



US 20120073774A1

(19) **United States**

(12) **Patent Application Publication**
Jehn-Rendu et al.

(10) **Pub. No.: US 2012/0073774 A1**

(43) **Pub. Date: Mar. 29, 2012**

(54) **METHOD FOR REDUCING DEPOSITS IN THE DRYING SECTION IN THE MANUFACTURE OF PAPER, PAPERBOARD, AND CARDBOARD**

(30) **Foreign Application Priority Data**

Jun. 16, 2009 (EP) 09162870.1

Publication Classification

(75) Inventors: **Christian Jehn-Rendu**, Eppelheim (DE); **Geert Andre Leon Vanhyfte**, Gent (BE)

(51) **Int. Cl.**
D21H 23/00 (2006.01)

(73) Assignee: **BASF SE**, Ludwigshafen (DE)

(52) **U.S. Cl.** **162/164.6**

(21) Appl. No.: **13/375,781**

(57) **ABSTRACT**

(22) PCT Filed: **Jun. 11, 2010**

(86) PCT No.: **PCT/EP2010/058193**

§ 371 (c)(1),
(2), (4) Date: **Dec. 2, 2011**

A process for reducing deposits in the dry section in the production of paper, board and cardboard by adding (a) at least one water-soluble cationic polymer and (b) at least one aqueous dispersion of a polymer size to a paper stock, draining the paper stock with sheet formation and drying the paper products.

**METHOD FOR REDUCING DEPOSITS IN
THE DRYING SECTION IN THE
MANUFACTURE OF PAPER, PAPERBOARD,
AND CARDBOARD**

[0001] The invention relates to a process for reducing deposits in the dry section in the production of paper, board and cardboard by adding (a) at least one water-soluble cationic polymer and (b) at least one aqueous dispersion of a polymer size to a paper stock, draining the paper stock with sheet formation and drying the paper products.

[0002] In papermaking, deposits are caused as a rule by impurities which occur in particular during recycling of wastepaper. Such deposits are also referred to as stickies. These stickies originate, for example, from contact adhesives, the coating of paper or cardboard or from resins which were not removed in the fiber production. These stickies cause a considerable reduction in the runnability of the paper machine, due firstly to a substantial increase in the cationic demand in the paper process and secondly to deposits in the dry section. Increase in the cationic demand reduces the efficiency of the paper process chemicals, such as, for example, the retention aids, while the deposits in the dry section lead to tears in the papermaking process.

[0003] The literature has already disclosed some papermaking processes which are concerned with the problem of deposits of impurities.

[0004] U.S. Pat. No. 3,081,219 discloses a process for the production of paper based on sulfite groundwood, in which control of the deposits of impurities is to be achieved by the addition of a sequestering agent, such as polyphosphates, or of a dispersant, such as formaldehyde sulfonic acid or naphthalenesulfonic acid-formaldehyde condensate.

[0005] U.S. Pat. No. 4,871,865 describes a process for the production of paper in which a water-soluble polymer having methyl ether groups, such as, for example, methylcellulose, is added in order to achieve control of the deposits of stickies.

[0006] The control of impurity deposits in papermaking is likewise disclosed in U.S. Pat. No. 4,871,424. There, the metering of water-soluble polymers carrying hydroxyl groups, such as, for example, polyvinyl alcohol, is recommended.

[0007] DE 42 40 110 A1 discloses a process for the production of paper in which control of the impurity deposits is brought about by the addition of water-soluble polyethyleneimines.

[0008] U.S. Pat. No. 6,387,215 teaches the use of water-soluble copolymers of acrylamide and vinyl acetates for controlling the impurity deposits.

[0009] Since in particular tears in the dry section which are caused by deposits lead again and again to problems in the ongoing papermaking process, there is a continuous demand for the reduction of deposits, in particular in the dry section in the production of paper, board and cardboard.

[0010] It was therefore the object of the present invention to provide a process for reducing deposits in the dry section in the production of paper, board and cardboard, in which the ongoing papermaking process is impaired to a lesser extent by tears. This process should be suitable in particular for newspapers and cardboard produced from wastepaper (comprising deinked wastepaper).

[0011] The object is achieved by a process for reducing deposits in the dry section in the production of paper, board

and cardboard by adding (a) at least one water-soluble cationic polymer and (b) at least one aqueous dispersion of a polymer size to a paper stock, draining the paper stock with sheet formation and drying the paper products.

[0012] Said components (a) and (b) can be added to the paper stock in any desired sequence or as a mixture.

[0013] The cationic polymers (a) are water-soluble. The solubility in water under standard conditions (20° C., 1013 mbar) and at pH 7 is, for example, at least 5% by weight, preferably at least 10% by weight.

[0014] The charge density of the cationic polymers (without counterion) is, for example, at least 0.5 meq/g and is usually in the range from 1 to 22 meq/g.

[0015] Water-soluble cationic polymers (a) in the context of the invention are those polymers which may comprise cationic, neutral or anionic structural units, but in which the cationic structural units have an excess of at least 5 mol %, preferably of at least 10 mol % and particularly preferably of at least 20 mol % compared with the anionic structural units.

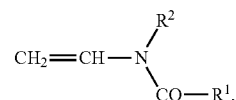
[0016] The molar masses M_w of the cationic polymers are, for example, at least 1000 dalton. They are, for example, generally in the range from 5000 to 5 million dalton.

[0017] Suitable water-soluble cationic polymers (a) are all compounds carrying amino or ammonium groups. The amino groups may be primary, secondary, tertiary or quaternary groups. Substantially polymers, polyaddition compounds or polycondensates are suitable for the polymers, it being possible for the polymers to have a linear or branched structure including hyperbranched or dendritic structures. Furthermore, graft polymers can also be used.

[0018] The water-soluble cationic polymer (a) is usually selected from the group consisting of the polymers comprising vinylamine units, cationic homo- and copolymers of (meth)acrylamide, polyallylamines, polyaminoalkyl vinyl ethers, polyamidoamine compounds and polyamine compounds reacted with epihalohydrin, amphoteric polymers having an overall cationic charge, polymers comprising ethyleneimine units and homopolymers having cationic or protonatable groups.

[0019] Such water-soluble cationic polymers (a) are, for example, polymers comprising vinylamine units, cf. DE 35 06 832 A1 and DE 10 2004 056 551 A1. In the process according to the invention, reaction products which are obtainable

[0020] by polymerization of at least one monomer of the formula



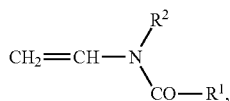
[0021] in which R^1 , R^2 are H or C_1 - to C_6 -alkyl, and subsequent partial or complete elimination of the groups $-\text{CO}-\text{R}^1$ from the units of the monomers (I) incorporated in the form of polymerized units into the polymer with formation of amino groups,

and/or

[0022] by Hofmann degradation of polymers which have acrylamide and/or methacrylamide units are used as polymers comprising vinylamine units.

[0023] In an embodiment of the invention, for example, the reaction products which are obtainable by polymerization of

[0024] (1.) at least one monomer of the formula



[0025] in which R^1 , R^2 are H or C_1 - to C_6 -alkyl,

[0026] (2.) optionally, at least one other monoethylenically unsaturated monomer and

[0027] (3.) optionally, at least one crosslinking monomer having at least two double bonds in the molecule and subsequent partial or complete elimination of the groups $-\text{CO}-\text{R}^1$ from the units of the monomers (I) incorporated in the form of polymerized units into the polymer, with formation of amino groups, are used as polymers comprising vinylamine units.

[0028] Preferably, the reaction products which are obtainable by polymerization of N-vinylformamide and subsequent elimination of formyl groups from the vinylformamide units incorporated in the form of polymerized units into the polymer, with formation of amino groups, are used as polymers comprising vinylamine units or the reaction products which are obtainable by copolymerization of

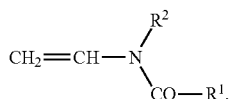
(1.) N-vinylformamide and

[0029] (2.) acrylonitrile

and subsequent elimination of formyl groups from the vinylformamide units incorporated in the form of polymerized units into the copolymer, with formation of amino groups, are used.

[0030] In another embodiment of the invention, the polymers comprising vinylamine units may also be amphoteric if they have a total cationic charge. The content of cationic groups in the polymer should be at least 5 mol %, preferably at least 10 mol %, above the content of anionic groups. Such polymers are obtainable, for example, by polymerization of

[0031] (1.) at least one monomer of the formula



[0032] in which R^1 , R^2 are H or C_1 - to C_6 -alkyl,

[0033] (2.1) at least in each case one monomer carrying an acid function and selected from monoethylenically unsaturated sulfonic acids, monoethylenically unsaturated phosphonic acids and monoethylenically unsaturated carboxylic acids having 3 to 8 carbon atoms in the molecule and/or the alkali metal, alkaline earth metal or ammonium salts thereof.

[0034] (2.2) optionally, at least one other neutral and/or a cationic monomer and

[0035] (3.) optionally, at least one crosslinking monomer having at least two double bonds in the molecule and subsequent partial or complete elimination of the groups $-\text{CO}-\text{R}^1$ from the units of the monomers (I) incorporated in

the form of polymerized units into the polymer, with formation of amino groups, the content of amino groups in the copolymer being at least 5 mol % above the content of acid groups of the monomers (2.1) incorporated in the form of polymerized units.

[0036] Also of interest are amphoteric polymers which comprise vinylamine units, carry an overall cationic charge and are obtainable, for example, by copolymerization of

[0037] (1.) N-vinylformamide,

[0038] (2.1) acrylic acid, methacrylic acid and/or the alkali metal, alkaline earth metal or ammonium salts thereof and

[0039] (2.2) optionally, acrylonitrile and/or methacrylonitrile

and subsequent partial or complete elimination of formyl groups from the N-vinylformamide incorporated in the form of polymerized units into the polymer, with formation of amino groups, the content of amino groups in the copolymer being at least 5 mol % above the content of acid groups of the monomers (2.1) which are incorporated in the form of polymerized units.

[0040] Examples of monomers of the formula (I) are N-vinylformamide, N-vinyl-N-methylformamide, N-vinylacetamide, N-vinyl-N-methylacetamide, N-vinyl-N-ethylacetamide, N-vinylpropionamide and N-vinyl-N-methylpropionamide and N-vinylbutyramide. The monomers of group (a) can be used alone or as a mixture in the copolymerization with the monomers of the other groups. A preferably used monomer of this group is N-vinylformamide.

[0041] These polymers may optionally be modified by copolymerizing the N-vinylcarboxamides (1.) together with (2.) at least one other monoethylenically unsaturated monomer and then hydrolyzing the copolymers with formation of amino groups. If anionic monomers are used in the copolymerization, the hydrolysis of the vinylcarboxamide units incorporated in the form of polymerized units is continued until the molar excess of amine units relative to the anionic units in the polymer is at least 5 mol %.

[0042] Examples of monomers of the group (2.) are esters of α,β -ethylenically unsaturated mono- and dicarboxylic acids with C_1 - C_{30} -alkanols, C_2 - C_{30} -alkanediols and C_2 - C_{30} -aminoalcohols, amides of α,β -ethylenically unsaturated monocarboxylic acids and the N-alkyl and N,N-dialkyl derivatives thereof, nitriles of α,β -ethylenically unsaturated mono- and dicarboxylic acids, esters of vinyl alcohol and allyl alcohol with C_2 - C_{30} -monocarboxylic acids, N-vinylacetams, nitrogen-containing heterocycles having α,β -ethylenically unsaturated double bonds, vinylaromatics, vinyl halides, vinylidene halides, C_2 - C_8 -monoolefins and mixtures thereof.

[0043] Suitable representatives are, for example, methyl (meth)acrylate (in which (meth)acrylate in the context of the present invention denotes both acrylate and methacrylate), methyl ethacrylate, ethyl(meth)acrylate, ethyl ethacrylate, n-butyl (meth)acrylate, isobutyl(meth)acrylate, tert-butyl (meth)acrylate, tert-butyl ethacrylate, n-octyl(meth)acrylate, 1,1,3,3-tetramethylbutyl(meth)acrylate, ethylhexyl (meth)acrylate and mixtures thereof.

[0044] Suitable additional monomers of group (2.) are furthermore the esters of α,β -ethylenically unsaturated mono- and dicarboxylic acids with aminoalcohols, preferably C_2 - C_{12} -aminoalcohols. These may be C_1 - C_8 -monoalkylated or -dialkylated on the amine nitrogen. Suitable acid components of these esters are, for example, acrylic acid, methacrylic acid, fumaric acid, maleic acid, itaconic acid, crotonic

acid, maleic anhydride, monobutyl maleate and mixtures thereof. Acrylic acid, methacrylic acid and mixtures thereof are preferably used. These include, for example, N-methylaminomethyl(meth)acrylate, N-methylaminoethyl(meth)acrylate, N,N-dimethylaminomethyl(meth)acrylate, N,N-dimethylaminoethyl(meth)acrylate, N,N-diethylaminomethyl(meth)acrylate, N,N-dimethylaminopropyl(meth)acrylate, N,N-diethylaminopropyl(meth)acrylate and N,N-dimethylaminocyclohexyl(meth)acrylate.

[0045] Furthermore, 2-hydroxyethyl(meth)acrylate, 2-hydroxyethyl ethacrylate, 2-hydroxypropyl(meth)acrylate, 3-hydroxypropyl(meth)acrylate, 3-hydroxybutyl(meth)acrylate, 4-hydroxybutyl(meth)acrylate, 6-hydroxyhexyl(meth)acrylate and mixtures thereof are suitable as monomers of group (2.).

[0046] Suitable additional monomers of group (2.) are furthermore acrylamide, methacrylamide, N-methyl(meth)acrylamide, N-ethyl(meth)acrylamide, N-propyl(meth)acrylamide, N-butyl(meth)acrylamide, N-(tert-butyl)(meth)acrylamide, N-octyl(meth)acrylamide, N-(1,1,3,3-tetramethylbutyl)(meth)acrylamide, N-(ethylhexyl)(meth)acrylamide and mixtures thereof.

[0047] In addition, N-[2-(dimethylamino)ethyl]acrylamide, N-[2-(dimethylamino)ethyl]methacrylamide, N-[3-(dimethylamino)propyl]acrylamide, N-[3-(dimethylamino)propyl]methacrylamide, N-[4-(dimethylamino)butyl]acrylamide, N-[4-(dimethylamino)butyl]methacrylamide, N-[2-(diethylamino)ethyl]acrylamide, N-[2-(diethylamino)ethyl]methacrylamide and mixtures thereof are suitable as further monomers of group (2.).

[0048] Further examples of monomers of group (2.) are nitriles of α,β -ethylenically unsaturated mono- and dicarboxylic acids, such as, for example, acrylonitrile and methacrylonitrile. The presence of units of these monomers in the copolymer leads, during or after the hydrolysis, to products which have amidine units, cf., for example, EP 0 528 409 A1 or DE 43 28 975 A1. In the hydrolysis of N-vinylcarboxamide polymers, amidine units are in fact formed in a secondary reaction in that the vinylamine units react with a neighboring vinylformamide unit or—if a nitrile group is present as a neighboring group of the polymer—react therewith. Below, the statement “vinylamine units in the amphoteric copolymers or in unmodified homo- or copolymers” always means the sum of vinylamine and amidine units.

[0049] Suitable monomers of group (2.) are furthermore N-vinyl lactams and derivatives thereof which may have, for example, one or more C_1 - C_6 -alkyl substituents (as defined above). These include N-vinylpyrrolidone, N-vinylpiperidone, N-vinylcaprolactam, N-vinyl-5-methyl-2-pyrrolidone, N-vinyl-5-ethyl-2-pyrrolidone, N-vinyl-6-methyl-2-piperidone, N-vinyl-6-ethyl-2-piperidone, N-vinyl-7-methyl-2-caprolactam, N-vinyl-7-ethyl-2-caprolactam and mixtures thereof.

[0050] Furthermore, N-vinylimidazoles and alkylvinylimidazoles are suitable as monomers of group (2.), in particular methylvinylimidazoles, such as, for example, 1-vinyl-2-methylimidazole, 3-vinylimidazole N-oxide, 2- and 4-vinylpyridine N-oxides and betaine derivatives and quaternization products of these monomers and ethylene, propylene, isobutylene, butadiene, styrene, α -methylstyrene, vinyl acetate, vinyl propionate, vinyl chloride, vinylidene chloride, vinyl fluoride, vinylidene fluoride and mixtures thereof.

[0051] The abovementioned monomers can be used individually or in the form of any desired mixtures. Typically,

they are used in amounts of from 1 to 90 mol %, preferably from 10 to 80 mol % and particularly preferably from 10 to 60 mol %.

[0052] For the preparation of amphoteric copolymers, anionic monomers, which are designated above as monomers (2.1), are also suitable as other monoethylenically unsaturated monomers of group (2.). They can, optionally, be copolymerized with the neutral and/or cationic monomers (2.2) described above. The amount of anionic monomers (2.1) is, however, not more than 45 mol %, so that the resulting amphoteric copolymer has a cationic charge overall.

[0053] Examples of anionic monomers of group (2.1) are ethylenically unsaturated C_3 - to C_8 -carboxylic acids, such as, for example, acrylic acid, methacrylic acid, dimethacrylic acid, ethacrylic acid, maleic acid, fumaric acid, itaconic acid, mesaconic acid, citraconic acid, methylenemalononic acid, allylactic acid, vinylacetic acid and crotonic acid. Other suitable monomers of this group are monomers comprising sulfo groups, such as vinylsulfonic acid, acrylamido-2-methylpropanesulfonic acid and styrenesulfonic acid, and monomers comprising phosphonic groups, such as vinylphosphonic acid. The monomers of this group can be used alone or as a mixture with one another, in partly or completely neutralized form in the copolymerization. For example, alkali metal or alkaline earth metal bases, ammonia, amines and/or alkanolamines are used for the neutralization. Examples of these are sodium hydroxide solution, potassium hydroxide solution, sodium carbonate, potassium carbonate, sodium bicarbonate, magnesium oxide, calcium hydroxide, calcium oxide, triethanolamine, ethanolamine, morpholine, diethylenetriamine or tetraethylenepentamine.

[0054] A further modification of the copolymers is possible by using, in the copolymerization, monomers of group (3.) which comprise at least two double bonds in the molecule, e.g. triallylamine, methylenebisacrylamide, glycol diacrylate, glycol dimethacrylate, glyceryl triacrylate, pentaerythritol triallyl ether, polyalkylene glycols at least diesterified with acrylic acid and/or methacrylic acid or polyols, such as pentaerythritol, sorbitol or glucose. These are so-called crosslinking agents. If at least one monomer of the above group is used in the polymerization, the amounts used are up to 2 mol %, e.g. from 0.001 to 1 mol %.

[0055] Furthermore, it may be expedient for the modification of the polymers to combine the use of the above crosslinking agents with the addition of chain-transfer agents. Typically, from 0.001 to 5 mol % are used. All chain-transfer agents known from the literature, for example sulfur compounds such as mercaptoethanol, 2-ethylhexyl thioglycolate, thioglycolic acid and dodecyl mercaptan, and sodium hypophosphite, formic acid or tribromochloromethane and terpinolene, can be used.

[0056] The polymers comprising vinylamine units also include hydrolyzed graft polymers of, for example, N-vinylformamide on polyalkylene glycols, polyvinyl acetate, polyvinyl alcohol, polyvinylformamides, polysaccharides, such as starch, oligosaccharides or monosaccharides. The graft polymers are obtainable, for example, by subjecting N-vinylformamide to free radical polymerization in an aqueous medium in the presence of at least one of said grafting bases, optionally together with copolymerizable other monomers, and then hydrolyzing the grafted-on vinylformamide units in a known manner to give vinylamine units.

[0057] The hydrolysis of the copolymers described above can be carried out in the presence of acids or bases or enzy-

matically. In the hydrolysis with acids, the vinylamine groups forming from the vinylcarboxamide units are present in salt form. The hydrolysis of vinylcarboxamide copolymers is described in detail in EP 0 438 744 A1, page 8, line 20 to page 10, line 3. The statements made there apply correspondingly to the preparation of the purely cationic and/or amphoteric polymers comprising vinylamine units to be used according to the invention and having an overall cationic charge.

[0058] As described above, other suitable polymers comprising vinylamine units are the reaction products which are obtainable by Hofmann degradation of homo- or copolymers of acrylamide or of methacrylamide in an aqueous medium in the presence of sodium hydroxide solution and sodium hypochlorite and subsequent decarboxylation of the carbamate groups of the reaction products in the presence of an acid. Such polymers are disclosed, for example, in EP 0 377 313 and WO 2006/075115 A1. The preparation of polymers comprising vinylamine groups is discussed in detail, for example, in WO 2006/075115 A1, page 4, line 25 to page 10, line 22 and in the examples on pages 13 and 14. The statements made there apply to the characterization of the polymers prepared by Hofmann degradation and comprising vinylamine units.

[0059] There, polymers which comprise acrylamide and/or methacrylamide units are used as starting materials. These are homo- or copolymers of acrylamide and methacrylamide. Suitable comonomers are, for example, dialkylaminoalkyl (meth)acrylamides, diallylamine, methylallylamine and the salts of the amines and the quaternized amines. Also suitable as comonomers are dimethyldiallylammonium salts, acrylamidopropyltrimethylammonium chloride and/or methacrylamidopropyltrimethyl-ammonium chloride, N-vinylformamide, N-vinylacetamide, N-vinylpyrrolidone, vinyl acetate and acrylates and methacrylates. Optionally, other suitable comonomers are anionic monomers, such as acrylic acid, methacrylic acid, maleic anhydride, maleic acid, itaconic acid, acrylamidomethylpropanesulfonic acid, methallylsulfonic acid and vinylsulfonic acid and the alkali metal, alkaline earth metal and ammonium salts of said acidic monomers, not more than 5 mol % of these monomers being used in the polymerization. The amount of water-insoluble monomers is chosen in the polymerization so that the resulting polymers are soluble in water.

[0060] Optionally, crosslinking agents may also be used as comonomers, for example ethylenically unsaturated monomers which comprise at least two double bonds in the molecule, such as triallylamine, methylenebisacrylamide, ethylene glycol diacrylate, ethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, triallylamine and trimethylol trimethacrylate. If a crosslinking agent is used, the amounts used are, for example, from 5 to 5000 ppm. The polymerization of the monomers can be effected by all known processes, for example by free radical solution, precipitation or suspension polymerization. Optionally, the procedure can be effected in the presence of customary polymerization chain-transfer agents.

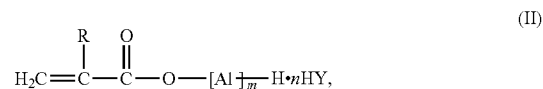
[0061] In the Hofmann degradation, for example, from 20 to 40% strength by weight aqueous solutions of at least one polymer comprising acrylamide and/or methacrylamide units are used as starting material. The ratio of alkali metal hypochlorite to (meth)acrylamide units in the polymer is decisive for the resulting content of amine groups in the polymer. The molar ratio of alkali metal hydroxide to alkali metal hypochlorite is, for example, from 2 to 6, preferably from 2 to 5. The amount of alkali metal hydroxide required for

the degradation of the polymer is calculated for a certain amine group content in the degraded polymer.

[0062] The Hofmann degradation of the polymer takes place, for example, in the temperature range from 0 to 45° C., preferably from 10 to 20° C., in the presence of quaternary ammonium salts as stabilizer, in order to prevent a secondary reaction of the resulting amino groups with the amide groups of the starting polymer. After the end of the reaction with alkali metal hydroxide/alkali metal hypochlorite, the aqueous reaction solution is passed into a reactor in which an acid for the decarboxylation of the reaction product is present. The pH of the reaction product comprising vinylamine units is adjusted to a value of from 2 to 7. The concentration of the degradation product comprising vinylamine units is, for example, more than 3.5% by weight, in general above 4.5% by weight. The aqueous polymer solutions can be concentrated, for example, with the aid of ultrafiltration.

[0063] Further suitable water-soluble cationic polymers (a) are cationic homo- and copolymers of (meth)acrylamide and can be prepared by polymerization of the above-described monomers of group (2.), the quaternization products of these monomers with C₁- to C₈-alkyl chloride, C₁-C₈-dialkyl sulfate, C₁-C₁₆-epoxides and benzyl chloride also being suitable.

[0064] Allylamine, dialkyldiallylammonium chlorides, in particular dimethyldiallylammonium chloride and diethyldiallylammonium chloride, and the monomers of the formula (II)



which are disclosed in WO 01/36500 A1 and comprise alkyleneimine units,

in which

[0065] R is hydrogen or C₁- to C₄-alkyl,

[0066] $-\text{[Al]}_m-$ is a linear or branched oligoalkyleneimine chain having m alkyleneimine units,

[0067] m is an integer in the range from 1 to 20, and the number average m in the oligoalkyleneimine chains is at least 1.5,

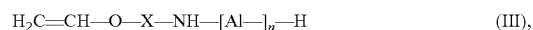
[0068] Y is the anion equivalent of a mineral acid and

[0069] n is a number $1 \leq n \leq m$,

are suitable for the preparation of polyallylamines as water-soluble cationic polymers (a).

[0070] Monomers or monomer mixtures in which the number average of m is at least 2.1, in general from 2.1 to 8, in the abovementioned formula (II) are preferred. They are obtainable by reacting an ethylenically unsaturated carboxylic acid with an oligoalkyleneimine, preferably in the form of an oligomer mixture. The resulting product can, optionally, be converted into the acid addition salt with a mineral acid HY. Such monomers can be polymerized in an aqueous medium in the presence of an initiator which initiates a free radical polymerization, to give cationic homo- and copolymers.

[0071] Further suitable water-soluble cationic polymers (a) are polyaminoalkyl vinyl ethers. Monomers suitable for this purpose are disclosed in the prior EP application with the application number 07 117 909.7. They are aminoalkyl vinyl ethers comprising alkyleneimine units and of the formula (III)



in which

[Al—] is a linear or branched oligoalkyleneimine chain having *n* alkyleneimine units,

n is a number of at least 1 and

X is a straight-chain or branched C₂- to C₆-alkylene group, and salts of the monomers (III) with mineral acids or organic acids and quaternization products of the monomers (III) with alkyl halides or dialkyl sulfates. These compounds are obtainable by an addition reaction of alkyleneimines with amino-C₂- to C₆-alkyl vinyl ethers.

[0072] The abovementioned monomers can be polymerized alone to give water-soluble cationic homopolymers (a) or together with at least one other neutral monomer to give water-soluble cationic copolymers or with at least one monomer having acid groups to give amphoteric copolymers which, in the case of a molar excess of cationic monomers incorporated in the form of polymerized units, carry an overall cationic charge.

[0073] Suitable neutral monomers which are copolymerized with the abovementioned cationic monomers for the preparation of cationic polymers are, for example, esters of α,β -ethylenically unsaturated mono- and dicarboxylic acids with C₁-C₃₀-alkanols, C₂-C₃₀-alkanediols, amides of α,β -ethylenically unsaturated monocarboxylic acids and the N-alkyl and N,N-dialkyl derivatives thereof, esters of vinyl alcohol and allyl alcohol with saturated C₁-C₃₀-monocarboxylic acids, vinylaromatics, vinyl halides, vinylidene halides, C₂- to C₈-monoolefins and mixtures thereof.

[0074] Further suitable comonomers are, for example, methyl(meth)acrylate, methyl ethacrylate, ethyl(meth)acrylate, ethyl ethacrylate, n-butyl(meth)acrylate, isobutyl(meth)acrylate, tert-butyl(meth)acrylate, tert-butyl ethacrylate, n-octyl(meth)acrylate, 1,1,3,3-tetramethylbutyl(meth)acrylate, ethylhexyl(meth)acrylate and mixtures thereof.

[0075] Also suitable are acrylamide, substituted acrylamides, methacrylamide, substituted methacrylamides, such as, for example, acrylamide, methacrylamide, N-methyl(meth)acrylamide, N-ethyl(meth)acrylamide, N-propyl(meth)acrylamide, N-(n-butyl)(meth)acrylamide, tert-butyl(meth)acrylamide, n-octyl(meth)acrylamide, 1,1,3,3-tetramethylbutyl(meth)acrylamide and ethylhexyl(meth)acrylamide, and acrylonitrile and methacrylonitrile and mixtures of said monomers.

[0076] Further monomers for the modification of the cationic polymers are 2-hydroxyethyl(meth)acrylate, 2-hydroxyethyl ethacrylate, 2-hydroxypropyl(meth)acrylate, 3-hydroxypropyl(meth)acrylate, 3-hydroxybutyl(meth)acrylate, 4-hydroxybutyl(meth)acrylate, 6-hydroxyhexyl(meth)acrylate, etc. and mixtures thereof.

[0077] Further suitable monomers for the copolymerization with the abovementioned cationic monomers are N-vinyl lactams and derivatives thereof which may have, for example, one or more C₁-C₆-alkyl substituents, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, etc. These include, for example, N-vinylpyrrolidone, N-vinylpiperidone, N-vinylcaprolactam, N-vinyl-5-methyl-2-pyrrolidone, N-vinyl-5-ethyl-2-pyrrolidone, N-vinyl-6-methyl-2-piperidone, N-vinyl-6-ethyl-2-piperidone, N-vinyl-7-methyl-2-caprolactam, N-vinyl-7-ethyl-2-caprolactam, etc.

[0078] Suitable comonomers for the copolymerization with the abovementioned cationic monomers are furthermore ethylene, propylene, isobutylene, butadiene, styrene, α -me-

thylstyrene, vinyl chloride, vinylidene chloride, vinyl fluoride, vinylidene fluoride and mixtures thereof.

[0079] In addition, polyamidoamine compounds and polyamine compounds reacted with epichlorohydrin, as disclosed in DE 24 34 816 A1 and in U.S. Pat. No. 3,258,393, are also suitable.

[0080] The German laid-open application describes nitrogen-containing condensates which are obtained by reacting polyamidoamine compounds with polyalkylene oxide derivatives which are reacted at the terminal hydroxyl groups with epichlorohydrin. For the preparation of such condensates, reference is made expressly and in its entirety to the disclosure of DE 24 34 816 A1, in particular to the passage on page 4, 3rd paragraph to page 6, inclusive.

[0081] Polyamine compounds reacted with epichlorohydrin are disclosed, for example, in U.S. Pat. No. 3,258,393. According to this, epichlorohydrin is reacted with a bifunctional or a polyfunctional amine. Suitable bifunctional amines are methylamine, ethylamine, ethanolamine, dimethylamine, N,N'-dimethylethylenediamine, aniline, piperazine and ethyl aminoacetate. Examples of polyfunctional amines are ethylenediamine, N-methylethylenediamine, ammonia, hydrazine, p-phenylenediamine and further amines mentioned in U.S. Pat. No. 3,258,393, in particular the polyfunctional amines disclosed in column 4. The bifunctional and polyfunctional amines are usually used in equimolar ratio. In addition to epichlorohydrin, other crosslinking agents, such as glyoxal, 1,2-dichloroethane, diglycidyl ether, methylenebisacrylamide and 1,4-dichlorobutene, and further crosslinking agents mentioned in column 4 of U.S. Pat. No. 3,258,393 are also suitable according to this US document. For the preparation of such condensates, reference is made expressly and in its entirety to the disclosure of U.S. Pat. No. 3,258,393.

[0082] Of course, the polyamine compounds reacted with epichlorohydrin can be prepared on the basis of only one bifunctional amine or of a polyfunctional amine.

[0083] As described above, cationic polymers are also understood as meaning amphoteric polymers which carry an overall cationic charge. In the case of the amphoteric polymers, the content of cationic groups is, for example, at least 5 mol % above the content of anionic groups in the polymer. Such polymers are obtainable, for example, by copolymerizing a cationic monomer, such as N,N-dimethylaminoethylacrylamide, in the form of the free base, in a form partly neutralized with an acid or in quaternized form with at least one monomer comprising acid groups, the cationic monomer being used in a molar excess so that the resulting polymers carry an overall cationic charge.

[0084] Furthermore, polymers comprising ethyleneimine units are suitable as water-soluble cationic polymers for the process according to the invention. These include all polymers which are obtainable by polymerization of ethyleneimine in the presence of acids, Lewis acids or haloalkanes, such as homopolymers of ethyleneimine or graft polymers of ethyleneimine, cf. U.S. Pat. No. 2,182,306 or U.S. Pat. No. 3,203,910. These polymers can, optionally, be subsequently subjected to crosslinking. Suitable crosslinking agents are, for example, all polyfunctional compounds which comprise groups reactive toward primary amino groups, for example polyfunctional epoxides, such as bisglycidyl ethers of oligo- or polyethylene oxides, or other polyfunctional alcohols, such as glycerol or sugars, polyfunctional carboxylic esters, polyfunctional isocyanates, polyfunctional acrylates or meth-

acrylates, polyfunctional acrylamides or methacrylamides, epichlorohydrin, polyfunctional acid halides, polyfunctional nitriles, α,ω -chlorohydrin ethers of oligo- or polyethylene oxides or of other polyfunctional alcohols, such as glycerol or sugars, divinyl sulfone, maleic anhydride or ω -halocarboxylic acid chlorides, polyfunctional haloalkanes, in particular α,ω -dichloroalkanes. Further crosslinking agents are described in WO 97/25367 A1, pages 8 to 16.

[0085] Polymers comprising ethyleneimine units are disclosed, for example, in EP 0411 400 A1, DE 24 34 816 A1 and U.S. Pat. No. 4,066,494.

[0086] For example, at least one water-soluble cationic polymer from the group consisting of

[0087] homopolymers of ethyleneimine,

[0088] polyethyleneimines reacted with at least bifunctional crosslinking agents,

[0089] polyamidoamines which are grafted with ethyleneimine and reacted with at least bifunctional crosslinking agents,

[0090] reaction products of polyethyleneimines with monobasic carboxylic acids to give amidated polyethyleneimines,

[0091] Michael adducts of polyethyleneimines with ethylenically unsaturated acids, salts, esters, amides or nitriles of monoethylenically unsaturated carboxylic acids,

[0092] phosphonomethylated polyethyleneimines,

[0093] carboxylated polyethyleneimines and

[0094] alkoxyated polyethyleneimines

is used as polymers comprising ethyleneimine units in the process according to the invention.

[0095] Polymers which are obtained by first condensing at least one polycarboxylic acid with at least one polyamine to give polyamidoamines, then effecting grafting with ethyleneimine and then crosslinking the reaction products with one of the abovementioned compounds are among the preferred compounds comprising polyethyleneimine units. A process for the preparation of such compounds is described, for example, in DE 24 34 816 A1, α,ω -chlorohydrin ethers of oligo- or polyethylene oxides being used as crosslinking agents.

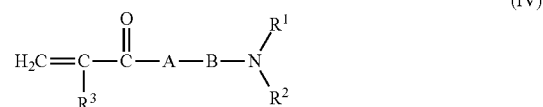
[0096] Products of the two above types, which were subjected to ultrafiltration and thus optimized in their molecular weight distribution, are particularly preferred. Such products which have been subjected to ultrafiltration are described in detail in WO 00/67884 A1 and WO 97/25367 A1. These publications and the disclosure present therein are hereby incorporated by reference.

[0097] Reaction products of polyethyleneimines with monobasic carboxylic acids to give amidated polyethyleneimines are disclosed in WO 94/12560 A1. Michael adducts of polyethyleneimines with ethylenically unsaturated acids, salts, esters, amides or nitriles of monoethylenically unsaturated carboxylic acids form the subject of WO 94/14873 A1. Phosphonomethylated polyethyleneimines are described in detail in WO 97/25367 A1. Carboxylated polyethyleneimines are obtainable, for example, with the aid of a Stecker synthesis by reaction of polyethyleneimines with formaldehyde and ammonia/hydrogen cyanide and hydrolysis of the reaction products. Alkoxyated polyethyleneimines can be prepared by reacting polyethyleneimines with alkylene oxides, such as ethylene oxide and/or propylene oxide.

[0098] In addition, homopolymers of cationic or basic (meth)acrylates which in each case have an amino group and/or quaternary ammonium group, or cationic or basic

(meth)acrylamides which in each case carry an amino group and/or quaternary ammonium group may also be used in the process according to the invention.

[0099] Such compounds having an amino group are those of the general formula (IV):



in which

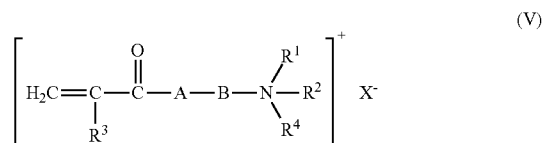
A is O, NH,

[0100] B is C_nH_{2m} , where n is an integer in the range from 1 to 8,

R^1, R^2 are $\text{C}_m\text{H}_{2m+1}$, m is an integer in the range from 1 to 4 and

R^3 is H, CH_3 ,

[0101] The compounds having quaternary ammonium groups can be characterized with the aid of the following formula (V):



in which

X— is OH—, Cl—, Br, $\text{CH}_3\text{—OSO}_3\text{—}$

[0102] R^4 is $\text{C}_m\text{H}_{2m+1}$, m is an integer in the range from 1 to 4, and

the other substituents have the abovementioned meaning.

[0103] The compounds of the formula (V) are designated as a rule as cationic monomers and those of the formula (IV) as basic monomers. Basic, ethylenically unsaturated monomers are, for example, acrylates and methacrylates of aminoalcohols, e.g. N,N-dimethylaminoethyl acrylate, N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl acrylate, N,N-diethylaminoethyl methacrylate, N,N-dimethylaminoethyl methacrylate, N,N-dimethylaminopropyl methacrylate, N,N-dimethylaminopropyl methacrylate, N,N-dimethylaminopropyl methacrylate, N,N-dimethylaminoneopentyl acrylate, derivatives of acrylamide or of methacrylamide which comprise amino groups, such as N,N-dimethylaminoethylacrylamide, N,N-dimethylaminoethylmethacrylamide, N,N-dimethylaminopropylacrylamide and N,N-dimethylaminopropylmethacrylamide.

[0104] The quaternary compounds of the formula (V) are obtained by reacting the basic monomers of the formula (IV) with known quaternizing agents, for example with methyl chloride, benzyl chloride, ethyl chloride, butyl bromide, dimethyl sulfate and diethyl sulfate or epichlorohydrin. These monomers lose their basic character in the quaternary form. The following may be mentioned as examples: N,N,N-trimethylammoniummethyl acrylate chloride, N,N,N-trimethylam-

moniummethyl methacrylate chloride, N,N,N-trimethylammoniummethylmethacrylamide chloride, N,N,N-trimethylammoniumpropylacrylamide chloride, N,N,N-trimethylammoniumpropylmethacrylamide chloride, N,N,N-trimethylammoniummethylacrylamide chloride and the corresponding methosulfates and sulfates.

[0105] The monomers of this group are preferably selected from N,N-dimethylaminopropylmethacrylamide, N,N-dimethylaminoethyl methacrylate, and N,N-dimethylaminoethyl acrylate, used in each case in the form of a salt with at least one mineral acid or carboxylic acid and/or in quaternary form. A preferred quaternizing agent is methyl chloride.

[0106] All of the abovementioned cationic homo- and copolymers can be prepared by solution, precipitation, suspension or emulsion polymerization. The solution polymerization in aqueous media is preferred. Suitable aqueous media are water and mixtures of water and at least one water-miscible solvent, for example an alcohol, such as methanol, ethanol, n-propanol, etc.

[0107] The polymerization temperatures are preferably in a range from about 30 to 200° C., particularly preferably from 40 to 110° C. Polymerization is usually effected under atmospheric pressure but may also take place under reduced or superatmospheric pressure. A suitable pressure range is from 0.1 to 5 bar.

[0108] For the preparation of polymers, the monomers can be polymerized with the aid of free radical initiators.

[0109] Initiators which may be used for the free radical polymerization are the peroxy and/or azo compounds customary for this purpose, for example alkali metal or ammonium peroxodisulfates, diacetyl peroxide, dibenzoyl peroxide, succinyl peroxide, di-tert-butyl peroxide, tert-butyl perbenzoate, tert-butyl perpivalate, tert-butyl peroxy-2-ethylhexanoate, tert-butyl permaleate, cumyl hydroperoxide, diisopropyl peroxodicarbamate, bis(o-toluoyl)peroxide, didecanoyl peroxide, dioctanoyl peroxide, dilauroyl peroxide, tert-butyl perisobutyrate, tert-butyl peracetate, di-tert-amyl peroxide, tert.-butyl hydroperoxide, azobisisobutyronitrile, azobis(2-amidinopropane)dihydrochloride or 2,2'-azobis(2-methylbutyronitrile). Initiator mixtures or redox initiator systems, such as, for example, ascorbic acid/iron(II) sulfate/sodium peroxodisulfate, tert-butyl hydroperoxide/sodium disulfite, tert-butyl hydroperoxide/sodium hydroxymethanesulfinate, H₂O₂/Cu(I) or iron(II) compounds, are also suitable.

[0110] For establishing the molecular weight, the polymerization can be effected in the presence of at least one chain-transfer agent. The customary compounds known to the person skilled in the art, such as, for example, sulfur compounds, e.g. mercaptoethanol, 2-ethylhexyl thioglycolate, thioglycolic acid, sodium hypophosphite, formic acid or dodecyl mercaptan and tribromochloromethane and other compounds which have a regulating effect on the molecular weight of the polymers obtained, can be used as chain-transfer agents.

[0111] All abovementioned cationic polymers can be modified by carrying out the polymerization of the cationic monomers and, optionally, of the mixtures of cationic monomers and the comonomers in the presence of at least one crosslinking agent. The crosslinking agents are understood as meaning those monomers which comprise at least two double bonds in the molecule, e.g. methylenebisacrylamide, glycol diacrylate, glycol dimethacrylate, glyceryl triacrylate, pentaerythrityl triallyl ether, polyalkylene glycols at least diesterified with acrylic acid and/or methacrylic acid or polyols,

such as pentaerythritol, sorbitol or glucose. If at least one crosslinking agent is used in the copolymerization, the amounts used are, for example, up to 2 mol %, for example from 0.001 to 1 mol %.

[0112] Furthermore, the cationic polymers can be modified by the subsequent addition of crosslinking agents, i.e. by the addition of compounds which have at least two groups reactive toward amino groups, such as, for example,

[0113] di- and polyglycidyl compounds,

[0114] di- and polyhalogen compounds,

[0115] compounds having two or more isocyanate groups, possibly blocked carbonic acid derivatives,

[0116] compounds which have two or more double bonds which are suitable for a Michael addition,

[0117] di- and polyaldehydes,

[0118] monoethylenically unsaturated carboxylic acids and the esters and anhydrides thereof.

[0119] The at least one water-soluble cationic polymer (a) is used in the process according to the invention for reducing deposits in the dry section in the production of paper, for example in an amount of from 0.005 to 2.0% by weight, preferably from 0.005 to 1% by weight, particularly preferably from 0.01 to 0.3% by weight, based in each case on the solids content of the paper stock.

[0120] In principle, all polymer sizes which are known to the person skilled in the art and are used both as surface sizes and as engine sizes in papermaking are suitable as aqueous dispersions of polymer sizes in the process according to the invention.

[0121] Finely divided, cationic or amphoteric, aqueous polymer dispersions, which are frequently obtainable by a two-stage polymerization, are preferably suitable. In the first polymerization stage, a prepolymer is prepared as a dispersant or protective colloid and an emulsion polymerization is then carried out in an aqueous solution of the prepolymer in the presence of ethylenically unsaturated monomers.

[0122] Such finely divided, cationic, aqueous polymer dispersions are known to the person skilled in the art and are disclosed, inter alia, in DE 24 25 585 A1, DE 24 54 397 A1, EP 0 051 144 A1, EP 0 058 313 A1, U.S. Pat. No. 4,659,431, EP 1 180 527 A1, WO 05/121195 A1, WO 08/071,690 A1 and in the prior EP application with the application number 09 161 929.6.

[0123] Usually, the prepolymers obtainable by solution polymerization of

[0124] (i) nitrogen-containing monomers which carry an amino group and/or quaternary ammonium group,

[0125] (ii) nonionic, hydrophobic, ethylenically unsaturated monomers,

[0126] (iii) optionally, ethylenically unsaturated monomers comprising acid groups, and

[0127] (iv) optionally, nonionic, hydrophilic, ethylenically unsaturated monomers.

[0128] The prepolymer obtained by this route is then subjected to an emulsion polymerization as a dispersant or protective colloid in the presence of ethylenically unsaturated monomers, a monomer mixture comprising nonionic, hydrophobic, ethylenically unsaturated monomers being used as the ethylenically unsaturated monomers.

[0129] Suitable (i) nitrogen-containing monomers which carry an amino group and/or quaternary ammonium group are those compounds which are used beforehand with the formulae (IV) and (V) as (a) water-soluble cationic polymers for the preparation of homopolymers of cationic or basic (meth)

acrylates, which in each case have an amino group and/or quaternary ammonium group, or cationic or basic (meth)acrylamides, which in each case carry an amino group and/or quaternary ammonium group. The abovementioned preferred compounds and the quaternization products thereof are also preferably used as (i) nitrogen-containing monomers.

[0130] The monomers of group (ii) for the preparation of the prepolymer are nonionic, hydrophobic, ethylenically unsaturated compounds. They are those monomers which are not markedly soluble in water and form hydrophobic polymers. Such monomers are, for example, vinylaromatic monomers, such as styrene and substituted styrenes, e.g. α -methylstyrene and ethylstyrene; carboxylates of ethylenically unsaturated C_3 - to C_6 -mono- and dicarboxylic acid with monohydric C_1 - to C_{18} -alcohols, such as, for example C_1 - to C_{18} -(meth)acrylates, such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, isopropyl acrylate, isopropyl methacrylate, n-butyl acrylate, isobutyl acrylate and tert-butyl acrylate, n-butyl methacrylate, isobutyl methacrylate and tert-butyl methacrylate, hexyl acrylate, hexyl methacrylate, ethylhexyl acrylate, ethylhexyl methacrylate, cyclohexyl acrylate, cyclohexyl methacrylate, n-decyl acrylate, decyl methacrylate, lauryl acrylate, lauryl methacrylate, stearyl acrylate and stearyl methacrylate; nitrites of C_3 - to C_6 -mono- and dicarboxylic acids, such as, for example, acrylonitrile and methacrylonitrile; vinyl esters of linear or branched C_1 - to C_{30} -carboxylic acids, such as vinyl laurate, vinyl stearate, vinyl propionate, vinyl versatate, vinyl acetate, vinyl propylheptanoate, vinyl neodecanoate (Veova® 10 from Hexion Specialty Chemicals), vinyl neononanoate (Veova® 9 from Hexion Specialty Chemicals) and vinyl pelargonate; alkenes having 2 to 10 carbon atoms, preferably having terminal double bonds, such as ethylene, or diolefins, such as butadiene and isoprene.

[0131] From this group of monomers, styrene, acrylates, methacrylates, acrylonitrile, methacrylonitrile, vinyl acetate, vinyl propionate and butadiene are preferably used. Individual preferred acrylates and methacrylates are methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, n-butyl acrylate, tert-butyl acrylate, ethylhexyl acrylate, lauryl acrylate and the corresponding esters of methacrylic acid.

[0132] It is of course possible, and also preferred, to use any desired mixtures of said monomers, for example mixtures of styrene and (meth)acrylates, such as n-butyl acrylate and/or tert-butyl acrylate, styrene and ethylhexyl acrylate, styrene and acrylonitrile and (meth)acrylates, such as n-butyl acrylate and/or tert-butyl acrylate.

[0133] Suitable monomers of group (iii) are ethylenically unsaturated C_3 - to C_6 -carboxylic acids, such as acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, ethacrylic acid, crotonic acid, monoesters of ethylenically unsaturated dicarboxylic acids, such as monomethyl maleate, monomethyl fumarate, monoethyl maleate, monoethyl fumarate, monopropyl maleate, monopropyl fumarate, mono-n-butyl maleate and mono-n-butyl fumarate, and styrenecarboxylic acids and ethylenically unsaturated anhydrides, such as maleic anhydride and itaconic anhydride. In addition, monomers comprising sulfo and phosphonic acid groups, such as 2-acrylamido-2-methylpropanesulfonic acid and vinylphosphonic acid, are suitable as monomers (iii). The monomers comprising acid groups can be used in the form of the free acid groups and in a form partly or completely neutralized with alkali metal bases, alkaline earth metal bases,

ammonia and/or amines. Preferably, acrylic acid and methacrylic acid or mixtures of acrylic acid and methacrylic acid in any desired ratio are used from this group of monomers.

[0134] Nonionic, hydrophilic, ethylenically unsaturated monomers, for example amides or substituted amides of ethylenically unsaturated mono- or dicarboxylic acids, such as, for example, acrylamide, methacrylamide, N-methylacrylamide, N-methylmethacrylamide, N-ethylacrylamide and N-ethylmethacrylamide, are used as monomers (iv), which are optionally used for modifying the properties of the prepolymer.

[0135] The prepolymer is usually prepared by a solution polymerization method from the abovementioned monomers (i) to (iv). This prepolymer is then diluted in water to a concentration of, for example, from 2 to 25% by weight and then subjected to the second polymerization stage.

[0136] In this second polymerization stage, the abovementioned monomers of group (ii) are subjected to an emulsion polymerization in the presence of the prepolymer. Styrene, acrylates, methacrylates, acrylonitrile, methacrylonitrile, vinyl acetate, vinyl propionate and butadiene, and individual acrylates and methacrylates, such as methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, n-butyl acrylate, tert-butyl acrylate, ethylhexyl acrylate, lauryl acrylate and the corresponding esters of methacrylic acid, are preferred from this group of monomers. It is particularly preferable to use any desired mixtures of said monomers, for example mixtures of styrene and (meth)acrylates, such as n-butyl acrylate and/or tert-butyl acrylate, styrene and ethylhexyl acrylate, styrene and acrylonitrile and (meth)acrylates, such as n-butyl acrylate and/or tert-butyl acrylate.

[0137] Such monomer mixtures may also be polymerized in the presence of a generally degraded starch.

[0138] Specifically, the finely divided, cationic or amphoteric, aqueous polymer dispersions and the preparation process thereof are to be found in the abovementioned literature, to which express reference is made at this point.

[0139] The at least one aqueous dispersion of a polymer size (b) is used in the process according to the invention for reducing deposits in the dry section in the production of paper, for example in an amount of from 0.005 to 5.0% by weight, preferably from 0.01 to 1% by weight, particularly preferably from 0.05 to 0.5% by weight, based in each case on the solids content of the paper stock.

[0140] In the process according to the invention, the sequence of addition of the components (a) and (b) is arbitrary, it being possible to add the components individually or as a mixture to the fiber suspension.

[0141] For example, in the process according to the invention, first the water-soluble cationic polymer (a) is metered into the paper stock. The addition can be effected to the high-consistency stock (fiber concentration >15 g/l, e.g. in the range from 25 to 40 g/l up to 60 g/l) or preferably to the low-consistency stock (fiber concentration <15 g/l, for example in the range from 5 to 12 g/l). The point of addition is preferably before the wires but may also be between a shearing stage and a screen or thereafter.

[0142] The aqueous dispersion of a polymer size (b) is generally added to the paper stock only after the addition of the water-soluble cationic polymer (a) but can also be added simultaneously and also as a mixture with (a) to the paper stock. Furthermore, it is also possible first to add the aqueous dispersion of a polymer size (b), and the metering of the water-soluble cationic polymer (a) is then effected.

[0143] In the process according to the invention, the process chemicals usually used in papermaking are used in the customary amounts, for example retention aid, drainage aid, other dry strength agents, such as, for example, starch, pigments, fillers, optical brighteners, antifoams, biocides and paper dyes.

[0144] The process according to the invention is suitable for reducing all types of impurities in the dry section, in particular of resin residues in the fiber suspension, assistants from the papermaking, adhesives, binders from the paper-coating and binders from printing inks. Such impurities or stickies, whose deposits in the dry section are substantially reduced by the process according to the invention, are described, for example, in U.S. Pat. No. 6,387,215 B1, column 2, from line 22 to column 3, line 26.

[0145] The present invention also relates to the papers and board and cardboard produced by the process described above.

[0146] Suitable fibers for the production of the pulps for papermaking are all qualities customary for this purpose, for example mechanical pulp, bleached and unbleached chemical pulp and paper stocks from all annual plants. Mechanical pulp includes, for example, groundwood pulp, thermomechanical pulp (TMP), chemo-thermomechanical pulp (CTMP), pressure groundwood, semichemical pulp, high-yield chemical pulp and refiner mechanical pulp (RMP). For example, sulfate, sulfite and soda pulps are suitable as chemical pulp. For example, unbleached chemical pulp, which is also referred to as unbleached kraft pulp, is used. Suitable annual plants for the production of paper stocks are, for example, rice, wheat, sugarcane and kenaf.

[0147] The process according to the invention is suitable in particular for the production of papers from wastepaper (comprising deinked wastepaper), which is used either alone or as a mixture with other fibers. It is also possible to start from fiber mixtures comprising a primary stock and recycled coated broke, for example bleached pine sulfate as a mixture with recycled coated broke. The process according to the invention is of industrial interest for the production of paper, board and cardboard from wastepaper and in specific cases also from deinked wastepaper, because it substantially increases the runnability of the paper machines through a reduction of deposits and consequently fewer tears.

[0148] The pH of the stock suspension is, for example, in the range from 4.5 to 8, in general from 6 to 7.5. For example, an acid, such as sulfuric acid, or aluminum sulfate can be used for adjusting the pH.

[0149] The invention is explained in more detail with reference to the following, non-limiting examples.

EXAMPLES

[0150] The stated percentages in the examples mean % by weight, unless stated otherwise.

[0151] In the examples and the comparative examples, the following polymers were used:

Polymer K1

[0152] Cationic polyethyleneimine, molecular weight about 1 200 000 dalton (Catiofast® SF from BASF SE)

Polymer K2

[0153] Cationic polyvinylamine, degree of hydrolysis 100 mol %, molecular weight about 400 000 dalton (Catiofast® VFH from BASF SE)

Polymer K3

[0154] Cationic polyamine (epichlorohydrin-dimethylamine condensate), molecular weight about 100 000 dalton (Catiofast® 8154 from BASF SE)

Polymer K4

[0155] Cationic polydiallyldimethylammonium chloride, molecular weight about 100 000 dalton (Catiofast® CS from BASF SE)

Polymer K5

[0156] Cationic polyacrylamide, molecular weight about 8 000 000 dalton (Catiofast® 8356 from BASF SE)

Polymer K6

[0157] Cationic polyvinyl amine, Hofmann degradation product, molecular weight about 20 000 dalton, solids content 24.2% by weight, viscosity 19 mPa·s (determined using a Brookfield Viscometer, LVT, spindle 1, 60 rpm, 20° C.), charge density 57.2 meq/g per 100 g of products (determined by polyelectrolyte titration) (RSL HF 70D from SNF SAS)

Polymer A1

[0158] Cationic dispersion of a styrene-acrylate-based polymer size (Basoplast® 270 D from BASF SE)

[0159] Production of the paper stock and sheet formation for the examples and comparative examples

[0160] A mixture of 50% of newsprint and 50% of label printing paper was disintegrated until speck-free with tapwater at a consistency of 4% in a laboratory pulper at 40° C. for 25 min and then diluted with water to a solids content of 0.5%.

[0161] The abovementioned polymers were added to the paper stock with stirring (500 rpm), in each case a contact time of 30 s being maintained. The metering of the polymers and the metered amounts (in percent by weight, based on the solids content of the paper stock used) are stated in each case in the tables. After the last addition of a polymer to the paper stock, as much stock was removed in an amount (about 500 ml) required to produce a sheet having a basis weight of 80 g/m² on a rapid-Köthen sheet former. As usual in the rapid-Köthen process, the sheets were couched. Thereafter, the still wet sheet was unrolled once and placed moist on a stainless steel screen, whose weight was determined beforehand, with a pore size of 100 µm.

[0162] Each of these sheets was dried on the stainless steel screen for 10 min on a laboratory drying drum at 90° C.

[0163] The following method was used for the quantitative determination of the deposits:

[0164] In each case strips having dimensions of 200×55 mm were cut from the sheets on the stainless steel screen. These were subjected to a tear-peel test in a Zwick Roell Z-module, paper web and screen being pulled off from one another in opposite directions with a speed of 400 mm/min. The adhesion energy in J/m² was determined as a characterizing quantity. In addition, the proportion of deposits remaining on the screen was determined by weighing the stainless steel screen. The aim was to find as far as possible no deposits

at all on the screen and at the same time to have as little adhesion as possible on the screen. The two quantities below were calculated for characterizing the samples:

% reduction of the adhesion energy=(energy of a sample-energy of an untreated sample)/energy of an untreated sample [in each case in J/m²]

% reduction of the deposits=(deposition on a sample-deposition on an untreated sample)/deposition on an untreated sample [in each case in g]

1. A process for producing a paper products product with reduced deposits, the process comprising: adding a water-soluble cationic polymer (a) and an aqueous dispersion of a polymer size (b) to a paper stock, draining the paper stock, to obtain a sheet, and drying the sheet, to obtain a paper product.
2. The process of claim 1, wherein the polymer (a) is at least one selected from the group consisting of a polymer comprising a vinylamine unit, a cationic homo-polymer comprising (meth)acrylamide, a cationic copolymer comprising (meth)

TABLE 1

Reduction of the adhesion energy						
Example	Cationic polymer	Dose [%]	Polymer size	Dose [%]	Adhesion energy [J/m ²]	Reduction of adhesion energy [%]
Comparison 0	—	—	—	—	13.16	0
Comparison 1	Polymer K1	0.1	—	—	10.53	-20.2
Comparison 2	Polymer K2	0.1	—	—	10.78	-18.3
Comparison 3	Polymer K3	0.1	—	—	12.51	-5.2
Comparison 4	Polymer K4	0.1	—	—	12.34	-6.5
Comparison 5	Polymer K5	0.1	—	—	12.22	-7.4
Comparison 6	Polymer K6	0.1	—	—	12.24	-7.2
Comparison 7	—	—	Polymer A1	0.5	10.41	-21.1
Example 1	Polymer K1	0.1	Polymer A1	0.5	7.35	-44.3
Example 2	Polymer K2	0.1	Polymer A1	0.5	7.76	-41.2
Example 3	Polymer K3	0.1	Polymer A1	0.5	9.88	-25.1
Example 4	Polymer K4	0.1	Polymer A1	0.5	9.86	-25.3
Example 5	Polymer K5	0.1	Polymer A1	0.5	9.70	-26.5
Example 6	Polymer K6	0.1	Polymer A1	0.5	9.35	-29.1
Example 7	Polymer K1	0.1	Polymer A1	1.0	6.90	-47.7
Example 8	Polymer K1	0.1	Polymer A1	2.0	8.25	-37.5

[0165] The synergistic effect of the (a) water-soluble cationic polymer with the (b) aqueous dispersion of the polymer size with regard to the reduction of the adhesion energy is evident from table 1.

TABLE 2

Reduction of the deposits					
Example	Cationic polymer	Dose [%]	Polymer size	Dose [%]	Reduction of deposits [%]
Comparison 0	—	—	—	—	0
Comparison 8	Polymer K1	0.1	—	—	-18.7
Comparison 9	—	—	Polymer A1	0.5	-21.9
Comparison 10	—	—	Polymer A1	1.0	-30.2
Comparison 11	—	—	Polymer A1	2.0	-27.4
Example 9	Polymer K1	0.1	Polymer A1	0.5	-69.1
Example 10	Polymer K1	0.1	Polymer A1	1.0	-76.4
Example 11	Polymer K1	0.1	Polymer A1	2.0	-68.3

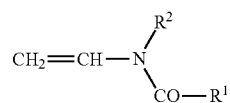
[0166] The efficiency and synergistic effect of the combination of a (a) water-soluble cationic polymer with a (b) aqueous dispersion of a polymer size is evident from table 2, in particular by a comparison of comparative examples 8 and 9 with example 9 according to the invention.

[0167] In addition, a comparison of examples 6, 7 and 8 according to the invention with examples 9, 10 and 11 according to the invention shows that the reduction of the adhesion energy takes place in parallel with the reduction of the deposits.

acrylamide, a polyallylamine, a polyaminoalkyl vinyl ether, a polymer obtained by a process comprising reacting a polyamidoamine compound with epihalohydrin, a polymer obtained by a process comprising reacting a polyamine compound with epihalohydrin, an amphoteric polymer having an overall cationic charge, a polymer comprising an ethyleneimine unit and a homopolymer comprising a cationic or protonatable group.

3. The process of claim 2, wherein the polymer (a) is a polymer comprising a vinylamine unit obtained by at least one process selected from the group consisting of:

- (i) polymerizing a monomer of formula (I)



wherein R¹, R² are H or C₁- to C₆-alkyl, to obtain an initial polymer; and subsequently eliminating, partially or completely, the CO—R¹ groups comprised, in polymerized form, in the initial polymer forming amino groups, and

- (ii) degrading, by Hofmann degradation, a polymer comprising at least one selected from the group consisting of an acrylamide and a methacrylamide unit.

4. The process of claim 2, wherein the polymer (a) is at least one polymer comprising an ethyleneimine unit selected from the group consisting of:

a homopolymer of ethyleneimine;

a polymer obtained by a process comprising reacting a polyethyleneimine with an at least bifunctional crosslinking agent;

a polymer obtained by a process comprising reacting a polyamidoamine grafted with ethyleneimine with an at least bifunctional crosslinking agent;

an amidated polyethyleneimine obtained by a process comprising reacting a polyethyleneimine with a monobasic carboxylic acid,

a Michael adduct obtained by a process comprising reacting a polyethyleneimine with an ethylenically unsaturated acid, salt, ester, an amide, or a nitrile of a monoethylenically unsaturated carboxylic acid;

a phosphonomethylated polyethyleneimine,

a carboxylated polyethyleneimine; and

an alkoxyated polyethyleneimine.

5. The process of claim 1, wherein the aqueous dispersion (b) is a finely divided, cationic or amphoteric, aqueous polymer dispersion obtained by a process comprising:

- a first polymerizing of monomers, to obtain a prepolymer; and then
- a second polymerizing, by emulsion polymerization, of the prepolymer,

wherein the second polymerizing is carried out in an aqueous solution and in the presence of ethylenically unsaturated monomers.

6. The process of claim 4, wherein the first polymerizing is by solution polymerization and the monomers comprise:

- (i) a nitrogen-comprising monomer which carry comprising at least one selected from the group consisting of an amino group and a quaternary ammonium group,
- (ii) a nonionic, hydrophobic, ethylenically unsaturated monomer,
- (iii) optionally, an ethylenically unsaturated monomer comprising an acid group; and
- (iv) optionally, a nonionic, hydrophilic, ethylenically unsaturated monomer, and

wherein the ethylenically unsaturated monomers, in the second polymerizing, comprise a monomer mixture comprising nonionic, hydrophobic, ethylenically unsaturated monomers.

7. The process of claim 1, wherein, during the adding, the polymer (a) and the aqueous dispersion (b) are added to the paper stock in any desired sequence or as a mixture.

8. The process of claim 1, wherein the adding comprises: adding the polymer (a) to the paper stock; and then adding the aqueous dispersion (b) to the paper stock.

9. The process of claim 1, wherein, during the adding, the aqueous dispersion (b) and the polymer (a) are simultaneously added to the paper stock.

10. The process of claim 1, wherein the adding comprises: adding the aqueous dispersion (b) to the paper stock; and then

adding, by metering in, the polymer (a) to the paper stock.

11. The process of claim 1, wherein the polymer (a) is a cationic homo-polymer comprising (meth)acrylamide.

12. The process of claim 1, wherein the polymer (a) is a cationic copolymer comprising (meth)acrylamide.

13. The process of claim 1, wherein the polymer (a) is a polyallylamine.

14. The process of claim 1, wherein the polymer (a) is a polyaminoalkyl vinyl ether.

15. The process of claim 1, wherein the polymer (a) is obtained by a process comprising reacting a polyamidoamine compound with epihalohydrin.

16. The process of claim 1, wherein the polymer (a) is obtained by a process comprising reacting a polyamine compound with epihalohydrin.

17. The process of claim 1, wherein the polymer (a) is an amphoteric polymer having an overall cationic charge.

18. The process of claim 1, wherein the polymer (a) is a polymer comprising an ethyleneimine unit.

19. The process of claim 1, wherein the polymer (a) is a homopolymer comprising a cationic or protonatable group.

20. The process of claim 1, wherein the paper products are at least one selected from the group consisting of paper, board, and cardboard.

* * * * *