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(54) **Process for dyeing pulp**

(57) The invention relates to a process for dyeing pulp comprising bleached pulp comprising adding a cationic dye to the pulp, and then adding a fluorescent whitening agent, followed by forming the paper sheet. Further, the invention relates to a paper obtained by this process.

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Description

[0001] The present invention relates to a process for dyeing pulp and a paper obtained by this process.

[0002] It is known in the art to use cationic dyes for dyeing paper. The cationic dyes used are usually di- or triarylmethine dyes, which are also known as triaryl methane dyes or triaryl carbenium ions, oxazine dyes, thiazine dyes, acridine, xanthene, or thioxanthene dyes, rhodamine dyes, azo dyes having basic groups, such as C.I. Basic Brown 1, styryl dyes, such as Basic Yellow 90, as described in P. Rys, H. Zollinger, Fundamentals of the Chemistry and Application of Dyes, Wiley Interscience, London, 1972. Commonly used dyes are further described in Klaus Hunger (Editor), Industrial Dyes, Wiley-VCH, Weinheim, 2003.

[0003] US-A- 4 374 643 describes colour salts or complexes consisting of an optical brightener component having an anionic group and a colour component having a basic group capable of forming a salt with the anionic group. These salts are hardly or not soluble in water, and can be used for colouring various fibrous articles.

[0004] The abovementioned cationic dyes exhibit a large affinity to wood-containing, unbleached paper fibres. Therefore, they are used for dyeing wood-containing papers, e.g. packaging, kraft, sleeve, and envelope papers. On the other hand, it is also known that bleached, wood-free pulp exhibits insufficient dyeing behaviour with respect to cationic dyes (Klaus Hunger (Editor), Industrial Dyes, Wiley-VCH, Weinheim, 2003, page 460).

[0005] Surprisingly, it has been found that this problem can be overcome by using a fluorescent whitening agent (FWA).

[0006] Accordingly, the present invention relates to a process for dyeing pulp comprising bleached pulp, comprising adding at least one cationic dye to the pulp, and then adding at least one fluorescent whitening agent to the pulp, followed by forming the paper sheet. Further, the invention relates to a paper obtainable by the process according to the invention. Preferred embodiments of the invention are described in the description hereinafter, the examples and the dependent claims.

[0007] The pulp that can be used in the process of the invention is any pulp or pulp suspension which comprises bleached pulp or is at least partially bleached pulp. The pulp can be produced from softwood or pine wood, hardwood, grasses, used or waste paper, or exotic fibres, such as hemp, jute, cotton, palms, agave, sisal, or coconut, according to conventional processes, e.g. as described in M. J. Kocurek, Pulp and Paper Manufacture, Vol. 1, Joint textbook Committee of the Paper Industry; Tappi CPPA 1983. In the production of wood-free pulp the cellulose is obtained by removing the lignin components during pulping and other interfering substances during bleaching. A pulp can be produced by reacting or cooking wood chips with an alkaline cooking liquid at elevated temperature. The cooking liquor may be a kraft, soda, alkali, sulfite or polysulfide cooking liquor, or a modification thereof, for example an anthraquinone modified cooking liquor. Known processes are e.g. the sulfate or sulfite processes, or bleaching processes, such as described e.g. in J. S. Gratzl, Chemische Grundlagen der Zellstoffbleiche mit Sauerstoff, Wasserstoffperoxid und Ozon, Das Papier 46, V1-V8(1992), Nr. 10A. Lignin, which is a component of the wood used, is dissolved by the cooking liquor. The character of the pulp produced is dependent on the amount of lignin removal from the wood used, and thus depends on the residual lignin content of the final pulp. The Kappa number represents a measure for the residual lignin content of a pulp. The Kappa number can be determined by the standard test method ISO 302:2004 Pulps - Determination of Kappa number. Higher Kappa numbers indicate higher residual lignin contents.

[0008] Pulps suitable in the process of the invention are pulps which contain at least 10 % by weight of bleached pulp based on 100 % by weight of the pulp used. Depending on how far the effects of the invention should be obtained, it is also possible to work with lower amounts of bleached pulp. Preferred pulps contain at least 20 % by weight of bleached pulp, based on 100 % by weight of the pulp. In particular, there is used a pulp containing 50 to 100 % by weight, preferably 90 to 100 % by weight, more preferably 95 to 100 % by weight, of bleached pulp, based on 100 % by weight of the pulp used. In a preferred embodiment, the pulp used consists of bleached pulp or is a wood-free pulp. The term "wood-free" as employed in the paper making art and as used herein means pulps which are free or essentially free of lignin, and in particular pulps which have a lignin content of less than 1 % by weight. If a pulp is bleached, it is necessarily also wood-free.

[0009] Pulps suitable in the process of the invention are pulps containing 0.1 to 50 % by weight, preferably 0.5 to 40 % by weight, in particular 1 to 10 % by weight of fibers, based on 100 % by weight of the pulp. In terms of the Kappa number, pulps suitable in the process of the invention are pulps having Kappa numbers up to 160, preferably in the range of 135 to 0, more preferably 100 to 0, most preferably 50 to 0.

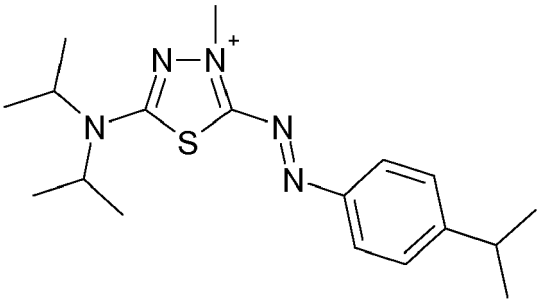
[0010] Cationic dyes which can be used in the process of the invention are the cationic dyes as known from the prior art and as described above. In the present invention, "cationic dye" means, in line with the common understanding in the art, that the dye is derived from dye bases. Cationic dyes form positively charged ions (cations) by dissociation in water. The term "cationic dye" does not refer to the pH reaction of these dyes.

[0011] Suitable cationic dyes are the following cationic dyes, which are described according to the Color Index: Basic Blue 3, Basic Blue 26, Basic Blue 41, Basic Blue 54, Basic Blue 64, Basic Blue 100, Basic Blue 140, Basic Blue 159, Basic Blue 163, Basic Green 1, Basic Green 4, Basic Orange 1, Basic Orange 2, Basic Orange 21, Basic Orange 60, Basic Orange 64, Basic Orange 160, Basic Red 1, Basic Red 12, Basic Red 14, Basic Red 18, Basic Red 29, Basic Red

46, Basic Red 49, Basic Red 51, Basic Red 108, Basic Red 111, Basic Violet 1, Basic Violet 3, Basic Violet 4, Basic Violet 10, Basic Violet 14, Basic Violet 16, Basic Violet 49, Basic Yellow 1, Basic Yellow 11, Basic Yellow 13, Basic Yellow 15, Basic Yellow 21, Basic Yellow 28, Basic Yellow 29, Basic Yellow 40, Basic Yellow 51, Basic Yellow 70, Basic Yellow 94, Basic Yellow 96, Basic Brown 1, Basic Brown 22, and Basic Brown 23. Preferred cationic dyes are Basic Blue 159, Basic Blue 26, Basic Red 12, Basic Violet 16, Basic Red 49, Basic Violet 1, and Basic Yellow 90. The following cationic dyes which are indicated by their formulas are also preferred.

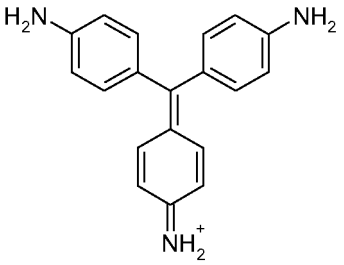
Basic Blue 159

[0012]



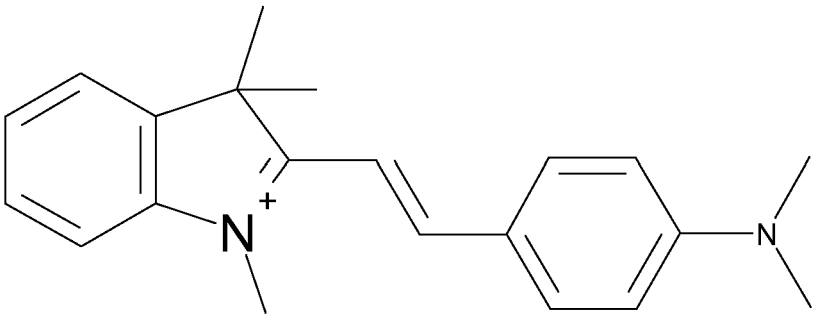
Basic Violet 1

[0013]



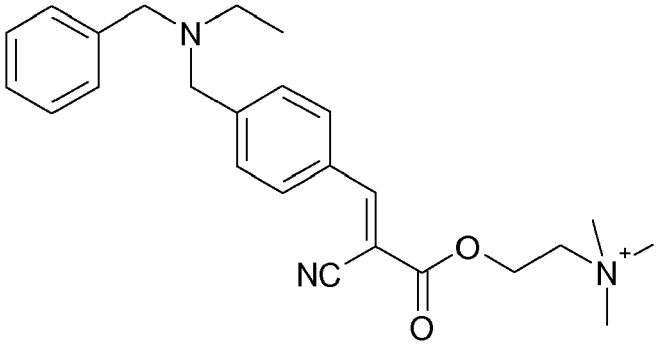
Basic Red 49

[0014]



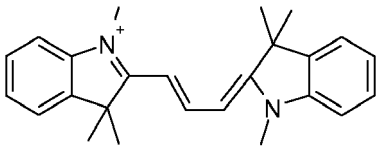
Basic Yellow 90

[0015]



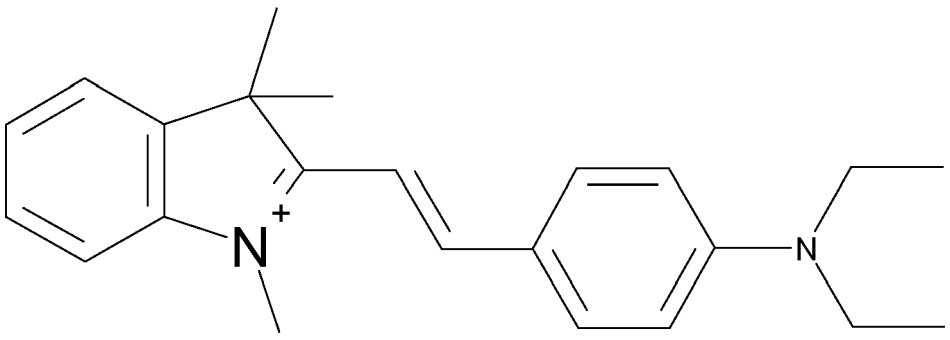
Basic Red 12

[0016]



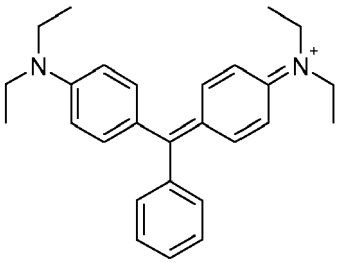
Basic Violet 16

[0017]



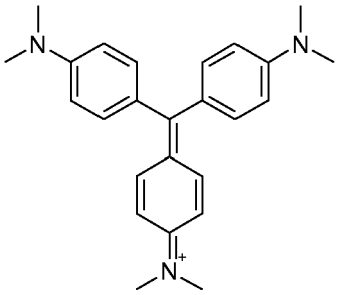
Basic Green 1

[0018]



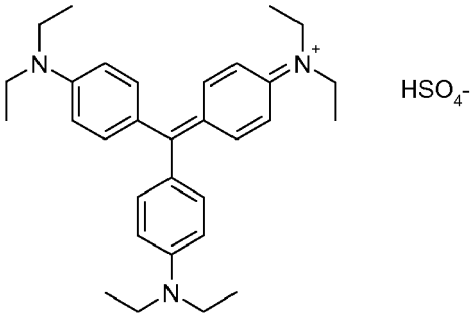
Basic Violet 3

[0019]



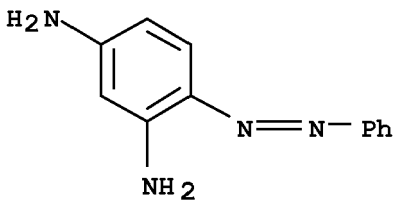
Basic Violet 4

[0020]



Basic Orange 2

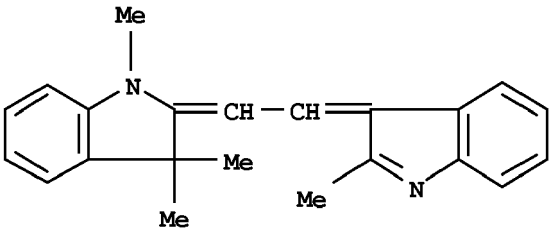
[0021]



· HCl

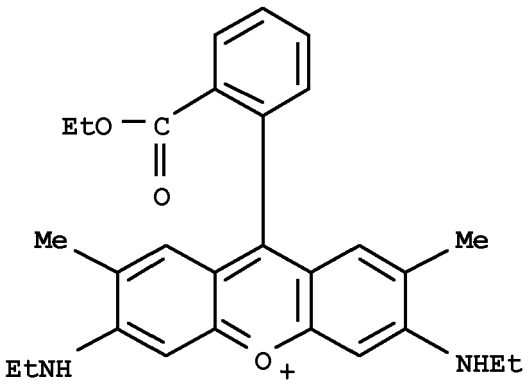
Basic Orange 21

[0022]



Basic Red 1

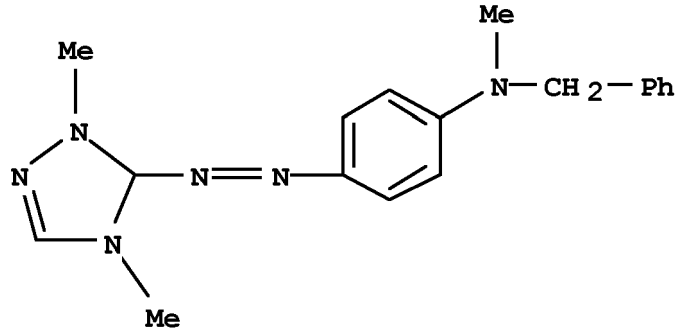
[0023]



· Cl $^-$

Basic Red 46

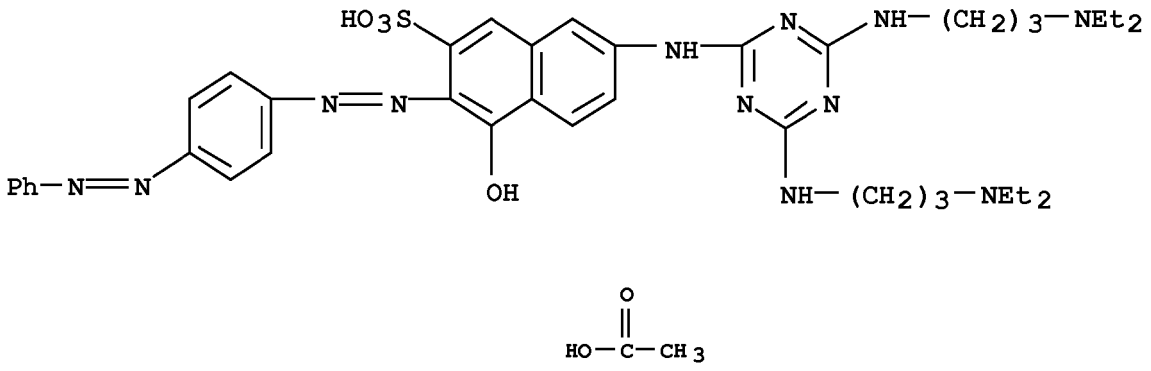
[0024]



· Br⁻

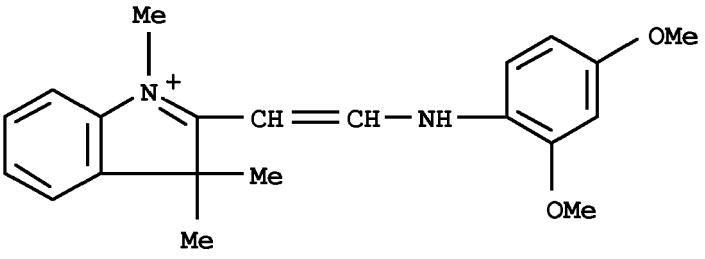
Basic Red 111

[0025]



Basic Yellow 11

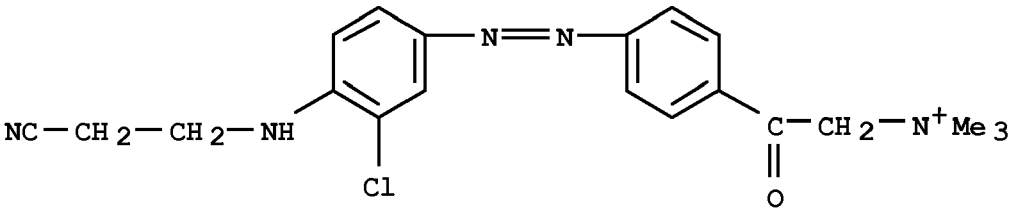
[0026]

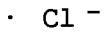


· Cl⁻

Basic Yellow 15

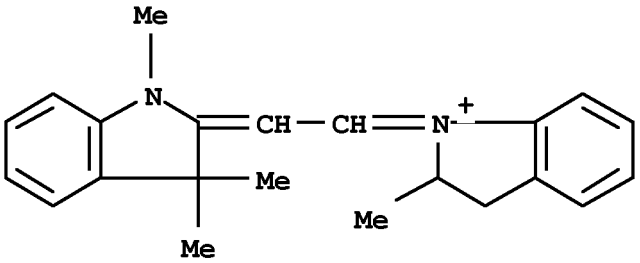
[0027]

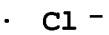




Basic Yellow 21

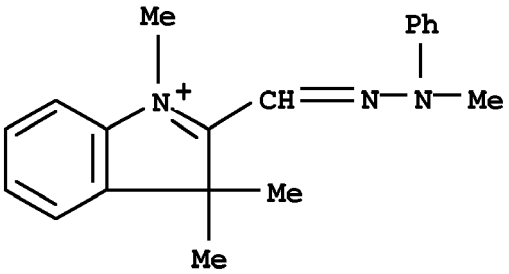
[0028]





Basic Yellow 51

[0029]



[0030] Suitable amounts of cationic dye are within a range of 0.01 to 20 % by weight based on 100 % by weight of the pulp used. In a preferred embodiment of the invention, the cationic dye is used in an amount of 0.01 to 1 % by weight

or in an amount of 0.05 to 10 % by weight, preferably 0.1 to 1 % by weight, more preferred 0.2 to 0.5 % by weight, based on 100 % by weight of the pulp. One or more cationic dyes can be used as a cationic dye.

[0031] The fluorescent whitening agents that can be used in the process of the invention are known fluorescent whitening agents and are subject to no limitations. Suitable fluorescent whitening agents are described in e.g. Klaus Hunger (Editor), Industrial Dyes, Wiley-VCH, Weinheim, 2003, Chapter 7.2, pages 590-610. In particular, fluorescent whitening agents having sulfonic acid residues are suitable. Preferably, there are used sulfonic acid groups-containing distyrylbenzenes, distyrylbiphenyls, divinylstilbenes, triazinylaminostilbenes, stilbenyl-2H-triazoles, stilbenyl-2H-naphtho[1,2-d]triazoles, bis(1,2,3-triazol-2-yl)stilbenes, benzoxazoles, stilbenylbenzoxazoles, bis-benzoxazoles, bis(benzo[b]furan-2-yl)biphenyls, benzimidazoles, 1,3-diphenyl-2-pyrazolines, coumarins, und naphthalimides.

[0032] Most preferably, the fluorescent whitening agent is a derivative of 4,4'-diaminostilbene-2,2'-disulfonic acid, in particular a 1,3,5-triazinyl derivative of 4,4'-diaminostilbene-2,2'-disulfonic acid or salts thereof. Most preferred are the disodium salt of 4,4'-bis[(4-anilino-6-diethanolamino-1,3,5-triazine-2-yl)amino]-stilbene-2,2'-disulfonic acid, the tetrasodium and hexasodium salt of 4,4'-bis[(4-p-sulfoanilino-6-diethanolamino-1,3,5-triazine-2-yl)amino]-stilbene-2,2'-disulfonic acid, and the hexasodium salt of 4,4'-bis[(4-(2,5-disulfoanilino)-6-diethanolamino-1,3,5-triazine-2-yl)amino]-stilbene-2,2'-disulfonic acid.

[0033] Suitable amounts of fluorescent whitening agent are within a range of 0.001 to 10 % by weight based on 100 % by weight of the pulp. In a preferred embodiment of the invention, the fluorescent whitening agent is used in an amount of 0.01 to 5 % by weight, preferably 0.1 to 1 % by weight, more preferably 0.2 to 0.4 % by weight, based on 100 % by weight of the pulp. As fluorescent whitening agent one or more fluorescent whitening agents can be used.

[0034] The process of the invention is carried out by adding the cationic dye to the pulp, and then adding the fluorescent whitening agent. The cationic dye and/or fluorescent whitening agent are suitably added by mixing or agitating. If the fluorescent whitening agent is added to the pulp with the added cationic dye too fast, a precipitate of fluorescent whitening agent and cationic dye is formed. Therefore, according to the invention the fluorescent whitening agent is suitably added to the pulp with the added cationic dye at a time at which no such precipitate is formed. This is usually after an agitation time in which the cationic dye has been sufficiently distributed in the pulp, and this depends on the agitation performance. Preferably, the fluorescent whitening agent is added some seconds or minutes, e.g. 30 seconds, or 1, 2, 3, 5, 10, 15 or 20 minutes, after the cationic dye has been added. In particular, the fluorescent whitening agent is added 5 to 10 minutes after the cationic dye addition. After that the paper sheet is formed.

[0035] It is preferred to add the cationic dye and/or fluorescent whitening agent by using a metering pump. The dye and/or fluorescent whitening agent can be added to the pulp in the paper machine in the pulper, in the mixing vat, in the stuff chest, before the headbox, or in the size press. The process of the invention can be carried out continuously, discontinuously (batch), or a combination of both by split dyeing. In the discontinuous process the dyeing is usually carried out batch wise in the pulper or the mixing vat. In the continuous process the dyeing is usually carried out by adding the dye and fluorescent whitening agent to the pulp stream. The dye and fluorescent whitening agent can be added in the thick matter area and/or thin (dilute) matter area. It is further possible to dye both in the pulp and on the surface. Surface dyeing or dipping can be carried out by using coating colours and e.g. a size press. It is possible to use coating colors with dye and fluorescent whitening agent. Further, it is possible to soak the base paper with dyeing solution and fluorescent whitening agent in a dipping tank, or to carry out a dyeing application in the plane using suitable printing procedures.

[0036] As shown by the following examples, the present invention surprisingly overcomes the problem that bleached wood-free pulp is insufficiently dyed by cationic dyes.

[0037] The following examples illustrate the invention without restricting its scope.

EXAMPLES

[0038] About 0.2 % by weight (based on 100 % by weight of pulp) of cationic dye is added to a bleached wood-free pulp containing about 2.5 % by weight of fibers, the remainder being mainly water. After an agitation period of 5 to 10 minutes a fluorescent whitening agent is added in an amount as indicated in the Tables below (the amount refers to % by weight based on 100 % by weight of the pulp). After 20 to 30 seconds the sheet is formed. The fluorescent whitening agent used is BLANKOPHOR DS, which contains the disodium salt of 4,4'-bis[(4-anilino-6-diethanolamino-1,3,5-triazine-2-yl)amino]-stilbene-2,2'-disulfonic acid.

COMPARATIVE EXAMPLES

[0039] In the comparative examples the anionic fixing agents MESITOL P, which is a commercial polycondensate of naphthalene sulfonic acid and formaldehyde, and MESITOL NBS, which is a commercial polycondensate of phenol sulfonic acid, 4,4'-dihydroxydiphenyl sulfone and formaldehyde, are used instead of the fluorescent whitening agent. Both fixing agents are present as sodium salts.

[0040] The % data hereinafter refer to percent by weight. The colour measurements are carried out with the CIELab system according to DIN 6174.

[0041] The following data have been measured:

Sample	L	A	B	C
ASTRA Blue B (Basic Blue 159)	81,88	-6,69	-14,59	16,05
Addition of	ΔL	Δa	Δb	ΔC
0,3% BLANKOPHOR DS	-7,34	0,87	-15,13	14,24
0,3% MESITOL NBS*	-6,20	1,95	-7,20	6,25
0,3% MESITOL P*	2,01	1,00	2,38	-2,58
Sample	L	A	B	C
ASTRA Brill. Red 4BC (Basic Red 49)	80,22	47,50	-12,04	49,00
Addition of	ΔL	Δa	Δb	ΔC
0,3% BLANKOPHOR DS	-1,00	3,27	-11,76	7,07
0,3% MESITOL NBS*	-2,50	-11,64	-3,24	-10,02
0,3% MESITOL P*	1,99	-7,24	1,33	-7,34
Sample	L	A	B	C
ASTRA Blue 6RL (Basic Violet 1)	62,93	16,61	-38,34	41,78
Addition of	ΔL	Δa	Δb	ΔC
0,3% BLANKOPHOR DS	-1,90	3,92	-6,64	7,66
0,3% MESITOL NBS*	-6,09	5,68	-3,36	5,50
0,3% MESITOL P*	9,39	-7,53	10,87	-12,85
Sample	L	A	B	C
ASTRA Yellow 4GN (Basic Yellow 90)	95,88	-6,90	19,51	20,69
Addition of	ΔL	Δa	Δb	ΔC
0,3% BLANKOPHOR DS	0,27	-3,39	7,97	8,65
0,3% MESITOL NBS*	-1,08	-1,87	14,21	4,15

(continued)

Addition of	ΔL	Δa	Δb	ΔC
0,3% MESITOL P*	-0,16	-0,24	2,67	2,61
* Comparative sample				

[0042] The higher ΔC is the more brilliant is the colour. The samples of the invention with fluorescent whitening agent exhibit higher ΔC values. Thus, in these samples the colour is more brilliant, compared to the comparative samples with the anionic fixing agents MESITOL, which result in less brilliant colourings.

[0043] Accordingly, dyeing bleached wood-free pulp with cationic dyes results in brilliant dyeing when using fluorescent whitening agents.

Claims

1. A process for dyeing pulp comprising bleached pulp, comprising adding at least one cationic dye to the pulp, and then adding at least one fluorescent whitening agent to the pulp, followed by forming the paper sheet.

2. The process of claim 1, wherein a pulp containing at least 20 % by weight, preferably 50 to 100 % by weight, in particular 90 to 100 % by weight, of bleached pulp based on 100 % by weight of the pulp is used.

3. The process of claim 1 or 2, wherein a wood-free pulp is used.

4. The process of claim 1 or 2, wherein a pulp containing 0.1 to 50 % by weight, preferably 1 to 10 % by weight, of fibers based on 100 % by weight of the pulp is used.

5. The process of claim 1 or 2, wherein a pulp having a Kappa number up to 160, in particular a Kappa number in the range of 100 to 0, is used.

6. The process of any of the preceding claims, wherein the cationic dye is added in an amount of 0.01 to 20 % by weight, preferably 0.01 to 1 % by weight, based on 100 % by weight of the pulp.

7. The process of any of the preceding claims, wherein the cationic dye is selected from Basic Blue 26, Basic Blue 159, Basic Red 12, Basic Red 49, Basic Violet 1, Basic Violet 16, and Basic Yellow 90.

8. The process of any of the preceding claims, wherein the fluorescent whitening agent is added in an amount of 0.001 to 10 % by weight, preferably 0.1 to 1 % by weight, based on 100 % by weight of the pulp.

9. The process of any of the preceding claims, wherein the fluorescent whitening agent is derived from 4,4'-diaminostilbene-2,2'-disulfonic acid, in particular wherein the whitening fluorescent agent is a 1,3,5-triazinyl derivative of 4,4'-diaminostilbene-2,2'-disulfonic acid.

10. Paper obtainable by a process according to any of the preceding claims.

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 09 16 3790

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	US 3 742 012 A (BAUMAN D) 26 June 1973 (1973-06-26) * column 1, line 5 - line 9; claims 1-4; example 20 * -----	1-10	INV. D21H21/28 D21H21/30
A	US 4 540 523 A (BEECKEN HERMANN [DE]) 10 September 1985 (1985-09-10) * column 22, line 63 - column 23, line 4; claims 1-8 * -----	1-10	
A	WO 2007/104128 A (FP INNOVATIONS [CA]; JIANG ZHI-HUA [CA]; BERRY RICHARD MCKINNON [CA]) 20 September 2007 (2007-09-20) * paragraphs [0001], [0005] - [0010]; claims 1-15 * -----	1-10	
A	EP 0 899 373 A (CIBA GEIGY AG [CH]) 3 March 1999 (1999-03-03) * paragraphs [0001], [0014] - [0016]; tables 1-38 * -----	1-10	
			TECHNICAL FIELDS SEARCHED (IPC) D21H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	27 July 2009	Hindia, Evangelia

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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