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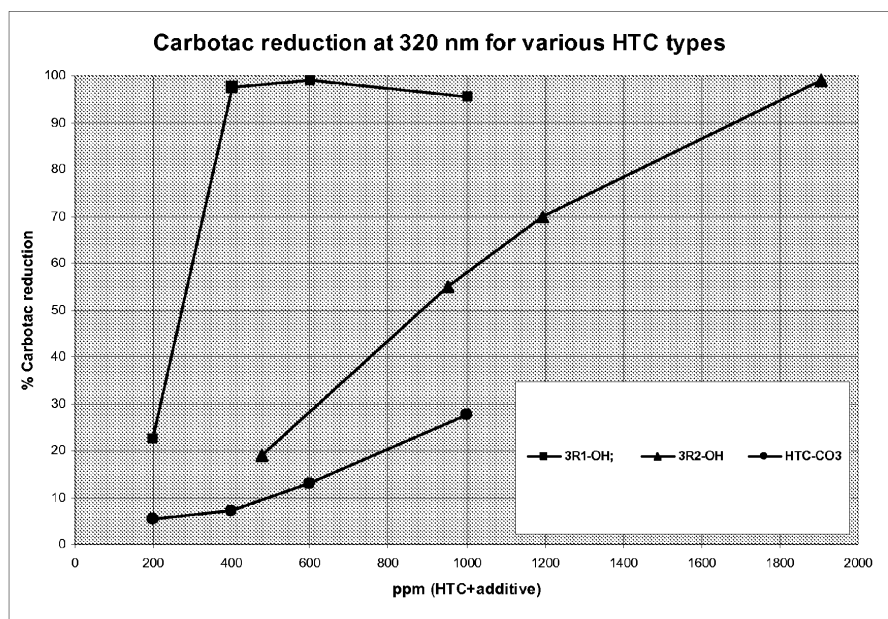
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(54) **Process for the production of a cellulosic product**

(57) The present invention pertains to a process for the production of a cellulosic product which comprises (i) providing an aqueous suspension containing cellulosic fibres and, optionally, a filler; (ii) adding to the suspension a clay having 3R₁ stacking and interlayers which com-

prise hydroxide; and (iii) dewatering the obtained suspension. Further, it pertains to the use of a clay having 3R₁ stacking and interlayers which comprise hydroxide for removing disturbing and detrimental substances such as pitch and stickies from an aqueous cellulosic pulp suspension.

Figure 1



Description

[0001] The present invention relates to a process for the production of a cellulosic product which comprises treating cellulosic fibres with a clay having 3R₁ stacking and interlayers which comprise hydroxide.

[0002] Pulp suspensions are widely used for making cellulosic products such as, for example, pulp and paper and apart from cellulosic fibres also contain compounds which have a negative impact on the production process. Such compounds are found in cellulosic suspensions originating from both virgin pulp and recycled pulp.

[0003] In virgin pulp suspensions such disturbing/detrimental substances are primarily hemicellulose, lignin, as well as lipophilic and hydrophilic extractives. Apart from the cellulose, these substances are to a varying extent dissolved or colloiddally dispersed into the process waters during the pulping and bleaching operations. Compounds which are released during pulping and bleaching operations are commonly referred to as pitch.

[0004] Examples of pitch include wood resins such as lipophilic extractives (fatty and resin acids, sterols, stearyl esters, triglycerides), and also fats, terpenes, terpenoids, waxes, etc.

[0005] In recycled pulp suspensions the compounds having a negative influence on the paper making process mainly consist of glues, hot-melt plastics, inks, and latex among others; compounds commonly referred to as stickies. Apart from pitch and stickies, the suspension also contains charged contaminants such as salts and various wood polymers of which the charged, low-charged or non-charged compounds compete with the cellulose with respect to adsorption of and interaction with added performance chemicals such as drainage and retention aids, sizing agents, etc. Usually such disturbing compounds are referred to as anionic trash.

[0006] All of the above-mentioned compounds interfere with the pulp and paper making processes in various ways. For instance, some of them precipitate due to changes in the properties of the pulp suspension and are eventually deposited on various mechanical parts of the paper machine such as, for example, screens and felts. Over time, the deposits will lead to breakdowns on the paper machine, often in the form of breaking of the paper web, as a result of which the paper machine has to be stopped for cleaning. Furthermore, paper mills tend to re-circulate white water to a greater extent than previously, which increases the presence of disturbing and detrimental substances in the suspension.

[0007] Various additives have been used in order to decrease the negative impact of the above-mentioned detrimental/disturbing substances. For example, talc has been widely used for adsorbing pitch and stickies. Also various types of clays have been employed for reducing the impact of detrimental compounds.

[0008] Japanese laid-open patent application No. 1985-94687, for instance, relates to a pitch-adsorbing agent containing hydrotalcite.

[0009] WO 2004/046464 describes a process for the production of a cellulosic product wherein use is made of a clay having 3R₂ stacking which allows for adsorption and removal of disturbing and detrimental substances.

[0010] The object of the present invention is to provide a process which allows for improved adsorption and removal of disturbing and detrimental substances. Surprisingly, it has now been found that this objective can be realized when cellulosic fibres are treated with a clay having 3R₁ stacking and interlayers which comprise hydroxide and optionally also carbonate.

[0011] Accordingly, the present invention relates to a process for the production of a cellulosic product which comprises:

- (i) providing an aqueous suspension containing cellulosic fibres and, optionally, a filler ;
- (ii) adding to the suspension a clay having 3R₁ stacking and interlayers which comprise hydroxide; and
- (iii) dewatering the obtained suspension.

[0012] It has been found that the negative impact on pulp and paper making processes caused by the presence of disturbing and detrimental substances in aqueous cellulosic pulp suspensions, more specifically problems caused by pitch and stickies, can indeed be further reduced compared to the process known from WO 2004/046464 by treating the cellulosic fibres with a clay according to the invention.

[0013] Further, it has been found that slurries containing clays having 3R₁ stacking and interlayers which comprise hydroxide are more stable and easier to process than slurries which contain clays having 3R₂ stacking, such as those, for instance, described in WO 2004/046464.

[0014] The present invention further relates to a cellulosic product obtainable by the process according to the present invention. The cellulosic product produced is preferably pulp and/or paper.

[0015] The present invention also relates to a process for the production of a cellulosic product which comprises (i) providing an aqueous suspension containing cellulosic fibres; (ii) adding to the suspension a clay having 3R₁ stacking and interlayers which comprise hydroxide, and, optionally, one or more drainage (dewatering) and retention aids; and (iii) dewatering the obtained suspension.

[0016] It has surprisingly also been found that the addition to cellulosic suspensions of a clay having 3R₁ stacking and interlayers which comprise hydroxide in conjunction with additives used for pulp and paper making not only allows for adsorption and removal of disturbing substances, but also improves the performance of the additives used in the process, as compared to the situation when the clay is not added. Examples of such additives for which improved performance is observed include retention and dewatering aids, sizing agents, etc. Preferably, the clay is used together with one or more drainage and retention aids comprising at least one cat-

ionic polymer. Thus, the present invention provides improved drainage (dewatering) and retention in pulp and paper making processes as well as improved sizing in paper making processes, while simultaneously further reducing the content of disturbing and detrimental substances in the cellulosic suspension.

[0017] The clay according to the invention can be derived from naturally occurring clays, chemically and/or physically modified naturally occurring clays, and synthetic clays.

[0018] Naturally occurring clays normally have an essentially crystalline structure. However, synthetically obtained clays may also additionally contain amorphous material having essentially the same chemical composition as the crystalline structures. The amount of amorphous material present in synthetic clay depends mainly on the reaction parameters used. The term "clay", as used herein, refers to clays having an essentially crystalline structure and also to clays containing both crystalline and amorphous structures.

[0019] Clays are characterized by a layered structure wherein atoms within the layers (lamellae) are cross-linked by chemical bonds, while the atoms of adjacent layers interact mainly by physical forces. The layers of the clay may be non-charged or charged depending on the types of atoms present in the layers. If the layers are charged, then the space between these layers, also designated as the interlayer space, will contain ions which have the opposite charge to the charge of the layers. The term "cationic clay", as used herein, refers to clays having positively charged layers and anions present in the interlayer space. The term "anionic clay", as used herein, refers to clays having negatively charged layers and cations present in the interlayer space. Usually, the ions in the interlayer space are exchangeable.

[0020] The layer or lamella of the clay suitably comprises at least two different metal atoms having different valences. Suitably, one metal atom is divalent and the other metal atom is suitably trivalent. However, the layer may also comprise more than two metal atoms. The charge of the layer is governed by the ratio of metal atoms having different valences. For instance, a higher amount of trivalent metals will render a layer having an increased density of the positive charge. Suitably, the clay of the invention comprises layers containing divalent and trivalent metals in a ratio so that the overall charge of the layers is cationic, and the interlayers comprise anions. In other words, the layers essentially consist of divalent and trivalent metals in such a ratio that the overall charge of the layers is cationic.

[0021] Preferred synthetically produced and naturally occurring clays according to the invention can be characterized by the general formula: $[M_m^{2+} M_n^{3+} (OH)_{2m+2n}] X_{n/z}^{z-} bH_2O$, wherein m and n, independently of each other, are integers having a value such that m/n is in the range of from 1 to 10, preferably 1 to 6, more preferably 2 to 4, and most preferably have values around 3; b is an integer having a value in the range of from 0 to 10,

suitably a value from 2 to 6, and often a value about 4; $X_{n/z}^{z-}$ is an anion wherein z is an integer from 1 to 10, preferably from 1 to 6; M^{2+} is a divalent metal atom selected from the group consisting of Be, Mg, Cu, Ni, Co, Zn, Fe, Mn, Cd, and Ca; and M^{3+} is a trivalent metal atom selected from the group consisting of Al, Ga, Ni, Co, Fe, Mn, Cr, V, Ti and In.

[0022] Examples of suitable cationic clays according to the invention include hydrotalcite, pyroaurite, stichtite, takovite, reevesite, desautelsite, meixnerite, iowaite, etc. Examples of terms also used to describe these clays include hydrotalcite-like compounds and layered double hydroxide compounds. Preferably, use is made of hydrotalcite.

[0023] According to the present invention, the clay has a specific stacking, namely a $3R_1$ stacking, and has interlayers which comprise hydroxide; this type of clay is also referred to herein as " $3R_1$ -OH clay" (see S.P. Newman, W. Jones, P. O'Connor, D. Stamires Synthesis of the $3R_2$ polytype of a hydrotalcite-like mineral in J. Mater. Chem. 2002, 72, 153-155). The $3R_1$ -OH clay is preferably cationic, and the clay can be any of those mentioned above. The $3R_1$ -OH clay suitably has a three-layer repeating unit. The $3R_1$ stacking polytype of clay has a different layer arrangement/stacking than the $3R_2$ clay as described in WO 2004/046464, herein also referred to as " $3R_2$ clay". The $3R_1$ and $3R_2$ clays can be distinguished from each other in X-ray diffraction/reflections patterns by the intensities of the 107 and 108 d_{hkl} reflections. The $3R_2$ clay has a stronger d_{hkl} 107 reflection close to 45° 2 theta (according to Drits and Bookin (A.S. Bookin, V.A. Drits, Clays Clay Miner, 41:551 and A.S. Bookin, V.I. Cherkashin, V.A. Drits, Clays Clay Miner, 41:558), employing Cu $K\alpha$ -radiation), whereas the $3R_1$ clay has a stronger d_{hkl} reflection close to 47° 2 theta (the d_{hkl} 108 reflection). The presence of a reflection at 54.5 (1 0 10), is a direct evidence for the presence of $3R_2$ -stacked moieties. The presence of peaks at both 45° 2 theta and 47° 2 theta indicates the presence of a mixture of $3R_1$ and $3R_2$ clays. It is understood that the precise 2 theta values for the 107 and 108 d_{hkl} reflections will depend on the lattice "a" and "c" structural parameters for the clay, here the data are given for a Mg-Al based clay (employing Cu $K\alpha$ -radiation as X-ray source). Of course, there are some other differences in the X-ray diffraction patterns as well, but it is believed that this is the best range of the d_{hkl} reflections to make such a distinction.

[0024] An exact determination of the amount of $3R_2$ remains an analytical challenge. In practice, for the materials according to the invention the criterion is used that no significant X-ray reflection is observed at 2 theta ~54.4.

[0025] According to one preferred embodiment of the invention, the clay having $3R_1$ stacking and interlayers which comprise hydroxide is added to an aqueous suspension containing cellulosic fibres in a process for the production of cellulosic products such as pulp and paper. It has been observed that if the $3R_1$ -OH clay is added to

such a suspension, improved removal of disturbing substances such as pitch and stickies is achieved over the addition of conventional clays having a 3R₂ stacking.

[0026] The clay is suitably mixed with cellulosic fibres by being added to an aqueous suspension containing cellulosic fibres (herein also referred to as "aqueous cellulosic suspension" and "cellulosic suspension") either as a slurry (suspension) or as a powder which can be easily dispersed in water. The suspension or powder of clay may further also contain other components such as, for example, dispersing and/or protecting agents, which can contribute to the overall effect of the clay. Such agents can have a non-ionic, anionic or cationic character. Examples of suitable protective agents or colloids include water-soluble cellulose derivatives, e.g. hydroxyethyl- and hydroxypropyl-, methylhydroxypropyl- and ethyl-hydroxyethyl cellulose, methyl- and carboxymethyl cellulose, gelatine, starch, guar gum, xanthan gum, polyvinyl alcohol, etc. Examples of suitable dispersing agents include non-ionic agents, e.g. ethoxylated fatty acids, fatty acids, alkyl phenols or fatty acid amides, ethoxylated and non-ethoxylated glycerol esters, sorbitan esters of fatty acids, non-ionic surfactants, polyols and/or their derivatives; anionic agents, e.g. as alkyl or alkylaryl sulphates, sulphonates, ethersulphonates, polyacrylic acid; and cationic agents, e.g. esterquats obtained by reacting alkanolamines with mixtures of fatty acids and dicarboxylic acids, optionally alkoxyating the resulting esters and quaternizing the products, quaternized fatty acid amides, betaines, dimethyl dialkyl or dialkylaryl ammonium salts, and cationic gemini dispersing agents.

[0027] The clay can be added at any point in the cellulosic product production process starting from the point where wood chips are disintegrated up to the point in the process where dewatering of the cellulosic suspension takes place. The cellulosic product can be in any form such as, for example, in the form of a web or sheet, e.g. pulp sheets and paper sheets.

[0028] According to a preferred embodiment of the invention, the clay is added to a cellulosic suspension of a pulp making process. The clay can be added prior to or after the pulping process, which can be a kraft, mechanical, thermo-mechanical, chemomechanical, chemo-thermo-mechanical pulping process. The clay can be added just before the pulping process or directly to the pulping process, for instance to the digester. However, it is preferred that the clay is added to the cellulosic suspension subsequent to chemical digestion, for instance downstream of the brown stock washer, or after refining of the (chemo-)mechanical pulp. Usually, the cellulosic pulp is bleached in a multistage bleaching process comprising different bleaching stages and the clay can be added to any bleaching sequence. Examples of suitable bleaching stages include chlorine bleaching stages, e.g. elementary chlorine and chlorine dioxide bleaching stages, non-chlorine bleaching stages, e.g. peroxide stages like ozone, hydrogen peroxide, and peracetic acid, and

combinations of chlorine and non-chlorine bleaching and oxidizing stages, optionally in combination with reducing stages such as treatment with dithionite. The clay can be added directly to the cellulosic suspension during a bleaching stage, preferably to the mixer upstream of the bleaching tower, at any point between the bleaching and washing stages, and also to a washing stage where the clay may be partly or wholly removed, e.g. in the displacement section.

[0029] According to another preferred embodiment of the invention, the clay is added to a cellulosic suspension of a paper making process. The clay can be added to the cellulosic suspension at any point of the paper making process, such as to the thick stock, the thin stock, or to the white water before it is recycled, e.g. upstream of the thin stock feed box. Preferably, the clay is added to the thick stock. The cationic clay can also be added at more than one point of the pulp and/or paper making processes. For instance, in integrated pulp and paper mills, the clay can be added in the process for pulp production, and optionally also in the process for paper production, and one or more drainage and retention aids can be added in the process for paper production. Such processes can include dewatering the cellulosic suspension containing clay, diluting the suspension obtained, adding to the diluted suspension one or more drainage and retention aids and dewatering the suspension containing the drainage and retention aids.

[0030] The term "paper", as used herein, includes not only paper and the production thereof, but also other cellulosic fibre-containing sheet or web-like products, such as for example board and paperboard, and the production thereof. The process can be used in the production of paper from different types of aqueous suspensions of cellulosic (cellulose-containing) fibres, and the suspensions should suitably contain at least 25% by weight and preferably at least 50% by weight of such fibres, based on a dry substance.

[0031] The cellulosic fibres can be based on virgin and/or recycled fibres, and the suspension can be based on fibres from chemical pulp such as sulphate, sulphite, and organosolve pulps, mechanical pulp such as thermo-mechanical pulp, chemo-thermo-mechanical pulp, refiner pulp, and ground wood pulp, from both hardwood and softwood, and can also be based on recycled fibres, optionally from de-inked pulps, and mixtures thereof. If recycled fibres are used, the suspended, recycled fibres are commonly treated in order to separate the non-fibre components such as, for example, printing inks and various paper surface treatment compounds, e.g. latex, from the fibres. In a preferred embodiment, the clay is suitably added to such a de-inking treatment process.

[0032] According to the invention, the clay is suitably added to the cellulosic suspension in an amount of from about 0.01 % by weight to about 5% by weight, preferably from about 0.05% by weight up to about 2% by weight, calculated as dry clay on a dry cellulosic suspension.

[0033] The present invention also relates to a process

for the production of cellulosic products, e.g. pulp and paper, which comprises adding to the suspension a clay having 3R₁ stacking and interlayers which comprise hydroxide, and optionally one or more drainage (dewatering) and retention aids. In a preferred embodiment, the drainage and retention aids comprise at least one cationic polymer. In another preferred embodiment, the drainage and retention aid comprises a cationic polymer and an anionic material. Examples of suitable anionic materials include anionic microparticulate materials, e.g. anionic inorganic and organic particles, and anionic organic polymers, e.g. anionic vinyl addition polymers such as anionic acrylamide-based polymers. It is preferred that the clay and the drainage and retention aids are used in a process for the production of paper.

[0034] The term "drainage and retention aid", as used herein, refers to a component (agent, additive) which when added to an aqueous cellulosic suspension, gives better drainage and/or retention than is obtained when said component is not added.

[0035] The term "cationic polymer", as used herein, refers to an organic polymer having one or more cationic groups, preferably an overall cationic charge. The cationic polymer may also contain anionic groups, and such polymers are commonly also referred to as amphoteric polymers.

[0036] The cationic polymer according to the invention can be derived from natural and synthetic sources. Examples of suitable cationic polymers derived from natural sources include polysaccharides, e.g. starches, guar gums, celluloses, chitins, chitosans, glycans, galactans, glucans, xanthan gums, pectins, mannans, dextrans, preferably starches and guar gums. Examples of suitable starches include potato, corn, wheat, tapioca, rice, waxy maize, barley, etc. Examples of suitable synthetic cationic polymers include chain-growth polymers, e.g. vinyl addition polymers like acrylate-, acrylamide-, and vinylamide-based polymers, and step-growth polymers, e.g. polyurethanes. Suitably, the cationic polymer is selected from polysaccharides, e.g. starches, and vinyl addition polymers, e.g. acrylamide-based polymers, and mixtures thereof.

[0037] The cationic polymer, more specifically cationic polysaccharides and vinyl addition polymers, may also comprise aromatic groups which can be present in the polymer backbone or, preferably, the aromatic groups can be a pendent group attached to or extending from the polymer backbone or be present in a pendent group that is attached to or extending from the polymer backbone (main chain). Examples of suitable aromatic groups include aryl, aralkyl and alkaryl groups, e.g. phenyl, phenylene, naphthyl, naphthylene, xylylene, benzyl and phenylethyl; nitrogen-containing aromatic (aryl) groups, e.g. pyridinium and quinolinium, as well as derivatives of these groups, preferably benzyl.

[0038] Examples of suitable cationic organic polymers having an aromatic group that can be used according to the invention include those described in International Pat-

ent Application Publication Nos. WO 99/55964, WO 99/55965, WO 99/67310, and WO 02/12626, which are hereby incorporated herein by reference. Examples of cationically charged groups that can be present in the cationic polymer as well as in monomers used for preparing the cationic polymer include quaternary ammonium groups, tertiary amino groups, and acid addition salts thereof.

[0039] The term "chain-growth polymer", as used herein, refers to a polymer obtained by chain-growth polymerization, also referred to as chain reaction polymer and chain reaction polymerization, respectively. Examples of suitable cationic chain-growth polymers include vinyl addition polymers prepared by the polymerization of one or more monomers having a vinyl group or ethylenically unsaturated bond, for example a polymer obtained by polymerizing a cationic monomer or a monomer mixture comprising a cationic monomer.

[0040] Examples of suitable cationic monomers include diallyldialkyl ammonium halides, e.g. diallyldimethyl ammonium chloride, acid addition salts and quaternary salts of dialkylaminoalkyl (meth)acrylate, e.g. quaternary monomers obtained by treating dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, and dimethylaminohydroxypropyl (meth)acrylate, and dialkylaminoalkyl (meth)acrylamides, e.g. dimethylaminoethyl (meth)acrylamide, diethylaminoethyl (meth)acrylamide, dimethylaminopropyl (meth)acrylamide, and diethylaminopropyl (meth)acrylamide, with acids, e.g. organic and inorganic acids, alkyl halides, e.g. methyl chloride, and aryl halides, e.g. benzyl chloride. Preferred cationic monomers include dimethylaminoethylacrylate benzyl chloride quaternary salt and dimethylaminoethylmethacrylate benzyl chloride quaternary salt. The cationic monomer can be copolymerized with one or more non-ionic and/or anionic monomers. Suitable copolymerizable non-ionic monomers include (meth)acrylamide; acrylamide-based monomers like N-alkyl (meth)acrylamides, N, N-dialkyl (meth)acrylamides, and dialkylaminoalkyl (meth)acrylamides, acrylate-based monomers like dialkylaminoalkyl (meth)-acrylates, and vinylamides. Suitable copolymerizable anionic monomers include acrylic acid, methacrylic acid, and various sulphonated vinylic monomers such as styrene sulphonate. Preferred copolymerizable monomers include acrylamide and methacrylamide, i.e. (meth)acrylamide, and the cationic or amphoteric organic polymer preferably is an acrylamide-based polymer.

[0041] The weight average molecular weight of the cationic polymer can vary within wide limits dependent on, *inter alia*, the type of polymer used, and usually it is at least about 5,000 and often at least 10,000. More often, it is above 150,000, normally above 500,000, suitably above about 700,000, preferably above about 1,000,000 and most preferably above about 2,000,000. The upper limit is not critical; it can be about 200,000,000; usually it is 150,000,000 and suitably 100,000,000.

[0042] Anionic inorganic microparticulate materials

that can be used according to the invention include anionic silica-based particles and anionic clays of the smectite type. It is preferred that the anionic inorganic particles are in the colloidal range of particle size.

[0043] Preferably, anionic silica-based particles, i.e. particles based on SiO_2 or silicic acid, are used and such particles are usually supplied in the form of aqueous colloidal dispersions, so-called sols. Examples of suitable silica-based particles include colloidal silica and different types of polysilicic acid, either homo- or copolymerized. The silica-based sols can be modified and contain other elements, e.g. aluminium, boron, nitrogen, zirconium, gallium, titanium and the like, which can be present in the aqueous phase and/or in the silica-based particles. Suitable silica-based particles of this type include colloidal aluminium-modified silica and aluminium silicates. Mixtures of such suitable silica-based particles can also be used. Drainage and retention aids comprising suitable anionic silica-based particles include those disclosed in U.S. Patent Nos. 4,388,150; 4,927,498; 4,954,220; 4,961,825; 4,980,025; 5,127,994; 5,176,891; 5,368,833; 5,447,604; 5,470,435; 5,543,014; 5,571,494; 5,573,674; 5,584,966; 5,603,805; 5,688,482; and 5,707,493; which are hereby incorporated herein by reference.

[0044] Anionic silica-based particles suitably have an average particle size below about 100 nm, preferably below about 20 nm, and more preferably in the range of from about 1 to about 10 nm. As is conventional in silica chemistry, the particle size refers to the average size of the primary particles, which may be aggregated or non-aggregated. The specific surface area of the silica-based particles is suitably above $50 \text{ m}^2/\text{g}$ and preferably above $100 \text{ m}^2/\text{g}$. Generally, the specific surface area can be up to about $1,700 \text{ m}^2/\text{g}$ and preferably up to $1,000 \text{ m}^2/\text{g}$. The specific surface area is measured by means of titration with NaOH in a well-known manner, e.g. as described by G. W. Sears in *Analytical Chemistry* 28 (1956): 12, 1981-1983 and in U.S. Patent No. 5,176,891. The given area thus represents the average specific surface area of the particles.

[0045] According to a preferred embodiment of the invention, the anionic silica-based particles have specific surface area within the range of from 50 to $1,000 \text{ m}^2/\text{g}$, preferably from 100 to $950 \text{ m}^2/\text{g}$. Sols of silica-based particles of these types also encompass modifications, for example with any of the elements mentioned above. Preferably, the silica-based particles are present in a sol having a S-value in the range of from 8 to 50%, preferably from 10 to 40%, containing silica-based particles with a specific surface area in the range of from 300 to $1,000 \text{ m}^2/\text{g}$, suitably from 500 to $950 \text{ m}^2/\text{g}$, and preferably from 750 to $950 \text{ m}^2/\text{g}$, which sols can be modified as mentioned above. The S-value can be measured and calculated as described by Iler & Dalton in *J. Phys. Chem.* 60 (1956), 955-957. The S-value indicates the degree of aggregation or microgel formation and a lower S-value is indicative of a higher degree of aggregation.

[0046] According to another preferred embodiment of

the invention, the silica-based particles are selected from polysilicic acid, either homo- or copolymerized, having a high specific surface area, suitably above about $1,000 \text{ m}^2/\text{g}$. The specific surface area can be within the range of from $1,000$ to $1,700 \text{ m}^2/\text{g}$ and preferably from $1,050$ to $1,600 \text{ m}^2/\text{g}$. The sols of modified or copolymerized polysilicic acid can contain other elements as mentioned above. In the art, polysilicic acid is also referred to as polymeric silicic acid, polysilicic acid microgel, polysilicate, and polysilicate microgel, which all are encompassed by the term polysilicic acid used herein. Aluminium-containing compounds of this type are commonly also referred to as **polyaluminosilicate** and polyaluminosilicate microgel, which are both, encompassed by the terms colloidal aluminium-modified silica and aluminium silicate used herein.

[0047] According to yet another preferred embodiment of the invention, the drainage and retention aids comprise anionic clay of the smectite type. Examples of suitable smectite clays include natural clays such as montmorillonite/bentonite, hectorite, beidellite, nontronite and saponite, as well as synthetic smectite-like clays such as laponite, etc., preferably bentonite, and especially bentonite which after swelling preferably has a surface area of from 200 to $800 \text{ m}^2/\text{g}$. Suitable anionic clays include those disclosed in U.S. Patent Nos. 4,753,710; 5,071,512; and 5,607,552, which are hereby incorporated herein by reference. Also mixtures of anionic silica-based particles and anionic clays of the smectite type can be employed.

[0048] Preferably, the drainage and retention aids comprise cationic polymer and anionic organic polymer. Anionic organic polymers according to the invention contain one or more negatively charged (anionic) groups. Examples of groups that can be present in the polymer as well as in the monomers used for preparing the polymer include groups carrying an anionic charge and acid groups carrying an anionic charge when dissolved or dispersed in water, the groups being collectively referred to herein as anionic groups, such as phosphate, phosphonate, sulphate, sulphonic acid, sulphonate, carboxylic acid, carboxylate, alkoxide, and phenolic groups, i.e. hydroxy-substituted phenyls and naphthyl. Groups carrying an anionic charge are usually salts of an alkali metal, alkaline earth or ammonia.

[0049] Anionic organic particles that can be used according to the invention include cross-linked anionic vinyl addition polymers, suitably copolymers comprising an anionic monomer like acrylic acid, methacrylic acid, and sulfonate or phosphonated vinyl addition monomers, usually copolymerized with non-ionic monomers like (meth)acrylamide, alkyl (meth)acrylates, etc. Useful anionic organic particles also include anionic condensation polymers, e.g. melamine-sulfonic acid sols.

[0050] Further anionic polymers that can form part of the drainage and retention system include anionic step-growth polymers, chain-growth polymers, polysaccharides, naturally occurring aromatic polymers and modifi-

cations thereof. The term "step-growth polymer", as used herein, refers to a polymer obtained by step-growth polymerization, also referred to as step-reaction polymer and step-reaction polymerization, respectively. The anionic organic polymers can be linear, branched or cross-linked. Preferably, the anionic polymer is water-soluble or water-dispersible. In a preferred embodiment, the anionic organic polymer also contains one or more aromatic groups. The aromatic group of the anionic polymer can be present in the polymer backbone or in a substituent group that is attached to the polymer backbone (main chain). Examples of suitable aromatic groups include aryl, aralkyl, and alkaryl groups and derivatives thereof, e.g. phenyl, tolyl, naphthyl, phenylene, xylylene, benzyl, phenylethyl, and derivatives of these groups.

Examples of suitable anionic chain-growth polymers include vinyl addition polymers comprising an anionic monomer having carboxylate groups like acrylic acid, methacrylic acid, ethylacrylic acid, crotonic acid, itaconic acid, maleic acid, and salts of any of the foregoing, anhydrides of the diacids, and sulfonate vinyl addition monomers, such as sulfonate styrene, usually copolymerized with non-ionic monomers like acrylamide, alkyl acrylates, etc., for example those disclosed in U.S. Patent Nos. 5,098,520 and 5,185,062, the teachings of which are hereby incorporated herein by reference.

[0051] Examples of suitable anionic aromatic step-growth polymers include condensation polymers, i.e. polymers obtained by step-growth condensation polymerization, e.g. anionic polyurethanes and condensates of an aldehyde such as formaldehyde with one or more (aromatic) compounds containing one or more anionic groups, and optionally other comonomers useful in condensation polymerization such as urea and melamine.

[0052] Examples of preferred anionic step-growth polymers according to the invention include anionic benzene-based and naphthalene-based condensation polymers, preferably naphthalene-sulphonic acid-based and naphthalene-sulphonate-based condensation polymers.

[0053] Examples of suitable anionic polysaccharides include starches, guar gums, celluloses, chitins, chitosans, glycans, galactans, glucans, xanthan gums, pectins, mannans, dextrans, preferably starches, guar gums, and cellulose derivatives, suitable starches including potato, corn, wheat, tapioca, rice, waxy maize, and barley, preferably potato.

[0054] Examples of suitable anionic organic polymers include those described in U.S. Patent Nos. 4,070,236 and 5,755,930; and International Patent Application Publication Nos. WO 95/21295, WO 95/21296, WO 99/67310, WO 00/49227, and WO 02/12626, which are hereby incorporated herein by reference.

[0055] The weight average molecular weight of the anionic polymer having aromatic groups can vary within wide limits dependent on, inter alia, the type of polymer used, and usually it is at least about 500, suitably above about 2,000, and preferably above about 5,000. The upper limit is not critical; it can be about 200,000,000, usu-

ally about 150,000,000, suitably about 100,000,000, and preferably about 10,000,000.

[0056] Further to the above-mentioned cationic polymers, anionic inorganic and organic particles, and anionic organic polymers, the drainage and retention aid can also comprise low molecular weight, highly cationically charged, organic polymers and/or inorganic aluminium compounds.

[0057] According to one preferred embodiment of the invention, the drainage and retention aid comprises a cationic polymer and an anionic inorganic microparticulate material, suitably anionic silica-based particles or anionic clay of the smectite type. According to another preferred embodiment of the invention, the drainage and retention aid comprises a cationic polymer and an anionic vinyl addition polymer, suitably an anionic acrylamide-based polymer. According to yet another preferred embodiment of the invention, the drainage and retention aid comprises a cationic polymer comprising aromatic groups. According to a still further preferred embodiment of the invention, the drainage and retention aid comprises a cationic polymer comprising aromatic groups and an anionic polymer comprising aromatic groups. In accordance with another preferred embodiment, the cationic polymer is cationic starch or a cationic acrylamide-based polymer.

[0058] The components of drainage and retention aids can be added to the cellulosic suspension in conventional manner and in any order. When using an anionic microparticulate material, it is preferred to add the cationic polymer to the suspension before adding the microparticulate material, though the reverse order of addition may be used as well.

[0059] It is further preferred to add the cationic polymer before a shear stage, which can be selected from pumping, mixing, cleaning, etc., and to add the anionic compound after that shear stage. When using an LMW cationic organic polymer and/or an aluminium compound, such components are preferably introduced into the suspension prior to introducing the cationic polymer and the anionic component, if used. Alternatively, the LMW cationic organic polymer and the cationic polymer can be introduced into the suspension essentially simultaneously, either separately or in admixture, e.g. as disclosed in U.S. Patent No. 5,858,174, which is hereby incorporated herein by reference.

[0060] If the clay according to the invention is used together with a drainage and retention aid, the clay can be added to the suspension prior to or after the addition of the drainage and retention aid. However, it is preferred that the cationic clay is added prior to the addition of drainage and retention aid and other performance chemicals. Suitably, the clay is added to the thick stock or the thin stock, and the drainage and retention aid is added to the thin stock. The clay can also be added to the recycled white water. If two or more drainage and retention aids are used, i.e. a cationic polymer together with an anionic material, e.g. silica-based particles or anionic

organic polymer, the clay may be added to the cellulosic suspension (stock) prior to, after or in between the addition of the drainage and retention aids, or together with any of the drainage and retention aids. The clay may also be added at several locations in the process, e.g. to the thick stock and again to the thin stock prior to the addition of the drainage and retention aid.

[0061] The drainage and retention aid(s) according to the invention can be added to the stock to be dewatered in amounts which can vary within wide limits depending on, inter alia, the types and number of components, the type of cellulosic suspension, the salt content, the types of salts, the filler content, the type of filler, the point of addition, the degree of white water closure, etc. Generally, the retention and drainage aid(s) are added in amounts that give better drainage and/or retention than is obtained when the components are not added. The cationic polymer is usually added in an amount of at least about 0.001% by weight, often at least about 0.005% by weight, based on the dry cellulosic suspension, and the upper limit is usually about 3% and suitably about 1.5% by weight. Commonly applied addition amounts of cationic polymer are from about 0.01% up to about 0.5% by weight. Anionic materials, e.g. anionic silica-based particles, anionic clays of the smectite type, and anionic organic polymers, are usually added in an amount of at least about 0.001 % by weight, often at least about 0.005% by weight, based on the dry cellulosic suspension, and the upper limit is usually about 1.0% and suitably about 0.6% by weight.

[0062] When using LMW cationic organic polymers in the process, they can be added in an amount of at least about 0.001% by weight, based on the dry cellulosic suspension.

Suitably, the amount is in the range of from about 0.07 up to about 0.5%, preferably in the range from about 0.1 up to about 0.35%. When using an aluminium compound in the process, the total amount introduced into the stock to be dewatered depends on the type of aluminium compound used and on other effects desired from it. It is for instance well known in the art to utilize aluminium compounds as precipitants for rosin-based sizing agents. The total amount added is usually at least about 0.05% by weight, calculated as Al₂O₃ and based on the dry cellulosic suspension. Suitably, the amount is in the range of from about 0.5 up to about 3.0%, preferably in the range from about 0.1 up to about 2.0%.

[0063] Further additives which are conventional in papermaking can of course be used in combination with the additive(s) according to the invention, such as, for example, dry strength agents, wet strength agents, optical brightening agents, dyes, sizing agents like rosin-based sizing agents and cellulose-reactive sizing agents, e.g. ketene dimers and succinic anhydrides, etc. The cellulosic suspension, or stock, can also contain mineral fillers of conventional types such as, for example, kaolin, china clay, titanium dioxide, gypsum, talc, and natural and synthetic calcium carbonates such as chalk, ground marble,

and precipitated calcium carbonate.

[0064] Furthermore, the process can also be useful in the manufacture of paper from cellulosic suspensions having high conductivity. In such cases, the conductivity of the suspension that is dewatered on the wire is usually at least 1.0 mS/cm, suitably at least 2.0 mS/cm, and preferably at least 3.5 mS/cm. Conductivity can be measured by standard equipment such as, for example, a WTW LF 539 instrument supplied by Christian Berner.

[0065] The values referred to above are suitably determined by measuring the conductivity of the cellulosic suspension that is fed into or present in the head box of the paper machine or, alternatively, by measuring the conductivity of white water obtained by dewatering the suspension.

[0066] The present invention further encompasses paper making processes where white water is extensively recycled, or recirculated, i.e. with a high degree of white water closure, for example where from 0 to 30 tons of fresh water are used per ton of dry paper produced, usually less than 20, suitably less than 15, preferably less than 10, and notably less than 5 tons of fresh water per ton of paper.

[0067] The present invention also relates to the use of a clay having 3R₁ stacking and interlayers which comprise hydroxide for removing disturbing and detrimental substances such as pitch and stickies from an aqueous cellulosic pulp suspension

[0068] The invention is further illustrated in the following Examples which, however, are not intended to limit the scope of the invention.

Example 1

[0069] In accordance with the present invention, four High Throughput Experiments (HTE) were conducted using a 50 wt% dispersion of Carbotac 26171 (a polyacrylate available from Lubrizol). In each of the tests, a 0.05 w% carbotac solution (1 g 50 wt% Carbotac/1 l demiwater) was stirred and heated to 50°C. In each test a fixed amount (1,000 or 1,250 ppm) of a solution containing hydrotalcite (HTC) 3R₁-OH was added and the mixture so obtained was stirred for 20 minutes. The HTC was prepared according to the procedure described in Example 1 of US 6,593,265. The HTC had a Mg/Al ratio of 2.2. The total run time was 4 hours. Subsequently, the reaction product so obtained was filtered and the filtrate was measured with UV-Vis. Moreover, turbidimetry measurements (a method for determining the concentration of a substance in a solution by measuring the loss in intensity of a light beam through a solution that contains suspended particulate matter) were performed. The HTE experiments were performed on a Chemspeed ASW2000 automated synthesizer workstation. The UV absorption of the filtrate was measured off-line with a UV-Vis spectrometer. The UV-Vis measurements of the HTE experiments and the turbidimetry measurements were carried out on a Varian Cary1 UV-Vis spectrometer. The samples

were measured in a 5 mm cuvet against a demiwater reference sample. The absorption value used for determination of the efficiency of the test was determined on either 280 nm or 320 nm. The UV reduction was calculated as $(A(\text{carbotac})-A(\text{filtrate})/A(\text{carbotac})) \times 100\%$. It will be understood that the Carbotac reduction is a measure to indicate the clay's effectiveness in the reduction of disturbing and detrimental substances such as pitch and stickies. The results obtained in Carbotac reduction are shown in Figure 1 (—■—).

Comparative Example 2

[0070] This Example was carried out in a similar manner as Example 1, except that no HCT 3R₁-OH was used but instead use was made of a HTC 3R₂-OH (a HTC having 3R₂ stacking and interlayers which comprise hydroxide, see e.g. WO 2004/046464). The HTC 3R₂-OH was prepared according to the procedure described in Example 2 of US 6,468,488. The results obtained in terms of Carbotac reduction are shown in Figure 1 (—▲—).

Comparative Example 3

[0071] This Example was carried out in a similar manner as Example 1, except that no HCT 3R₁-OH was used but instead use was made of a HTC 3R₁-CO₃ (a commercial sample of Alcamizer 1, ex Kisuma Chemicals BV, a HTC having 3R₁ stacking and interlayers which comprise carbonate, see e.g. WO 2004/046464). The results obtained in terms of Carbotac reduction are shown in Figure 1 (—●—).

[0072] From Figure 1 it will be clear that with the processes in accordance with the present invention (Example 1) a considerable improvement in terms of Carbotac reduction is obtained compared to when use is made of conventional processes in which HTCs are used which fall outside the scope of the present invention (Comparative Examples 2 and 3).

Claims

1. A process for the production of a cellulosic product which comprises:
 - (i) providing an aqueous suspension containing cellulosic fibres and, optionally, a filler;
 - (ii) adding to the suspension a clay having 3R₁ stacking and interlayers which comprise hydroxide; and
 - (iii) dewatering the obtained suspension.
2. A process according to claim 1, wherein the cellulosic product is paper.
3. A process according to claim 1 or 2, wherein the cellulosic product is pulp.
4. A process according to any one of claims 1-3, wherein the clay comprises layers and interlayers, said interlayers comprising anions, and said layers comprising divalent and trivalent metal atoms in such a ratio that the overall charge of said layers is cationic.
5. A process according to any one of claims 1-4, wherein the clay contains a divalent metal atom (M²⁺) which is magnesium and a trivalent metal ion (M³⁺) which is aluminium.
6. A process according to any one of claims 1-5, wherein the clay is **characterized by** the general formula: $[M_m^{2+} M_n^{3+} (\text{OH})_{2m+2n}] X_{n/z}^{z-} b\text{H}_2\text{O}$, wherein m and n, independently of each other, are integers having a value such that m/n is in the range of from 1 up to 10; b is an integer having a value in the range of from 0 to 10; 10, X_{n/z}^{z-} is an anion wherein z is an integer from 1 to 10; M²⁺ is a divalent metal atom selected from the group consisting of Be, Mg, Cu, Ni, Co, Zn, Fe, Mn, Cd, Ca, and mixtures thereof; and M³⁺ is a trivalent metal atom selected from the group consisting of Al, Ga, Ni, Co, Fe, Mn, Cr, V, Ti, In, and mixtures thereof.
7. A process according to any one of claims 1-6, wherein the clay is hydrotalcite, pyroaurite, stichtite, takovite, reevesite, desautelsite, meixnerite, iowaite, or mixtures thereof.
8. A process according to any one of claims 1-7, wherein the clay is hydrotalcite.
9. A process according to any one of claims 1-8, which further comprises adding to the suspension one or more drainage and retention aids.
10. A process according to claim 9, wherein the drainage and retention aids comprise at least one cationic polymer.
11. A process according to claim 9 or 10, wherein the drainage and retention aids comprise cationic polymer and anionic material.
12. A process according to any one of claims 10-11, wherein the drainage and retention aids comprise cationic polymer and anionic silica-based particles.
13. A process according to any one of claims 9-12, wherein the drainage and retention aids comprise cationic polymer and anionic organic polymer.
14. A cellulosic product obtainable by the process according to any one of claims 1-13.
15. Use of a clay having 3R₁ stacking and interlayers which comprise hydroxide for removing disturbing

and detrimental substances such as pitch and stickies from an aqueous cellulosic pulp suspension.

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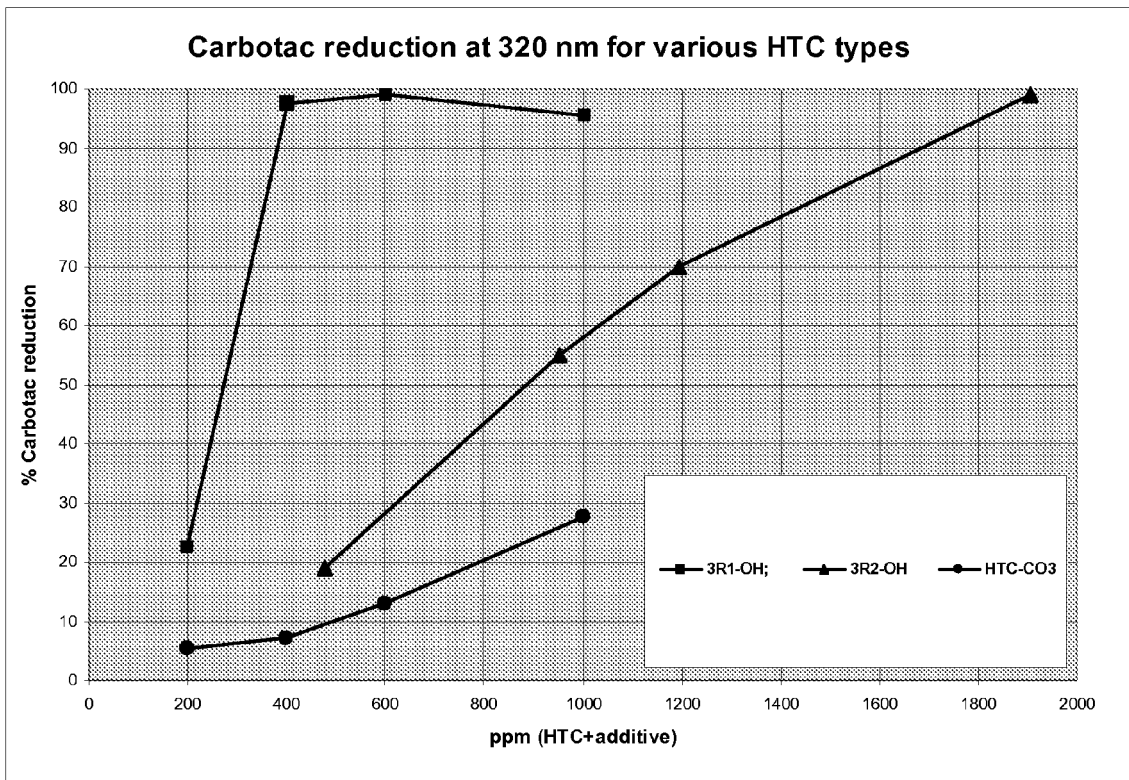
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Figure 1





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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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