soluble at alkaline extraction stage, such as steryl esters, sterols and/or betulinol. These neutral extractives are usually complicated to control and/or remove during the bleaching process, and they easily cause severe pitch agglomeration problems. Now it was unexpectedly observed that in the present invention the cationic groups of the polymer successfully interacts especially with these neutral extractives, but the neutral extractives can be effectively removed during the alkaline extraction stage, as they are liberated to the aqueous phase when the cationic groups of the polymer are hydrolysed.

In general, the method according to the present invention is suitable for all cellulosic pulps which are bleached. According to one embodiment the invention, the cellulosic fibres to be bleached may originate from hardwood, softwood, or their mixtures. Preferably the cellulosic fibres are hardwood fibres. Especially, the cellulosic fibres may originate from birch, eucalyptus, acacia, other tropical hardwood species, or any mixtures thereof. Cellulosic fibres are obtained from a pulping process and formed into an aqueous cellulosic fibre suspension. Preferably cellulosic fibres originate from a chemical pulping process, such as Kraft or sulphite pulping, preferably Kraft pulping. When the cellulosic fibres originate from Kraft pulping, the unbleached fibres are separated from the used cooking chemicals, so-called black liquor, by washing of the fibres (brownstock) with water. The obtained suspension of unbleached fibres is then transferred to a bleaching process.

The bleaching of the cellulosic fibre suspension is performed in a bleaching process comprising at least one acidic stage, where pH of the cellulosic fibre suspension is <6, preferably <5. The acidic stage may be, for example, an acid hydrolysis stage, commonly denoted as A-stage, and/or a chlorine dioxide stage, commonly denoted as D-stage. The bleaching process may comprise one or more acidic stages. The bleaching process further comprises one or more alkaline extraction stages, located after an acidic stage or between two acidic stages. In an alkaline extraction stage the pH of the cellulosic fibre suspension is raised at least pH 9, preferably at least pH 10.

The pitch control agent according to the present invention comprises at least one cationic polymer with cationic functional groups which are hydrolysed at pH 9 or higher. The pitch control agent is added to the cellulosic fibre suspension before an acidic stage of the bleaching process. The pitch control agent comprising at least one cationic polymer can be added to the cellulosic fibre suspension in any bleaching process stage and/or bleaching process location where talc is conventionally added to the cellulosic fibre suspension during the bleaching process. The pitch control agent may be added as one dose to the cellulosic fibre suspension, or it may be added to cellulosic fibre suspension as several dosages at several dosing locations along the bleaching process. According to one preferable

embodiment, when the cellulosic fibres originate from Kraft pulping, the pitch control agent is added to the cellulosic fibre suspension after the washing of the cellulosic fibres (brownstock) and before an acidic stage in the bleaching process. The pitch control agent may be added, for example, after the separation of used cooking chemicals and washing of the cellulosic fibres.

According to the invention the pitch control agent comprises at least one polymer, preferably cationic polymer, which comprises cationic functional groups which are hydrolysed at pH 9 or higher. When the cationic functional groups are hydrolysed at alkaline extraction stage, the pitch and pitch-like substances are effectively freed or released from the pitch control agent. This ensures good washing and/or deresination at the alkaline extractions stage and effective removal of pitch and pitch-like substances from the bleaching process.

In the context of the present application the term “cationic polymer” denotes a polymer, which may possess both cationic and anionic functional groups in an aqueous solution at pH 7, as long as the net charge of the polymer is cationic at pH 4. Cationic net charge means that the net charge of the polymer is positive, even if it contains anionic groups. The net charge of a polymer is calculated as the sum of the charges of the cationic and anionic groups present.

According to one embodiment the cationic polymer may comprise both cationic functional groups which are hydrolysed at pH 9 as well as cationic functional groups which remain unhydrolysed at pH 9. According to yet another embodiment the cationic polymer may comprise solely cationic functional groups which are hydrolysed at pH 9. The cationic functional groups efficiently interact with the pitch and pitch-like substances at the acidic bleaching stage, where the pH is <6, and prevent the agglomeration of pitch and pitch-like substances. At the following alkaline extraction stage, at least some or all of the cationic functionalized groups of the cationic polymer are hydrolysed, and the pitch and pitch-like substances are released and removed from the bleaching process.

According to one embodiment the pitch control agent may be a mixture of two or more cationic polymers, of which some comprise hydrolysable cationic functional groups. The pitch control agent may comprise at least 25 weight-%, preferably at least 50 weight-%, more preferably at least 75 weight-%, even more preferably at least 90 weight-%, of a cationic polymer, which comprises cationic functional groups which are hydrolysed at pH 9 or higher, calculated from the dry weight of total polymers of the pitch control agent. According to one preferable embodiment the pitch control agent consists of cationic polymer(s), which comprise(s) cationic functional groups which are hydrolysed at pH 9 or higher.

The pitch control agent may comprise a cationic polymer, preferably a copolymer of (meth)acrylamide, which has a weight average molecular weight MW of 1 500 000 – 6 000 000 g/mol, preferably 2 000 000 – 5 000 000 g/mol, more preferably 2 500 000 – 4 500 000 g/mol, even more preferably 2 700 000 – 4 300 000 g/mol. Sometimes the weight average molecular weight of the cationic polymer may be in a range of 3 000 000 – 5 000 000 g/mol or 3 500 000 – 5 500 000 g/mol. It has been observed that the defined molecular weight ensures proper interaction between the cationic polymer, pitch, and pitch-like substances in the acidic stage. In this application the value “weight average molecular weight” is used to describe the magnitude of the polymer chain length. Weight average molecular weight values are calculated from intrinsic viscosity results measured in a known manner in 1N NaCl at 25 °C by using an Ubbelohde capillary viscometer. The capillary selected is appropriate, and in the measurements of this application an Ubbelohde capillary viscometer with constant K=0.005228 was used. The average molecular weight is then calculated from intrinsic viscosity result in a known manner using Mark-Houwink equation $[\eta]=K \cdot Ma$, where $[\eta]$ is intrinsic viscosity, M molecular weight (g/mol), and K and a are parameters given in Polymer Handbook, Fourth Edition, Volume 2, Editors: J. Brandrup, E.H. Immergut and E.A. Grulke, John Wiley & Sons, Inc., USA, 1999, p. VII/11 for poly(acrylamide). Accordingly, value of parameter K is 0.0191 ml/g and value of parameter “a” is 0.71. The average molecular weight range given for the parameters in used conditions is 490 000 – 3 200 000 g/mol, but the same parameters are used to describe the magnitude of molecular weight also

outside this range. pH of the polymer solutions for intrinsic viscosity determination is adjusted to 2.7 by formic acid.

According to one preferable embodiment the pitch control agent may comprise polyacrylamide obtained by copolymerisation of (meth)acrylamide and cationic monomers. The cationic polyacrylamide which is suitable for use as a pitch control agent may be obtained by copolymerisation of (meth)acrylamide and at least one cationic monomer selected from a group consisting of 2-(dimethylamino)ethyl acrylate (ADAM), [2-(acryloyloxy)ethyl] trimethylammonium chloride (ADAM-Cl), 2-(dimethylamino)ethyl acrylate benzylchloride, 2-(dimethylamino)ethyl acrylate dimethylsulphate, 2-dimethylaminoethyl methacrylate (MADAM), [2-(methacryloyloxy)ethyl] trimethylammonium chloride (MADAM-Cl), 2-dimethylaminoethyl methacrylate dimethylsulphate, [3-(acryloylamino)propyl] trimethylammonium chloride (APTAC), [3-(methacryloylamino)propyl] trimethylammonium chloride (MAPTAC) and any of their combinations.

According to one preferable embodiment of the present invention the pitch control agent comprises cationic polyacrylamide which may be obtained by copolymerisation of (meth)acrylamide and at least one cationic monomer comprising functional groups that are hydrolysed at pH 9 or higher. Preferable monomers may be selected from the group consisting of 2-(dimethylamino)ethyl acrylate (ADAM), [2-(acryloyloxy)ethyl] trimethylammonium chloride (ADAM-Cl), 2-dimethylaminoethyl methacrylate (MADAM) and [2-(methacryloyloxy)ethyl] trimethylammonium chloride (MADAM-Cl). These monomers may be copolymerised together with acrylamide and/or methacrylamide monomers in order to obtain copolymers with cationic functional groups that are hydrolysed at pH 9 or higher and thus especially suitable for pitch control during bleaching of cellulosic fibres.

The pitch control agent may comprise a cationic polyacrylamide which is obtained by copolymerisation of (meth)acrylamide and 4 – 60 mol-%, preferably 5 – 50 mol-%, more preferably 5 – 40 mol-%, or sometimes even more preferably 5 – 25 mol-%, of cationic monomers, preferably cationic monomers that are hydrolysed at pH 9 or higher. According to one embodiment, cationic polyacrylamide which is obtained

by copolymerisation of (meth)acrylamide and 4 – 15 mol-%, preferably 5 – 13 mol-%, more preferably 6 – 12 mol-%, of cationic monomers. This means that in the latter embodiment the cationic polyacrylamide may have a total ionicity in a range of 4 – 15 mol-%, preferably 5 – 13 mol-%, more preferably 6 – 12 mol-%, even more preferably 6 – 10 mol-%.

According to one preferable embodiment of the present invention the pitch control agent may comprise a polymer, which is a net cationic amphoteric polyacrylamide. Net cationic amphoteric polyacrylamide may be obtained by copolymerisation of acrylamide or methacrylamide together with both anionic monomers and cationic monomers, which are hydrolysed at pH 9 or higher. Preferably amphoteric polyacrylamide is obtained by copolymerisation of acrylamide together with both anionic monomers and cationic monomers. According to one preferable embodiment the net cationic amphoteric polyacrylamide may obtained by gel polymerisation of (meth)acrylamide together with anionic monomers and cationic monomers. Without wishing to be bound by a theory, it is speculated that the anionic groups of the amphoteric polymer may improve the removal of pitch and pitch-like substances. When the cationic groups of the polymer are hydrolysed at pH 9 or higher, the pitch and pitch-like substances are released. At the same time, the anionic functional groups of the polymer exert a repelling force to the pitch and pitch-like substances. This may improve and make the removal of the pitch and pitch-like substances even more effective.

According to one embodiment, the pitch control agent may comprise a net cationic amphoteric polyacrylamide where 53 – 90 %, preferably 50 – 85 %, more preferably 60 – 80 %, of the charged groups of the amphoteric polyacrylamide are cationic groups, which are hydrolysed at pH 9 or higher.

If the pitch control agent comprises a net cationic amphoteric polyacrylamide, the anionic groups in the polymer structure may originate from monomers selected from unsaturated mono- or dicarboxylic acids, such as acrylic acid, maleic acid, fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid, crotonic acid, isocrotonic acid, angelic acid or tiglic acid. Preferably the anionic groups originate

from acrylic acid or itaconic acid. The cationic groups may originate from cationic monomers listed earlier in this application.

According to one embodiment the amphoteric polyacrylamide may comprise <80 mol-%, preferably <70 mol-%, more preferably <50 mol-% or <40 mol-% of structural units originating from anionic and cationic monomers. The amphoteric polymer may comprise 5 – 80 mol-%, preferably 7 – 70 mol-%, preferably 7 – 50 mol-% or 7 – 40 mol-% of structural units originating from anionic and cationic monomers. For example, the amphoteric polymer may comprise 5 – 30 mol-%, preferably 5 – 20 mol-% or 5 – 15 mol-% of structural units originating from cationic monomers, which are hydrolysed at pH 9 or higher, and/or 1 – 40 mol-%, preferably 3 – 30 mol-% or 5 – 20 mol-% of structural units originating from anionic monomers.

According to one embodiment, the amphoteric polyacrylamide may comprise at least 85 mol-% structural units derived from acrylamide and/or methacrylamide monomers and <15 mol-% of structural units originating anionic and cationic monomers. The percentage values are calculated from the total dry weight of the polymer. The total ionicity of the amphoteric polyacrylamide is in the range of 4 – 15 mol-%, preferably 5 – 13 mol-%, more preferably 6 – 12 mol-%, even more preferably 6 – 10 mol-%. Total ionicity includes all groups having ionic charge in the amphoteric polyacrylamide, most of the charged groups originating from the ionic monomers, but including also other charged groups originating from chain termination agents or the like. It has been observed that in some embodiments it is beneficial when the total ionicity of the amphoteric polymer is <15 mol-%, especially when the average molecular weight of the polymer is 2 000 000 – 6 000 000 g/mol.

According to one embodiment of the invention the pitch control agent which comprises the cationic polymer with hydrolysable functional groups is added in amount of <500 g cationic polymer/ton dry pulp, preferably <300 g cationic polymer/ton dry pulp, more preferably <200 g cationic polymer/ton dry pulp or <100 g/ton dry pulp. It is possible to use lower dosage of pitch control agent when it comprises cationic polymer.

Some embodiments of the invention are described in the following non-limiting example.

Example 1

In Example 1 unbleached, oxygen delignified birch pulp was bleached in the laboratory with a conventional D-E-D (chlorine dioxide – alkali extraction – chlorine dioxide) bleaching sequence. The bleaching conditions are described in Table 1.

To control the extractives, talc (reference) or pitch control agents A or B (according to the invention) were added to the pulp before each acidic bleaching stage (D).

Talc was commercial talc used for pulp applications.

Pitch control agent A was amphoteric polyacrylamide originating from about 7 mol-% of cationic monomers and 2 mol-% of anionic monomers; weight average weight about 4 000 000 g/mol; a net charge of about +0.6 meg/g at pH 7. The cationic functional groups of polyacrylamide hydrolysed at pH 9.

Pitch control agent B was a polymer mixture comprising poly-DADMAC and cationic polyacrylamide in ratio 1:1, total polymer content of the mixture was 35 weight-%. Poly-DADMAC had weight average molecular weight about 250 000 g/mol and charge density of about +6 meq/g. Cationic polyacrylamide originated from 10 mol-% of cationic monomers, had weight average molecular weight about 5 000 000 g/mol and a charge density of about +1.3 meq/g at pH 7. The functional groups of cationic polyacrylamide hydrolysed at pH 9. The pitch control agent B had a net charge of about 3.6 – 3.7 meg/g at pH 7

In addition, a further reference bleaching was done without any additives.

The amount of talc added to the pulp before each bleaching stage was 1 kg/t and the amount of the pitch control agent A and B were 300 g/t before each bleaching stage. After each bleaching stage the filtrates and washed pulps were sampled for

extractives. The pulp was washed afterthe bleaching stages with two times 20 amount of water in ratio to pulp.

Table 1 Bleaching sequence and conditions of Example 1.

	0-Reference	Talc (Ref.)	Agent A	Agent B	0-Reference	Talc (Ref)	Agent A	Agent B	0-Reference	Talc (Ref.)	Agent A	Agent B
Bleaching stage	D_0	D_0	D_0	D_0	E	E	E	E	D1	D1	D1	D1
T, °C	70	70	70	70	70	70	70	70	70	70	70	70
t, min	30	30	30	30	60	60	60	60	60	60	60	60
Consistency, %	10	10	10	10	10	10	10	10	10	10	10	10
pH, start	3.1	3.1	3.2	3.1	11.1	11.1	10.9	10.9	3.9	3.9	4.0	4.0
pH, end	3.1	3.2	3.2	3.1	11	10.6	10.4	10.8	3.6	3.2	3.4	3.2
$ClO_{2(akt\ Cl)}$, kg/tp	35	35	35	35					35	35	35	35
NaOH,kg/tp					10	10	10	10				

The results are shown in Table 2. It can be seen that talc and especially the pitch control agents A and B increased the amount of extractives in the pulp after D0 stage compared to the 0-reference. This is a clear indication that the extractives (=pitch and pitch-like substances) were retained in the pulp. This increase in extractive content in the pulp, obtainable with both talc and the pitch control agents A and B, was then removed in the E-stage, which can be seen as an increase in the extractive amount in the filtrates. After the final bleaching stage (D1) all pulps had roughly the same amount of extractive content indicating that the fixation in the acidic stages did not deteriorate the overall pitch washing efficiency.

Table 2 Results of Example 1

	Extractives					
Bleaching stage	D0	D0	E	E	D1	D1
	pulp [mg/g]	filtrate [mg/l]	pulp [mg/g]	filtrate [mg/l]	filtrate [mg/l]	pulp [mg/g]
0-REF	4.6.	76.5	0.40	170.9	0.3	4.1
Talc (ref.)	5.2	94.1	0.40	332.5	0.4	4.3
Agent A	6.7	68.0	0.50	596.4	0.5	4.5
Agent B	6.0	79.0	0.50	425.6	0.4	3.2

It is seen from Table 2 that both pitch control agent A and B remove extractives even more effectively than talc. Especially agent A, comprising only hydrolysable cationic functional groups, provided for an effective removal of extractives.

Example 2

In Example 2, oxygen delignified birch pulp was bleached in the laboratory with a conventional bleaching sequence, comprising an acidic chlorine dioxide stage (D_0) followed by alkali extraction stage (E). The bleaching conditions are given in Table 3.

Table 3 Bleaching conditions for Example 2.

Bleaching stage	D_0	E
T, °C	70	70
t, min	30	60
Consistency, %	10	10
pH, start	3.0	11.0
$ClO_{2(akt\ Cl)}$, kg/tp	35	
NaOH,kg/tp		10

To control the extractives, commercial talc for pulp applications (reference) or following cationic polymer were added to the pulp before the acidic bleaching stage (D0):

Poly A was an amphoteric polyacrylamide originating from about 7 mol-% of cationic monomers and 2 mol-% of anionic monomers; weight average weight about 4 000 000 – 5 000 000 g/mol; a net charge of about +0.7 meg/g at pH 7. The cationic functional groups of polyacrylamide hydrolysing at pH 9.

Poly B was a cationic polyacrylamide originating from about 9 mol-% of cationic monomers; weight average weight about 4 000 000 – 5 000 000 g/mol; a net charge of about +1.2 meg/g at pH 7. The cationic functional groups of polyacrylamide hydrolysing at pH 9.

Poly C was a cationic polyacrylamide originating from about 20 mol-% of cationic monomers; weight average weight about 4 000 000 – 5 000 000 g/mol; a net charge of about +2.1 meg/g at pH 7. The cationic functional groups of polyacrylamide hydrolysing at pH 9.

Poly D was a cationic polyacrylamide originating from about 50 mol-% of cationic monomers; weight average weight about 4 000 000 – 5 000 000 g/mol; a net charge

of about +3.8 meg/g at pH 7. The cationic functional groups of polyacrylamide hydrolysing at pH 9.

Poly E (reference) was a cationic poly-DADMAC, having a net charge about +6.2 meg/g at pH 7 and a weight average molecular weight about 250 000 g/mol. The cationic functional groups did not hydrolyse at pH 9 or higher.

Poly F (reference) was a cationic polyamine epichlorohydrin-dimethylamine polymer, having a net charge about +7.2 meg/g at pH 7 and a weight average molecular weight about 150 000 g/mol. The cationic functional groups did not hydrolyse at pH 9 or higher.

Poly G (reference) was a cationic polyethyleneimine polymer, having a net charge about +12 meg/g at pH 7 and a weight average molecular weight approximately 300 000 g/mol. The cationic functional groups did not hydrolyse at pH 9 or higher.

Poly H (reference) was a cationic polyacrylamide, originating from about 7 mol-% of cationic monomers; weight average weight about 4 000 000 – 5 000 000 g/mol; a net charge of about +0.9 meg/g at pH 7. The cationic functional groups of polyacrylamide did not hydrolyse at pH 9.

The amount of talc added to the pulp suspension before the D0-bleaching stage was 3 kg/t. The cationic polymers were added in amount of 200 g/t, except Poly A, for which addition amounts of 100 and 200 g/t were tested.

The pulp was washed after D0 and E stages with water two times. For each washing, water: pulp ratio was 20:1. The washed pulps were analysed for extractives by using gas chromatography. The results are shown in Table 4. The percentage value in Table 4 indicates amount of removed extractives. It can be seen that the pitch control agents according to present invention and comprising cationic polymers with functional groups which are hydrolysed at pH, provide as effective, or even improved, extractives removal than talc. It can be further seen that compared to the reference polymers from Poly E to Poly H, the polymers Poly A – Poly D which comprised hydrolysing cationic groups were significantly more effective in removal of neutral pitch and pitch-like substances such as sterols, steryl esters and betulinol. This means that by using the present invention the amount of total extractives which is removed, is increased.

Table 4 Results of Example 2: Extractives remaining in pulp after D0- and E-stages, respectively. Values given as mg/g.

	Total Extractives			Fatty Acids			Sterols & Betulinol			Steryl Esters		
	D0	E	%	D0	E	%	D0	E	%	D0	E	%
Talc (ref.)	1.07	0.63	42	0.23	0.08	66	0.52	0.32	39	0.32	0.23	28
Poly A (100 g/t)	1.12	0.49	56	0.31	0.07	77	0.53	0.31	42	0.28	0.11	60
Poly A (200 g/t)	1.26	0.65	48	0.28	0.09	69	0.56	0.37	35	0.41	0.20	52
Poly B	1.18	0.64	46	0.23	0.08	64	0.56	0.37	35	0.38	0.19	50
Poly C	1.19	0.56	53	0.26	0.15	40	0.58	0.32	45	0.35	0.09	75
Poly D	1.22	0.49	60	0.24	0.04	84	0.56	0.31	45	0.43	0.14	67
Poly E (ref.)	1.15	0.80	30	0.26	0.13	48	0.55	0.45	19	0.34	0.22	34
Poly F (ref.)	1.04	0.67	36	0.29	0.09	68	0.48	0.36	26	0.27	0.21	21
Poly G (ref.)	1.01	0.71	30	0.22	0.09	58	0.50	0.38	25	0.29	0.24	18
Poly H (ref.)	1.24	0.75	39	0.23	0.11	50	0.62	0.42	33	0.39	0.22	43

Even if the invention was described with reference to what at present seems to be the most practical and preferred embodiments, it is appreciated that the invention shall not be limited to the embodiments described above, but the invention is intended to cover also different modifications and equivalent technical solutions within the scope of the enclosed claims.

CLAIMS

1. Method for pitch control and/or pitch removal during bleaching of cellulosic fibres, in which method

- cellulosic fibres are obtained from a pulping process and formed into an aqueous cellulosic fibre suspension,
- bleaching of the cellulosic fibre suspension is performed in a bleaching process comprising at least one acidic stage, where pH of the cellulosic fibre suspension is <6, and
- a pitch control agent is added to the cellulosic fibre suspension before the acidic stage, wherein the pitch control agent comprises at least one cationic polymer comprising cationic functional groups which are hydrolysed at pH 9 or higher.

2. Method according to claim 1, **characterised** in that the pitch control agent comprises at least 25 weight-%, preferably at least 50 weight-%, more preferably at least 75 weight-%, of the cationic polymer comprising cationic functional groups which are hydrolysed at pH 9 or higher, calculated from the dry weight of total polymers of the pitch control agent.

3. Method according to claim 1 or 2, **characterised** in that the cationic polymer has a weight average molecular weight MW of 1 500 000 – 6 000 000 g/mol, preferably 2 000 000 – 5 000 000 g/mol, more preferably 2 500 000 – 4 500 000 g/mol, even more preferably 2 700 000 – 4 300 000 g/mol.

4. Method according to claim 1, 2 or 3, **characterised** in that the pitch control agent comprises polyacrylamide obtained by copolymerisation of (meth)acrylamide and cationic monomers.

5. Method according claim 4, **characterised** in that the pitch control agent comprises a cationic polyacrylamide which is obtained by copolymerisation of (meth)acrylamide and 4 – 60 mol-%, preferably 5 – 50 mol-%, more preferably 5 – 40 mol-%.

6. Method according to claim 4 or 5, **characterised** in that the cationic polyacrylamide has a total ionicity in a range of 4 – 15 mol-%, preferably 5 – 13 mol-%, more preferably 6 – 12 mol-%, even more preferably 6 – 10 mol-%.

7. Method according to claims 4, 5 or 6, **characterised** in that the cationic polyacrylamide is a net cationic amphoteric polyacrylamide, preferably obtained by gel polymerisation of (meth)acrylamide together with anionic and cationic monomers.

8. Method according to claim 7, **characterised** in that 53 – 90 %, preferably 50 – 85 %, more preferably 60 – 80 %, of the charged groups of the amphoteric polyacrylamide are cationic.

9. Method according to any of preceding claims 4 – 8, **characterised** in that the cationic polyacrylamide is obtained by copolymerisation of (meth)acrylamide and at least one cationic monomer selected from a group consisting of 2-(dimethylamino)ethyl acrylate (ADAM), [2-(acryloyloxy)ethyl] trimethylammonium chloride (ADAM-Cl), 2-(dimethylamino)ethyl acrylate benzylchloride, 2-(dimethylamino)ethyl acrylate dimethylsulphate, 2-dimethylaminoethyl methacrylate (MADAM), [2-(methacryloyloxy)ethyl] trimethylammonium chloride (MADAM-Cl), 2-dimethylaminoethyl methacrylate dimethylsulphate, [3-(acryloylamino)propyl] trimethylammonium chloride (APTAC), and [3-(methacryloylamino)propyl] trimethylammonium chloride (MAPTAC).

10. Method according to any of preceding claims 1 – 9, **characterised** in that the cellulosic fibres originate from chemical pulping process, such as Kraft pulping process.

11. Method according to claim 10, **characterised** in that the pitch control agent is added after a separation of used cooking chemicals and washing of the cellulosic fibres.

12. Method according to any of preceding claims 1 – 11, **characterised** in that the pitch control agent is added in amount of <500 g/ton dry pulp, preferably <300 g/ton dry pulp, more preferably <200 g/ton dry pulp or <100 g/ton dry pulp.

13. Use of cationic polymer comprising cationic functional groups which are hydrolysed at pH 9 or higher as pitch control agent in a bleaching process of cellulosic fibres.

14. Use according to claim 13, **characterised** in that the cationic polymer is cationic polyacrylamide obtained by copolymerisation of (meth)acrylamide and at least one cationic monomer.

15. Use according to claim 13 or 14, **characterised** in that the cationic polymer is used as pitch control agent for steryl esters, sterols and/or betulinol.

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2021/050441

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21C9/08 D21C9/10 D21H17/37 D21H21/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D21C D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2018/096211 A1 (KEMIRA OYJ [FI]) 31 May 2018 (2018-05-31)	1-15
Y	claims 1-20; examples 1,2	1,13
Y	US 2018/363247 A1 (LI XIAOJIN HARRY [US] ET AL) 20 December 2018 (2018-12-20) claims 1-36	1,13
Y	US 2006/000570 A1 (SONG ZHIQIANG [US] ET AL) 5 January 2006 (2006-01-05) claims 1-20	1,13
A	WO 2016/120524 A1 (KEMIRA OYJ [FI]) 4 August 2016 (2016-08-04) the whole document	1-15

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 August 2021	30/08/2021

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INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2021/050441

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2012/118523 A1 (LU CHEN [US] ET AL) 17 May 2012 (2012-05-17) the whole document -----	1-15
A	US 5 256 252 A (SARKAR JAWED M [US] ET AL) 26 October 1993 (1993-10-26) the whole document -----	1-15

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/FI2021/050441

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2018096211 A1	31-05-2018	AU 2017365745 A1	23-05-2019
		BR 112019007678 A2	02-07-2019
		CA 3039741 A1	31-05-2018
		CN 109983177 A	05-07-2019
		EP 3545130 A1	02-10-2019
		FI 127289 B	15-03-2018
		JP 2019535923 A	12-12-2019
		KR 20190087429 A	24-07-2019
		RU 2019118796 A	24-12-2020
		WO 2018096211 A1	31-05-2018
US 2018363247 A1	20-12-2018	US 2018363247 A1	20-12-2018
		WO 2018232115 A1	20-12-2018
US 2006000570 A1	05-01-2006	AU 2005259257 A1	12-01-2006
		BR PI0512845 A	08-04-2008
		CA 2569823 A1	12-01-2006
		EP 1763609 A1	21-03-2007
		JP 2008505257 A	21-02-2008
		TW 200617242 A	01-06-2006
		US 2006000570 A1	05-01-2006
		WO 2006003122 A1	12-01-2006
WO 2016120524 A1	04-08-2016	AU 2016211072 A1	06-07-2017
		BR 112017013525 A2	02-01-2018
		CA 2970133 A1	04-08-2016
		CN 107208376 A	26-09-2017
		EP 3250752 A1	06-12-2017
		ES 2735900 T3	20-12-2019
		FI 126610 B	15-03-2017
		JP 6574258 B2	11-09-2019
		JP 2018509492 A	05-04-2018
		KR 20170108943 A	27-09-2017
		RU 2017130146 A	28-02-2019
		TR 201910897 T4	21-08-2019
		TW 201638127 A	01-11-2016
		US 2018016746 A1	18-01-2018
		WO 2016120524 A1	04-08-2016
US 2012118523 A1	17-05-2012	CA 2817004 A1	24-05-2012
		CN 103210145 A	17-07-2013
		EP 2640895 A1	25-09-2013
		US 2012118523 A1	17-05-2012
		WO 2012067877 A1	24-05-2012
US 5256252 A	26-10-1993	CA 2100374 A1	16-01-1994
		EP 0584513 A1	02-03-1994
		FI 933202 A	16-01-1994
		JP H06173192 A	21-06-1994
		KR 940005853 A	22-03-1994
		US 5256252 A	26-10-1993