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(54) **PRODUCTION OF PAPER BOARD AND
CARDBOARD**

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(57) **ABSTRACT**

Paper, board and cardboard are produced by draining a paper stock in the presence of at least one cationic polymer on a wire by a process in which a mixture of at least one substantially linear, cationic polyelectrolyte and an optical brightener is added to the paper stock before sheet formation, said mixture containing at least two parts by weight of the polyelectrolyte per part by weight of the optical brightener.

PRODUCTION OF PAPER BOARD AND CARDBOARD

[0001] The present invention relates to a process for the production of paper and cardboard by draining a paper stock in the presence of at least one cationic polymer on a wire.

[0002] It is generally known that paper substantially comprises fibers, consisting of wood and/or of cellulose, and, if required, of mineral fillers, in particular calcium carbonate and/or aluminum silicate, and that the essential process in papermaking consists in separating these fibers and fillers from a dilute aqueous suspension of these substances with the aid of at least one wire. It is also known that certain chemicals are added to the suspension of fibers and fillers in water, both for improving the separation process and for achieving or improving certain properties of the paper. A very up-to-date overview of the paper chemicals which can be generally used and their use is to be found in—*Paper Chemistry*, J. C. Roberts ed., *Blackie Academic & Professional*, London, Second edition 1996 (ISBN 0 7514 0236 2)—and in—*Applications of Wet-End Paper Chemistry*, C.O. Au and I. Thorn eds., *Blackie Academic & Professional*, London, 1995 (ISBN 0 7514 0034 3). As is evident from the literature cited, many of the paper chemicals used are cationic water-soluble polymers or, in other words, cationic polyelectrolytes or are polycations preferably having a medium or high molecular weight. These products are added to the very dilute paper fiber suspension before the paper sheet is formed therefrom on the wire. Depending on their composition, they ensure, for example, that more fine material remains behind on the wire or that the water is separated off more rapidly on the wire or that certain substances are fixed on the paper fibers and hence do not enter the white water, it being possible for both cleanliness of the white water and the effect of the fixed substances, e.g. dyes or sizes, on the properties of the final paper product to be important in the case of the latter property. However, polycations can also increase the strength of the paper or impart improved residual strength to the paper in the wet state. If the object of a cationic polyelectrolyte is to retain more fine material on the wire and to accelerate the removal of the water on the wire, it is referred to as a retention aid. If the cationic polyelectrolyte is to bind undesired or desired substances, for example anionic oligomers and polymers, resins, tacky impurities, dyes, sizes, strength agents, etc., to the fibers, the term fixing agent is used. If the cationic polyelectrolyte improves a paper property relevant to strength, it is a strength agent.

[0003] One of the most important objects in the production of papers and cardboards which are to be written on or printed on, also referred to below as graphic arts papers, is a high level of whiteness of the surface of the paper or of the cardboard. A high level of whiteness not only imparts the impression of cleanliness and safety but also increases the legibility of the script as a result of the greater contrast to the ink, especially in poor illumination. A particular advantage of the high level of whiteness is evident if the paper or cardboard is to be printed on, written on or painted in color. The whiter the surface, the better and more natural is the color contrast, particularly when writing on, printing on or painting with light or translucent colors or pastel shades. As a result of the recently increasing use of wastepaper in the production of graphic arts papers, the papermaker's product is substantially grayer than with the use of fresh fibers.

[0004] For these reasons, the papermakers are making considerable efforts to increase the whiteness of their product, particularly if it is paper for graphic arts purposes. As early as during the preparation of the raw materials, whether chemical pulp, mechanical pulp, deinked wastepaper stock or pigment, a major effort is made to obtain these raw materials in as white a form as possible. During the actual papermaking, an attempt is made to avoid all assistants and conditions which might impair the whiteness of the paper.

[0005] A known method for increasing the whiteness and brightness of paper is the use of optical brighteners, which, according to the prior art to date, is added to the paper pulp during various operations of papermaking and of paper conversion or is applied to the paper.

[0006] These are dye-like fluorescent compounds which absorb shortwave, ultraviolet light invisible to the human eye and emit it again as longer-wave blue light, with the result that the human eye perceives a higher level of whiteness and the degree of whiteness is thus increased.

[0007] The optical brighteners used in the paper industry are generally 1,3,5-triazinyl derivatives of 4,4'-diaminostilbene-2,2'-disulfonic acid, which derivatives may carry additional sulfo groups, for example 2, 4 or 6 altogether. An overview of such brighteners is to be found, for example, in: Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition, 2000 Electronic Release, OPTICAL BRIGHTENERS—Chemistry of Technical Products. However, more recent brightener types are also suitable, for example derivatives of 4,4'-distyrylbiphenyl, as also described in the above-mentioned Ullmann's Encyclopedia of Industrial Chemistry.

[0008] The optical brighteners can be used in various phases of papermaking and paper conversion. The optical brighteners can be added, for example, to the paper pulp but also in a size press together with surface sizes or strength agents, e.g. starch, or together with further assistants. Most frequently, optical brighteners are used in paper coating slips with which paper and cardboard are coated. The use in the pulp is particularly advantageous when the uniformity of the brightening and good fastness to bleeding are important (cf. for example W. Bieber, A. Brockes, B. Hunke, J. Krüsemann, D. Loewe, F. Müller, P. Mummehoff, in *Blankophor®—Optische Aufheller für die Papierindustrie*, Bayer, Geschäftsbereich Farben, Leverkusen, SP 600, 8.89, page 51). Even when optical brighteners are used in the paper coating slips, adding optical brighteners to the paper pulp is advisable (see above, W. Bieber, et al.; K. P. Kreutzer, *Grundprozesse der Papiererzeugung 2: Grenzflächenvorgänge beim Einsatz chemischer Hilfsmittel*, H.-G. Völkel and R. Grenz (eds.), PTS Munich, 2000, PTS manuscript: PTS-GPE—SE 2031-2, Chapter 8, page 21).

[0009] However, the use of optical brighteners leads to optimum success only when they are present in the paper not only in an optimum distribution but also in optimum chemical structure and conformation, since, for example in the case of stilbenes, only the trans form is optically active and this exhibits maximum fluorescence only when it is distributed in monomolecular form and is fixed in a plane (see above, K. P. Kreutzer). When added to the paper pulp, this generally results through adsorption onto the cellulose. The brighteners used are chemically modified so that they have a high affinity to cellulose and therefore require no additional fixing agents or brightener enhancers, i.e. carriers. On

the contrary, when the optical brighteners are used in the paper pulp, it is necessary to pay greater attention to ensuring that no further chemicals in the pulp reduce the effects of the brighteners (cf. literature above). The presence of cationic polymers is considered to be particularly harmful to the action of optical brighteners. In the paper industry, they are generally considered as fluorescence extinguishers, cf. W. Bieber et al, Blankophor®—Optische Aufheller für die Papierindustrie, Bayer AG, SP600, 8.89, page 59.

[0010] EP-A-0 192 600 discloses stable solutions of optical brighteners. They contain from 10 to 500 parts by weight of a polyethylene glycol having an average molar mass of from 1 000 to 3 000 and at least 20% by weight, based on the total mixture, of water per 100 parts by weight of a brightener. The mixtures are used as optical brighteners in paper coating slips.

[0011] EP-A-0 071 050 discloses linear, basic polymers which contain 90-10 mol % of vinylamine units and 10-90 mol % of N-vinylformamide units in polymerized form. They are prepared by free radical polymerization of N-vinylformamide and subsequent partial hydrolysis of the polymer thus obtained. The partially hydrolyzed poly-N-vinylformamides are used, for example, as retention aids, drainage aids and flocculants in papermaking.

[0012] The prior German Application 101 38 631.1 discloses a process for the production of coated paper having a high level of whiteness, a base paper or a precoated paper being treated with at least one substance which enhances the efficiency of optical brighteners and then being coated with a paper coating slip which contains an optical brightener. Examples of compounds which enhance the efficiency of optical brighteners are homo- and copolymers of N-vinylcarboxamides or the polymers obtainable therefrom by hydrolysis and containing vinylamine units.

[0013] The prior German Application 101 42 887.1 discloses a process for the production of coated papers having a high level of whiteness, for example mixtures of

[0014] (i) from 0.05 to 5% by weight of at least one optical brightener,

[0015] (ii) from 1 to 30% by weight of at least one polymer which contains N-vinylcarboxamide units and

[0016] (iii) from 98.95 to 65% by weight of a solvent being applied to the surface of the paper.

[0017] It is an object of the present invention to provide an improved process for the production of paper, board and cardboard, products having a higher degree of whiteness compared with the known processes being obtained.

[0018] We have found that this object is achieved, according to the invention, by a process for the production of paper, board and cardboard by draining a paper stock in the presence of at least one cationic polymer on a wire, if a mixture of at least one substantially linear, cationic polyelectrolyte and an optical brightener is added to the paper stock before sheet formation, at least two parts by weight of the polyelectrolyte being used per part by weight of the optical brightener.

[0019] Cationic polyelectrolytes are to be understood as meaning polymers which carry positive charges and which

are distributed over the polymer chain. Cationic polyelectrolytes are furthermore to be understood as meaning those substances which may be nonionic in the dry state but, owing to their basic character, are protonated in water or other solvents and hence carry positive charges.

[0020] The mixtures which are added to the paper stock before sheet formation usually contain

[0021] (i) from 0.05 to 5, preferably from 0.1-3, particularly preferably 0.2-2,% by weight of an optical brightener,

[0022] (ii) from 1 to 30, preferably 2-20, particularly preferably 5-15,% by weight of at least one substantially cationic polymer and

[0023] (iii) from 98.5 to 65, preferably 97.9-77, particularly preferably 94.8-83,% by weight of at least one solvent,

[0024] the sum always being 100% by weight. If other assistants typical for paper (see below) are also present, the content of solvent iii) is reduced correspondingly.

[0025] The results obtained by the novel process were not to be expected because, according to the general knowledge, it was to be assumed that cationic polyelectrolytes would lead to extinguishing of the fluorescence of the conventional optical brighteners (cf. for example K. P. Kreutzer, loc. cit., Chapter 8, page 22; cf. W. Bieber et al., loc. cit., pages 58, 65 and 71; F. Colling, The use and mis-use of dyestuffs and fluorescent whitening agents, in *Applications of Wet-End Paper Chemistry*, C.O. Au and I. Thorn ed., Blackie Academic & Professional, London, 1995, ISBN 0 7514 034 3, pages 130, 132-135). In addition, it is known from the prior art that optical brighteners and cationic electrolytes are mutually precipitated (cf. W. Bieber et al., loc. cit., page 59). Besides, these views are widespread in the paper industry.

[0026] It is furthermore surprising that highly effective optical brighteners which, owing to poor substantivity, cannot be used in the paper pulp, for example stilbene derivatives having 6 sulfo groups, are also suitable for the novel process (S. G. Murray, Dyes and fluorescent whitening agents for paper, in *Paper Chemistry*, ed. J. C. Roberts, 2nd edition, Blackie Academic & Professional, Glasgow (1996), page 187). When they are used, no fluorescence is detectable in the white water.

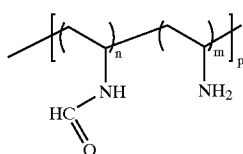
[0027] The cationic polyelectrolytes (ii) which can be used in the novel process are known. For example, polymers which are known by the following chemical trivial names can be used: polyvinylamine, polyallylamine, poly(diallyldimethylammonium chloride), cationic polyvinylformamide, cationic polyvinylpyrrolidone, cationic polyvinylacetamide, cationic polyvinylmethylformamide, cationic polyvinylmethylacetamide, poly(dimethylaminopropylmethacrylamide), poly(dimethylaminoethyl acrylate), poly(diethylaminoethyl acrylate), poly(acryloylethyltrimethylammonium chloride), poly(acrylamidopropyltrimethylammonium chloride), poly(methacrylamidopropyltrimethylammonium chloride), cationic polyacrylamide, poly(vinylpyridine), hexadimethrine bromide, poly(dimethylamine-co-epichlorohydrin), poly(dimethylamine-co-epichlorohydrin-co-ethylendiamine), poly(amidoamine-epichlorohydrin) and their salts if they are basic polymers. Polymers containing vinylamine units, such

as cationic polyvinylformamides and polyvinylamine, and furthermore cationic polyacrylamide and poly(diallyldimethylammonium chloride) are preferred. Polymers which contain vinylamine units and are in the form of the free bases or salts are particularly preferred.

[0028] The preparation of the cationic polyelectrolytes has long been very well known.

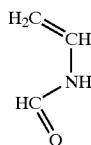
[0029] The cationic polyelectrolytes (ii) which can be used in the novel process have different molecular weights which are characterized below with the aid of the Fikentscher K values. The molecular weights of the cationic polyelectrolytes which can be used according to the invention are not limited. As a rule, they correspond to K values of from 20 to 200, preferably from 30 to 150, particularly preferably from 40 to 100 (the stated K values are determined according to H. Fikentscher in 5% strength aqueous sodium chloride solution at pH 7, 25° C. and a polymer concentration of 0.1% by weight).

[0030] The very particularly preferred polymers containing vinylamine units, such as cationic polyvinylformamides, contain vinylamine and vinylformamide units according to the formula (I)



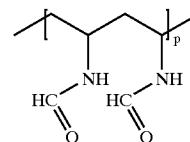
(I)

[0031] where the ratio n:m is from 99:1 to 1:99 and p may be from 30 to 30 000. Some or all of the vinylamine units of the polymers may be present as salts with mineral acids, such as hydrochloric acid, sulfuric acid or phosphoric acid, or as salts with organic acids (e.g. formic acid, acetic acid, propionic acid, toluenesulfonic acid, benzenesulfonic acid or methanesulfonic acid). The polymers containing vinylamine units are prepared by polymerizing, for example, N-vinylformamide of the formula (II)



(II)

[0032] to give a polyvinylformamide of the formula (III) and partly cleaving this with removal (or hydrolysis) of the formyl group to give the copolymer (I). On complete hydrolysis of the formyl groups of polyvinylformamides, polyvinylamines are obtained. The free bases of the polymers containing vinylamine units are formed if the hydrolysis is carried out using bases, such as sodium hydroxide solution or potassium hydroxide solution, whereas the vinylamine units of the polymers are present in salt form on hydrolysis with acids.



(III)

[0033] A preferred degree of hydrolysis of the carboxamido groups is from 5 to 90, particularly preferably from 10 to 50, mol %, based on the N-vinylcarboxamide units contained in the N-vinylcarboxamide polymers. The cleavage of the N-vinylcarboxamide units contained in the polymer is preferably effected in the presence of bases, for example sodium hydroxide, potassium hydroxide, alkaline earth metal hydroxides, ammonia or amines.

[0034] Cationic polymers of N-vinylformamide are obtained in a particularly suitable manner by hydrolytically cleaving homopolymers of N-vinylformamide with defined amounts of acid or base to give the desired degree of hydrolysis, as described in EP-B-0 071 050 mentioned as prior art. The amino groups formed thereby on the polymer chain are protonated to a greater or lesser extent depending on the pH of the solution and thus impart a more or less cationic character to the polymer.

[0035] If elimination of the formyl group is desired after the polymerization, this can be carried out, for example, in water. Elimination of the formyl group during the hydrolysis is effected in general at from 20 to 200° C., preferably from 40 to 180° C., in the presence of acids or bases. The hydrolysis in the presence of acids or bases is particularly preferably carried out at from 70 to 90° C.

[0036] From about 0.05 to 1.5 equivalents of an acid, such as hydrochloric acid, hydrobromic acid, phosphoric acid or sulfuric acid, per formyl group equivalent in the poly-N-vinylformamide are required, for example, with the acidic hydrolysis. The pH in the acidic hydrolysis is, for example, from 2 to 0, preferably from 1 to 0.

[0037] In addition the hydrolysis of the formyl groups of the poly-N-alkyl-N-vinylformamide can also be carried out in an alkaline medium, for example at a pH of from 11 to 14. This pH is preferably established by adding alkali metal bases, e.g. sodium hydroxide solution or potassium hydroxide solution. However, it is also possible to use ammonia, amines and/or alkaline earth metal bases. From 0.05 to 1.5, preferably from 0.4 to 1.0, equivalents of a base are used for the alkaline hydrolysis.

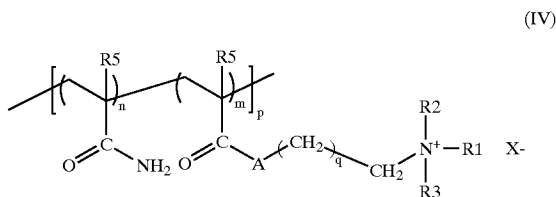
[0038] The cleavage can also be carried out at high temperatures, for example above 100° C., preferably from 120 to 180° C., particularly preferably from 140 to 160° C., in the presence of a solvent, e.g. water, in the absence of acids or bases. This is preferably carried out under conditions above the critical point of the solvent, for example using supercritical water.

[0039] In the hydrolysis (i.e. the formyl group is eliminated from the poly-N-vinylformamide in water in the presence of acids or bases), carboxylic acid, for example formic acid, or a salt thereof is obtained as the byproduct. The solutions thus obtainable can be used without further

working-up in the novel process, but the hydrolysis or solvolysis products can also be separated off. For separating off low molecular weight fractions, for example neutral salts, the solutions obtained are treated, for example, with ion exchangers or subjected to an ultrafiltration.

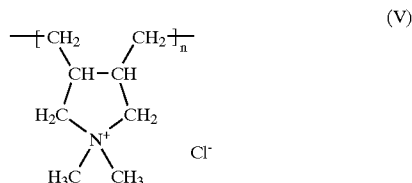
[0040] The cationic polyacrylamides which can be used for the novel process are known, cf. D. Horn, F. Linhart, in *Paper Chemistry*, ed. J. C. Roberts, 2nd edition, Blackie Academic & Professional, Glasgow (1996), pages 66-67, and literature cited there.

[0041] They frequently consist of polymers of the formula (IV),



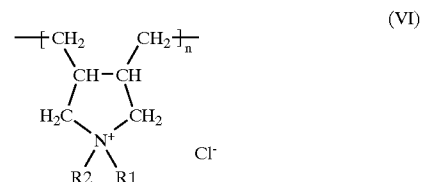
[0042] where A is oxygen or an NH group, R1 may be hydrogen or lower alkyl of 1-3 carbon atoms, R2 and R3 may be lower alkyl of 1-5 carbon atoms or benzyl and R5 may be hydrogen or methyl, the ratio n:m may be from 99:1 to 0:100, q may be 1 or 2, p may be from 50 to 50 000 and X⁻ may be any desired anion, e.g. chloride, bromide, ½ sulfate, hydrogen sulfate, methylsulfate, ethylsulfate, nitrate, formate, acetate or toluenesulfonate. In addition, acrylic acid or methacrylic acid can be incorporated as polymerized units into the polymer chain up to an amount such that the total charge of the polymer remains positive.

[0043] The poly(diallyldimethylammonium chloride) which can be used in the novel process can be characterized, for example, with the aid of the formula (V)



[0044] where n may be from 30 to 30 000. Such polymers have been known for many years, cf. D. Horn, F. Linhart, in *Paper Chemistry*, ed. J. C. Roberts, 2nd edition, Blackie Academic & Professional, Glasgow (1996), page 70; G. Butler, in *Polymeric Amines and Ammonium Salts*, ed. E. J. Goethals, Pergamon Press, Oxford 125, (1980).

[0045] Other diallyldialkylammonium chlorides are also suitable, for example those of the polymer formula (VI),



[0046] where R^1 and R^2 , independently of one another, may be alkyl of 2 to 4 carbon atoms, it also being possible for R^1 or R^2 to be hydrogen, and where n may be from 30 to 30 000.

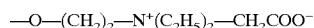
[0047] Preferably used cationic polyelectrolytes are hydrolyzed homopolymers of N-vinylformamide having a degree of hydrolysis of from 1 to 99 mol %, copolymers of acrylamide and cationic monomers (e.g. amino- or ammonium-containing monomers), polymers of diallyldimethylammonium chloride and the polyamidoamine/epichlorohydrin resins which can be used as wet strength agents.

[0048] Cationic polyelectrolytes which are obtainable by copolymerization of starting monomers of the abovementioned polyelectrolytes can of course also be used for the novel process. For example, copolymers of vinylformamide (formula (II)) and diallyldimethylammonium chloride or of vinylformamide and basic acrylates, as described in EP-B-0 464 043, and also copolymers of acrylamide and diallyldimethylammonium chloride or other diallyldialkylammonium chlorides can also be used. The solubility of the cationic polyelectrolytes in the solvent (iii) used is as a rule from at least 1% by weight to complete solubility, for example at 20° C.

[0049] The mixing ratios in the mixtures of the optical brighteners and the cationic polyelectrolytes may be from 1:2 to 1:100, but a substantial excess of cationic polyelectrolytes is advantageous. Particularly advantageous is the use of optical brighteners and cationic polyelectrolytes in the weight ratio of from 1:2 to 1:50, very particularly preferably from 1:5 to 1:20.

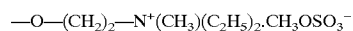
[0050] All optical brighteners (i) can be used for the novel process. For example, brighteners as described in Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition, 2000 Electronic Release, OPTICAL BRIGHTENERS—Chemistry of Technical Products, Section 2.1 to Section 2.9, can be used.

[0051] Suitable optical brighteners (i) belong, for example, to the group consisting of the distyrylbenzenes, for example cyano-substituted 1,4-distyrylbenzenes having cyano groups in the positions 2' and 3'[CAS Reg. No. 79026-03-2] or in positions 2' and 2"[13001-38-2], 3' and 3"[36755-00-7], 3' and 4"[79026-02-1] and 4' and 4"[13001-40-6], or amphoteric compounds, e.g. [84196-71-4], which carry a



[0052] group in each case in the 2' and 2" positions, to the group consisting of the distyrylbiphenyls, for example 4,4'-di(2-sulfostyryl)biphenyl disodium salt [27344-41-8], 4,4'-di(3-sulfostyryl)biphenyl disodium salt [51119-63-2], 4,4'-

di(4-chloro-3-sulfostyryl)biphenyl disodium salt [42380-62-1], 4,4'-di(6-chloro-3-sulfostyryl)biphenyl disodium salt [60477-28-3], 4,4'-di(2-methoxystyryl)biphenyl [40470-68-6] or a 4,4'-di(styryl)biphenyl which carries a



[0053] group in position 2 on the styryl radical [72796-88-4], to the group consisting of the divinylstilbenes, for example 4,4'-di(ethoxycarbonylviny)stilbene [60683-03-6] or 4,4'-di(cyanovinyl)stilbene [60682-87-3], to the group consisting of the triazinylaminostilbenes, e.g. 1,3,5-triazinyl derivatives of 4,4'-diaminostilbene-2,2'-disulfonic acid, such as anilino derivatives which carry the following radicals in each case in position 3 on the triazine rings: methoxy (CAS Reg. No. [3426-43-5]), aminomethyl [35632-99-6], ethylamino [24565-13-7], hydroxyethylamino [12224-16-7], N-hydroxyethyl-N-methylamino [13863-31-5], bis(hydroxyethyl)amino [4193-55-9], morpholino [16090-02-1], phenylamino [133-66-4], N-2-aminocarbonylethyl-N-2-hydroxyethylamino [68444-86-0] or such as anilinosulfonic acid derivatives which carry the following radicals in each case in position 3 on the triazine rings: N-hydroxyethylamino and additionally on the anilino group in position 5 of the triazine ring, sulfo in position 3 (CAS Reg. No. [61968-74-9]), N-bis(hydroxyethyl)amino and, additionally on the anilino group, sulfo in position 3 (CAS Reg. No. [12224-02-1]), N-bis(2-hydroxypropyl)amino and, additionally on the anilino group, sulfo in position 4 (CAS Reg. No. [99549-42-5]), N-bis(hydroxyethyl)amino and, additionally on the anilino group, sulfo in position 4 (CAS Reg. No. [16470-24-9]), N-hydroxyethyl-N-methyl-amino- and, additionally on the anilino group, sulfo in position 4 (CAS Reg. No. [74228-28-7]), diethylamino and, additionally on the anilino group, sulfo in positions 2 and 5 (CAS Reg. No. [83512-97-4]), N-bis(hydroxyethyl)amino and, additionally on the anilino group, sulfo in positions 2 and 5 (CAS Reg. No. [76482-78-5]), or morpholino and, additionally on the anilino group, sulfo in positions 2 and 5 (CAS Reg. No. [55585-28-9]), or to the group consisting of the stilbenyl-2H-triazoles, e.g. stilbenyl-2H-naphtho[1,2-d]triazoles, such as the sodium salt of 4-(2H-naphtho[1,2-d]triazol-2-yl)stilbene-2-sulfonic acid [6416-68-8] or those which carry sulfo in position 6 on the naphthol ring and at position 2 of the stilbene skeleton [2583-80-4], or cyano in position 2 and chlorine in position 4' on the stilbene skeleton [5516-20-1] or, for example, bis(1,2,3-triazol-2-yl)stilbenes, such as 4,4'-bis(4-phenyl-1,2,3-triazol-2-yl)stilbene-2,2'-disulfonic acid dipotassium salt [52237-03-3] or 4,4'-bis(4-(4'-sulfophenyl)-1,2,3-triazol-2-yl)stilbene-2,2'-disulfonic acid tetrasodium salt [61968-72-7], or to the group consisting of the benzoxazoles, e.g. stilbenylbenzoxazoles, for example 5,7-dimethyl-2-(4'-(4"-methoxycarbonyl)-phenylstilben-4-yl)-benzoxazole [18039-18-4] or those which carry other heterocycles in the 4" position, e.g. [64893-28-3], or bis-(benzoxazoles), e.g. ethylene-, thiophene-, naphthylene-, phenylethylene- or stilbene-bridged bisbenzoxazoles, such as those having the CAS numbers [1041-00-5], [2866-43-5], [7128-64-5], [5089-22-5], [1552-46-1], [1533-45-5] or [5242-49-9].

[0054] It is furthermore possible to use furans, benzo[b]furans and benzimidazoles, e.g. bis(benzo[b]furan-2-yl)biphenyls, for example sulfonated 4,4'-bis(benzo[b]furan-2-yl)biphenyls, or cationic benzimidazoles, for example 2,5-

di(1-methylbenzimidazol-2-yl)furan [4751-43-3], [72829-17-5], [74878-56-1], [74878-48-1] or [66371-25-3], or 1,3-diphenyl-2-pyrazolines, e.g. 1-(4-amidosulfonylphenyl)-3-(4-chlorophenyl)-2-pyrazoline [2744-49-2], [60650-43-3], [3656-22-2], [27441-70-9], [32020-25-0], [61931-42-8] or [81209-71-4], and tertiary and quaternary amine salts of 1,3-diphenyl-2-pyrazoline derivatives, e.g. [106359-93-7], [85154-08-1], [42952-22-7], [63310-12-3][12270-54-1] or [36086-26-7], and coumarins, e.g. 7-diethylamino-4-methylcoumarin [91-44-1] and [6025-18-9], [19683-09-1], [3333-62-8], [63660-99-1], [26867-94-7][52725-14-1] and naphthalimides, e.g. 4-acetylamino-N-(n-butyl)naphthalimide [3353-99-9], 4-methoxy-N-methylnaphthalimide [3271-05-4], [3271-05-4], [22330-48-9], [25826-31-7], [26848-65-7] or [60317-11-5], and 1,3,5-triazin-2-yl derivatives, for example (4,6-dimethoxy-1,3,5-triazin-2-yl)pyrene [3271-22-5] or 4,4'-di(4,6-diphenyl-1,3,5-triazin-2-yl)stilbene [6888-33-1].

[0055] 4,4'-Distyrylbiphenyl derivatives or stilbene derivatives which are substituted by up to 6, particularly preferably by 2, 4 or 6, sulfo groups can preferably be used, preferably the Blankophor® brands from Bayer AG, particularly preferably Blankophor® P and Blankophor® PSG, preferably furthermore the Tinopal® brands from Ciba Specialty Chemicals, particularly preferably Tinopal® MC liquid, Tinopal® ABP-Z liquid, Tinopals SPP-Z liquid and Tinopal® SK-B liquid and preferably furthermore the Leukophor® brands from Clariant AG, particularly preferably Leukophor® APN, UO, NS or SHR.

[0056] The optical brighteners and cationic polymers which contain polymerized vinylformamide units can be added separately from one another to the paper stock, the cationic polyelectrolyte being metered first, followed by the optical brightener, or the sequence of addition being reversed. Suitable solvents (iii) for the mixtures are, for example, water, methanol, ethanol, isopropanol, n-propanol, n-butanol, dimethylformamide and N-methylpyrrolidone, water being preferred. The concentration should be chosen so that the respective metering processes and subsequent dilution processes can be carried out optimally owing to, for example, the viscosity of the mixture. Optimum viscosities for various metering processes and dilution processes are known to a person skilled in the art. Customary concentrations of the mixtures are from 2 to 20% by weight.

[0057] The molecular weight of the cationic polyelectrolyte to be used according to the invention should be adapted to the respective desired profile of the polyelectrolytes. If the cationic polyelectrolyte is to act, for example, as a retention aid in papermaking, cationic polymers having a very high molecular weight are preferably used. If the cationic polymers are to be effective as fixing agents or as strength agents, cationic polymers having medium to low molecular weights are used. The addition of retention aids and drainage aids to the paper stock before drainage on the wire is part of the general prior art. The cationic polymers generally used have very high molecular weights of from 2 to 20 million Dalton (cf. F. Linhart, *Retention, PTS-Seminar—Grundlagen der Chemie für Papieringenieure*, Part 2, J. Weigl and R. Grenz (eds.), Munich: PTS Munich, 1991, CP—SE 111, Chapter 7, page 9). However, cationic polymers having molecular weights of from 500 000 to 2 million Dalton are also successfully used as retention aids. The amounts of these

polymers used are from 50 g/t to 5 kg/t, preferably from 100 g/t to 2 kg/t, based on dry paper stock.

[0058] The cationic fixing agents added in many cases to the paper stock have substantially lower molecular weights which differ very greatly depending on the chemical nature and the function of the polymer and are from 10 000 to 500 000 Dalton. The amounts of fixing agents used are from 100 g/t to 2 kg/t, based on dry paper stock. The molecular weights of polymeric cationic strength agents vary in the very wide range of from a few hundred Dalton, as is possible, for example, in the case of reactive wet-strength agents through 100 000 to 500 000 Dalton in the case of synthetic dry-strength agents (J. Marton, Dry-Strength Additives, in *Paper Chemistry*, J. C. Roberts ed., Blackie Academic & Professional, London, Second edition 1996, ISBN 0 7514 0236 2) to extremely high molecular weights in the case of cationic polysaccharides, such as starches or vegetable gums. In the case of the strength agents the amounts used may range from 0.5 to 100 kg/t.

[0059] The present invention also relates to the use of mixtures of

[0060] (i) from 0.05 to 5% by weight of at least one optical brightener,

[0061] (ii) from 1 to 30% by weight of at least one substantially cationic polymer and

[0062] (iii) from 98.95 to 65% by weight of at least one solvent

[0063] as an additive to the paper stock in the production of paper, board and cardboard having a high degree of whiteness. The mixtures may be dispersions or, preferably, solutions.

[0064] The mixtures of the two components (i) and (ii) are metered into the paper stock by the methods customary in the paper industry. This means that the mixtures are diluted with water continuously or batchwise to concentrations of from 0.01 to 1% by weight before addition to the paper stock, in order to achieve more rapid and more uniform mixing with the paper stock. However, this does not mean that the mixtures cannot be added undiluted or in less dilute form to the paper stock. The feed point of the mixtures depends on the requirements and on the desired profile of the cationic polyelectrolyte in the mixture. If the mixture is intended not only to increase the whiteness of the paper but also simultaneously to increase the retention and the drainage rate, addition in the low-density stock shortly before the head box, before or after the pressure screen, is appropriate. When the mixture is used as a whiteness-increasing fixing agent, the mixture can be added throughout the stock preparation region, for example also in the high-density stock, in the mixing chest, in the machine chest or to the individual stock components before they are mixed. If the cationic polyelectrolyte in the mixture is to act as a strength agent, it is advisable to add the mixture at a point which is customary for the addition of strength agents, for example in the mixing chest or machine chest, but also before the beater or in the low-density stock region. For all applications, the optimum metering point must be determined in each individual case by practical experiments.

[0065] The novel process is preferably used in the production of highly white papers and cardboards whose start-

ing materials should already have sufficient basic whiteness. Highly white fibers and fillers are therefore mainly used for this purpose. The fibers which may be used primarily include chemical pulps, for example bleached sulfate pulp based on conifers, birches or eucalyptus, and beech sulfite pulp, based on spruces and on beeches and other deciduous trees, but also chemical pulps which are obtained from wood by other processes. Bleached mechanical pulps, e.g. groundwood, pressure groundwood (PGW), refiner mechanical pulp (RMP), thermomechanical pulp (TMP) or chemothermomechanical pulp (CTMP, APTMP and further variants), based on conifers and aspen or other suitable deciduous trees, are furthermore suitable. Also suitable for this purpose are fibers from annuals, e.g. cotton, cotton linters, bleached straw pulp from straw of various cereal species, bleached bagasse pulp, hemp, flax, kenaf, etc. A very important fiber of the novel process is a bleached fiber freed from printing inks and based on waste graphic arts papers, i.e. deinked pulp (DIP). The fillers suitable for the novel process are generally aluminum silicates, such as kaolin or modifications obtained by further treatment thereof, magnesium silicates, e.g. talc, calcium carbonate in the form of ground marble or limestone or in the form of natural or ground chalk or in the form of precipitated calcium carbonate, calcium sulfate in the form of gypsum, or titanium dioxide.

[0066] The papers, boards or cardboards produced by the novel process can be printed on in conventional processes, for example offset, letterpress or gravure printing processes, flexographic printing processes or digital printing processes, e.g. laser printing or inkjet printing processes, but can also be otherwise processed or converted, e.g. coated.

[0067] The novel process helps the person skilled in the art to perform the difficult task of producing papers, boards and cardboards in an improved process or with higher quality and simultaneously increased whiteness with relatively simple means and high flexibility.

[0068] In the examples which follow, parts are by weight. The K values of the polymers were determined according to H. Fikentscher, *Cellulose-Chemie*, 13 (1932), 58-63 and 71-74, in 5% strength by weight aqueous solution at pH 7, 25° C. and a polymer concentration of 0.1% by weight.

EXAMPLE

[0069] A paper having a basis weight of 80 g/m² was produced according to the prior art on an experimental paper machine from an aqueous paper stock comprising 70 parts of birch sulfate pulp, 30 parts of pine sulfate pulp, 20 parts of chalk filler (Hydrocarb® 60 from Plüss-Staufer AG), 0.05 part of stock deaerator (Afrasil® SLO from BASF Aktiengesellschaft), 1.0 part of engine size (Basoplast® 2018 LC from BASF Aktiengesellschaft) and 0.5 part of soluble cationic starch (Solvitose® BPN from Avebe).

[0070] 1 part of an aqueous solution containing 10% by weight of a medium molecular weight polyvinylformamide having a K value of about 90 and a degree of hydrolysis of 30% and 0.5% (solid) of an optical brightener having 4 sulfo groups (Tinopal® ABP-Z liquid) was added as a retention aid, after the pressure screen. The retention was determined by comparison of the solids concentrations of the finally diluted paper pulp before the head box and of the white water (cf. F. Linhart, *Retention, PTS-Seminar—Grundlagen der Chemie für Papieringenieure*, Part 2, J. Weigl and R.

Grenz (eds.), Munich: PTS Munich, 1991, CP—SE 111, Chapter 7, page 1). The whiteness and the calorimetric values according to the CIELAB system (DIN 6174) were determined for the paper obtained as the end product. Furthermore, the paper obtained as the end product was checked visually for fluorescence by illumination with an ultraviolet lamp. The complete fixing of the brightener in the paper was investigated by impregnating a strip of highly absorptive white wood-free paper with white water and checking visually for fluorescence under illumination with ultraviolet light.

[0071] In the comparative experiment, 0.02 part of high molecular weight cationic polyacrylamide (Polymin® PR 8140 from BASF Aktiengesellschaft) was used according to the prior art as a retention aid before the pressure screen, and 0.3 part of bentonite activated with alkali (VO 004 from Erbsloh) was used after the pressure screen.

[0072] The results of the investigations are recorded in the table below.

TABLE

| | Invention | Comparative example |
|-------------------------------------|-----------|---------------------|
| Retention (%) | 95.1 | 80.5 |
| CIE whiteness according to DIN 6174 | 94.3 | 81.4 |
| a* (Red shift) | 1.18 | 0.38 |
| b* (Blue shift) | -0.53 | 2.39 |
| Fluorescence of the paper | strong | none |
| Fluorescence of the white water | none | none |

[0073] As is evident from the table, the novel process gives very good retention and simultaneously greatly increases the whiteness of the paper, the desired shift in hue to blue and red occurring. Particularly surprising is the extent of the increase in whiteness when it is considered that only 0.005 part of optical brightener, based on about 122 parts of solid paper stock, was used as a proportion of the mixture.

1. A process for the production of paper and cardboard comprising draining a paper stock in the presence of at least one cationic polymer on a wire, and wherein a mixture comprising at least one substantially linear, cationic polyelectrolyte selected from polymers containing vinylamine units, copolymers of acrylamide and cationic monomers or polymers of diallyldimethylammonium chloride, one or more optical brighteners, one or more solvents, and optionally, a retention and drainage aid, is added to the paper stock before sheet formation, and wherein at least two parts by weight of the polyelectrolyte is used per part by weight of the optical brightener.

2. The process as claimed in claim 1, wherein the at least one cationic polyelectrolyte is a hydrolyzed homopolymer of N-vinylformamide having a degree of hydrolysis from 1 to 99 mol %.

3. The process as claimed in claim 1, wherein the at least one cationic polyelectrolyte is selected from copolymers of acrylamide and cationic monomers, and wherein the cationic monomers are monomers containing an amino group or an ammonium group.

4. The process as claimed in claim 1, wherein at least 5 parts by weight of at least one cationic polymer is used per part by weight of optical brighteners.

5. The process as claimed in claim 1, wherein the mixture comprises:

(i) from 0.05 to 5% by weight of the one or more optical brighteners,

(ii) from 1 to 30% by weight of the at least one substantially cationic polymer,

(iii) from 98.95 to 65% by weight of the one or more solvents and optionally the retention and drainage aid.

6. A process for producing paper, board or cardboard, each having high degree of whiteness, comprising adding to paper stock a mixture comprising:

(i) from 0.05 to 5% by weight of at least one optical brightener,

(ii) from 1 to 30% by weight of at least one substantially cationic polymer selected from polymers containing vinylamine units, copolymers of acrylamide and cationic monomers or polymers of diallyldimethylammonium chloride, and

(iii) from 98.95 to 65% by weight of at least one solvent and optionally a retention and drainage aid.

7. A paper, board or cardboard obtained by a process as claimed in claim 1.

8. The process as claimed in claim 2, wherein at least 5 parts by weight of at least one cationic polymer is used per part by weight of optical brighteners.

9. The process as claimed in claim 3, wherein at least 5 parts by weight of at least one cationic polymer is used per part by weight of optical brighteners.

10. The process as claimed in claim 2, wherein the mixture comprises:

(i) from 0.05 to 5% by weight of the one or more optical brighteners,

(ii) from 1 to 30% by weight of the at least one substantially cationic polymer,

(iii) from 98.95 to 65% by weight of the one or more solvents and optionally the retention and drainage aid.

11. The process as claimed in claim 3, wherein the mixture comprises:

(i) from 0.05 to 5% by weight of the one or more optical brighteners,

(ii) from 1 to 30% by weight of the at least one substantially cationic polymer,

(iii) from 98.95 to 65% by weight of the one or more solvents and optionally the retention and drainage aid.

12. The process as claimed in claim 4, wherein the mixture comprises:

(i) from 0.05 to 5% by weight of the one or more optical brighteners,

(ii) from 1 to 30% by weight of the at least one substantially cationic polymer,

(iii) from 98.95 to 65% by weight of the one or more solvents and optionally the retention and drainage aid.

13. A paper, board or cardboard obtained by a process as claimed in claim 2.

14. A paper, board or cardboard obtained by a process as claimed in claim 3.

15. A paper, board or cardboard obtained by a process as claimed in claim 4.

16. A paper, board or cardboard obtained by a process as claimed in claim 5.

17. A composition comprising:

(i) from 0.05 to 5% by weight of at least one optical brightener,

(ii) from 1 to 30% by weight of at least one substantially cationic polymer selected from polymers containing vinylamine units, copolymers of acrylamide and cationic monomers or polymers of diallyldimethylammonium chloride, and

(iii) from 98.95 to 65% by weight of at least one solvent and optionally a retention and drainage aid.

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