



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
01.02.2012 Bulletin 2012/05

(51) Int Cl.:
D21H 21/30 (2006.01)

(21) Application number: **10171451.7**

(22) Date of filing: **30.07.2010**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK SM TR
Designated Extension States:
BA ME RS

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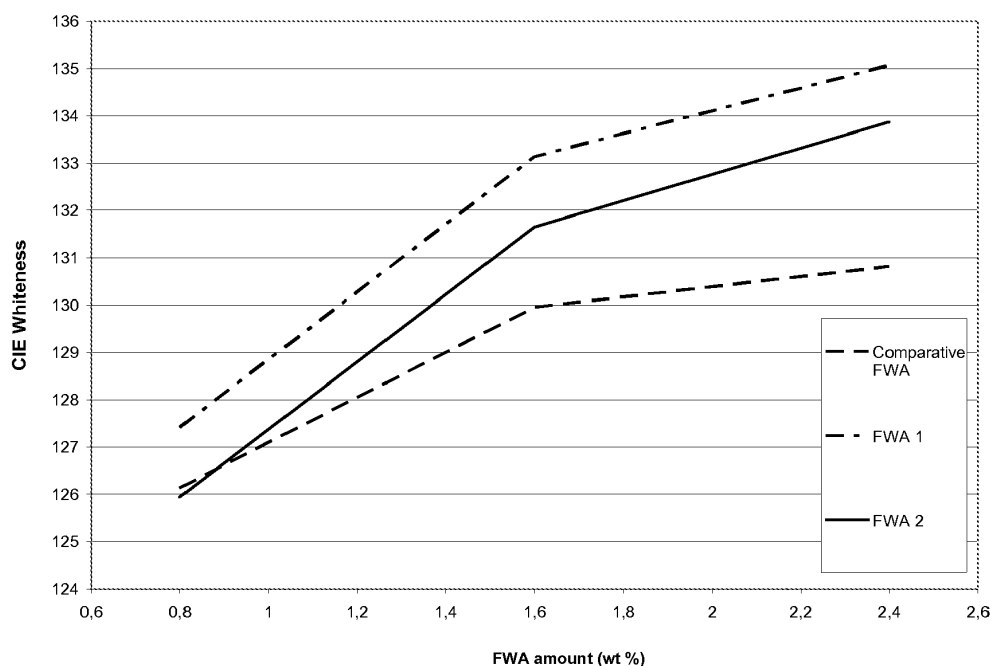
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(54) **Composition and process for whitening paper**

(57) The invention relates to a composition suitable for surface treatment of paper, wherein the composition contains a specified fluorescent whitening agent with a

combination of specific terminal groups, a salt of a bivalent cation, and a carrier. The composition is used for whitening paper, in particular in the size press.

Fig. 1



Description

[0001] The present invention relates to a composition suitable for surface treatment of paper, in particular a size press liquor, and a process for whitening paper using said composition.

[0002] In the production of paper, a sizing step is usually carried out for achieving good writing and printing properties and strength. Such a sizing step can take place, on the one hand, before the sheet formation in the paper pulp (internal sizing) and, on the other hand, after the sheet formation in the size press. A combination of both processes is also possible. In one or both production stages of paper, whitening of the pulp or of the paper sheet is usually also carried out by means of a fluorescent whitening agent (FWA). Usually, the size and fluorescent whitening agent are added separately to the paper pulp in the case of pulp application, whereas the fluorescent whitening agent is incorporated into the size press liquor and applied together with it to the paper sheet in the case of surface sizing.

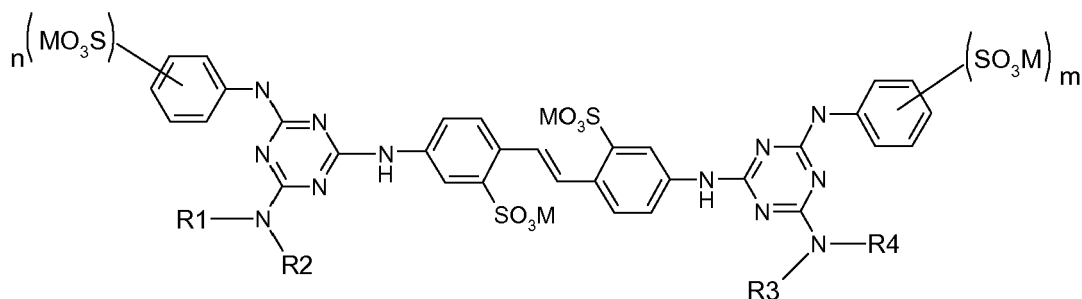
[0003] The combination of surface sizing and whitening of papers is widely used in the paper-producing industry. This method is widely used particularly in the printing and writing paper segment (copy, inkjet, offset, etc.). There is a continuing trend towards surface-sized papers having high whiteness and improved printing performance and consequently there is a demand for size press liquors which are as effective as possible. US 6,207,258 B1 discloses a composition and process for improved inkjet printing performance using a salt of a bivalent metal, in particular calcium chloride. Therefore, in order to achieve more brilliant and sharper printings, especially inkjet printings, the paper production industry uses nowadays calcium chloride in size press liquors. However, the use of that salt affects adversely the performance of the fluorescent whitening agents commonly used in size press liquors. In particular, the whitening effectiveness is decreased, the shade is moving to the greenish-yellowish direction, and additionally a loss of fluorescence is observed.

[0004] WO 2009/150180 A1 and EP 2 135 997 A1 disclose aqueous compositions containing specific bis-triazinylamino-stilbene compounds containing alkylsulfonic acid groups, a salt of a bivalent cation, and a carrier.

[0005] Surprisingly, it has been found that further specific bis-triazinylamino-stilbene compounds when used in combination with salts of bivalent cations, such as calcium chloride, in compositions suitable for surface treating of paper, such as size press liquors, also overcome problems of the prior art.

[0006] Therefore, the present invention relates to a composition suitable for surface treatment of paper, wherein the composition contains

(a) at least one fluorescent whitening agent of formula (I)



wherein n and m are, independently of each other, an integer of 1, 2, or 3;

R₁, R₂, R₃, and R₄ represent, independently of each other, hydrogen, C₁-C₄ alkyl, C₂-C₄ alkoxyalkyl, C₂-C₄ cyanoalkyl, or C₂-C₄ hydroxyalkyl; or R₁ and R₂ or R₃ and R₄ independently of each other together with N atom form morpholine, piperidine or pyrrolidine ring;

wherein at least one of R₁, R₂, R₃ and R₄ contains at least 3 carbon atoms;

M represents hydrogen, or one equivalent of a cation, in particular Li, Na, K, Ca, Mg, ammonium, or ammonium which is mono-, di-, tri- or tetra-substituted by C₁ - C₄ alkyl or C₂- C₄ hydroxyalkyl;

(b) at least one salt of a bivalent cation;

(c) at least one carrier; and

(d) water.

[0007] The invention further relates to a process for whitening paper, wherein a cellulose sheet is brought into contact with the above defined composition, preferably in the size press. Preferred embodiments of the invention are described in the description hereinafter, the claims and the figure.

[0008] Fig. 1 is a diagram showing the influence of calcium chloride on the performance of different fluorescent whitening agents according to Example 1.

[0009] In a preferred embodiment of the invention, the composition suitable for surface treatment of paper is a size press liquor, and the process is a process for whitening paper in the size press, wherein a cellulose sheet is brought into contact with the size press liquor.

[0010] In the context of this invention, size press is understood as meaning a surface application unit, preferably of the paper machine, in which the cellulose sheet formed is brought into contact with a size press liquor, and in which the proportion of the liquor which is to be taken up by the sheet (liquor absorption) can preferably be adjusted by means of the roll pressure.

[0011] Recent developments of the size press or film press, namely of the Speedsizer as well as of the Symsizer as well as Gate-roll, are likewise understood as being covered by the term size press.

[0012] According to the invention the composition contains at least one bis-triazinylamino-stilbene compound of the above defined formula (I), wherein n, m, R₁ to R₄, and M are as defined above. In the context of this invention, in the formula (I) the alkyl group can be linear or branched, and the possible substituents of the alkyl group, which are alkoxy, hydroxyl and/or cyano groups, can be attached at any position of the alkyl chain. In the present invention, C₂-C₄ alkoxyalkyl means C₂-C₄ alkyl substituted with C₂-C₄ alkoxy. In a preferred embodiment, n and m are integers from 1 to 2, most preferred 2. In another preferred embodiment, R₁, R₂, R₃ and R₄ represent, independently of each other, hydrogen, C₁-C₄ alkyl, C₂-C₄ cyanoalkyl, or C₂-C₄ hydroxyalkyl, in particular propyl, cyanoethyl, or hydroxypropyl. The -SO₃M groups at the terminal aromatic rings can be in o-, m-, or p-position. The preferred positions depend on the number of the -SO₃M groups. If n or m is 1, p-position is preferred. If n or m is 2, the 2,5-position is preferred. In a preferred embodiment, at least one of R₁, R₂, R₃ and R₄ is propyl, cyanoethyl or hydroxypropyl. In another preferred embodiment, R₁, R₂, R₃ and R₄ are propyl or hydroxypropyl, in particular all are either propyl or hydroxypropyl, wherein preferably n and m are 2. Most preferably, the hydroxypropyl group is a hydroxyisopropyl group. In another preferred embodiment, n and m are 2, and the two -SO₃M groups are in 2,5-position. In a further preferred embodiment, n and m are 2, R₁, and R₃ are hydroxyisopropyl, and R₂ and R₄ are cyanoethyl.

[0013] In the compound of formula (I), at least one of R₁, R₂, R₃ and R₄ contains at least 3 carbon atoms. Preferably, at least one of R₁ and R₂ and at least one of R₃ and R₄ contain at least 3 carbon atoms. In a further preferred embodiment, at least one of R₁, R₂, R₃ and R₄, in particular at least one of R₁ and R₂ and at least one of R₃ and R₄, represent(s) C₃-C₄ alkyl, C₃-C₄ alkoxyalkyl, C₃-C₄ cyanoalkyl, or C₃-C₄ hydroxyalkyl. In the present invention, C₃-C₄ alkoxyalkyl means C₃ or C₄ alkyl substituted with C₃ or C₄ alkoxy.

[0014] Preferred embodiments of M are hydrogen, Na, K, Ca, Mg, in particular M is Na or K, most preferred is Na.

[0015] The fluorescent whitening agents of formula (I) can be produced by known procedures, and are used as free acids or as salts thereof, preferably alkali metal salts. Generally, the compounds are prepared by reacting cyanuric chloride with 4,4'-diaminostilbene-2,2'-disulfonic acid or a salt thereof, and an appropriate aniline derivative containing a phenyl ring substituted with -SO₃M group(s), and substituted aliphatic amines or heterocyclic compounds. For example, EP 0 860 437 A1 describes the preparation of such compounds.

[0016] The composition of the invention can contain more than one, preferably two or three, most preferred three, of the fluorescent whitening agents of formula (I).

[0017] Component (a) of the composition can contain, in addition to the at least one fluorescent whitening agent of formula (I), one or more known bis-triazinylamino-stilbene or distyryl-biphenyl based fluorescent whitening agents.

[0018] The salt of component (b) of the composition of the invention comprises bivalent cations, preferably cations of an earth alkaline metal, in particular calcium or magnesium. Preferably, the counterions of the bivalent cations are mono- or multivalent anions, in particular halide, sulphate, hydrosulphate, phosphate, hydro-phosphate, dihydrophosphate, carbonate, hydrocarbonate, nitrate, acetate, or a mixture thereof, preferably chloride or sulphate, most preferably chloride. The salts disclosed in US 6,207,258 B1 are also suitable. A preferred salt is calcium chloride, magnesium chloride, magnesium sulphate, or a mixture thereof; more preferred is calcium chloride, magnesium chloride, or a mixture thereof; most preferred is calcium chloride.

[0019] The carrier of component (c) is any compound known in the art to be suitable as a carrier, in particular carriers suitable for size press liquors. Preferred carriers are carboxymethylcellulose (CMC), polyvinyl alcohol (PVA), starch or mixtures thereof, with starch being particularly preferred. Suitable carrier substances are, for example, hydrophilic polymers having the ability to form hydrogen bridge bonds. Preferred carrier substances are starch, polyvinyl alcohols, carboxymethyl-celluloses and polyethylene glycols having a number average molecular weight of from 200 to 8000 g/mol, as well as any desired mixtures of these substances, it being possible for these polymers optionally to be modified. Preferred polyvinyl alcohols are those having a degree of hydrolysis >85%, preferred carboxymethyl-celluloses are those having a degree of substitution DS of >0.5. Polyethylene glycols having a number average molecular weight Mn of from

200 to 8000 g/mol are particularly preferred. Suitable starches are based e.g., but not exclusively, on potato starch, rice starch, wheat starch, maize starch or tapioca starch. In particular, starches whose molecular weights have already been reduced by partial degradation and/or which have been obtained by derivatization are preferably used instead of natural starches. Furthermore, starches for which both modification steps have been combined, i.e. which have been partially degraded and additionally derivatized, are suitable. Typical methods for starch degradation are, for example, enzymatic, oxidative, thermal or hydrolytic treatment. Examples of suitable starch derivatives are hydroxyethyl starch or cationic starch.

[0020] The composition of the invention contains as component (d) water and, optionally, can contain sizing agents, such as alkenyl ketene dimer, alkyl ketene dimer (AKD), alkenyl succinic anhydride (ASA), rosin size, styrene maleic anhydride copolymers, styrene acrylate, styrene acrylic acid copolymers, polyurethane or ethylene acrylic acid copolymers, or other common paper chemicals, such as styryl-acrylate copolymers, latex, pigments, defoamers, or salts, such as NaCl or NaHCO_3 , or mixtures of two or more thereof.

[0021] The composition of the invention contains preferably component (a) in an amount of 0.02 to 3, more preferably 0.05 to 2, most preferably 0.1 to 1, weight-% based on 100 weight-% of the composition. If fluorescent whitening agents other than those of formula (I) are used, their amount is 5 to 95 weight-% based on 100 weight-% of component (a). Component (b) is preferably contained in an amount of 0.2 to 8, in particular 0.5 to 6, most preferably 1 to 5, weight-% based on 100 weight-% of the composition. Component (c) is preferably contained in an amount of 3 to 20, in particular 5 to 15, most preferably 6 to 12, weight-% based on 100 weight-% of the composition. The composition of the invention contains preferably water in an amount of 75 to 96.78, in particular 79 to 94.45, most preferably 82.5 to 92.9, weight-% based on 100 weight-% of the composition.

[0022] Optionally, the composition contains a sizing agent, preferably in an amount of 0 to 5, in particular 0 to 4, most preferably 0 to 3, in each case weight-% based on 100 weight-% of the composition.

[0023] In addition, relatively small amounts, usually amounts of less than 5% by weight, of further auxiliaries, such as, for example, dispersants, thickeners, antifreezes, preservatives, complexing agents, etc., or organic byproducts from the fluorescent whitening agent synthesis which were not completely removed in the working-up, may be contained in the composition of the invention.

[0024] Suitable compositions are also described in US 6,207,258 B1, wherein according to the invention as component (a) at least one fluorescent whitening agent of formula (I) is used.

[0025] The production of the composition is effected by known methods and preferably effected by combining an aqueous solution of the fluorescent whitening agent used as component (a), which preferably has a suitable pH value, with the other components, such as carrier substances, sizing agents, binders, pigments, salts or standardizing agents. Preferably, an aqueous preparation of carrier component (c) is prepared, to which preparation an aqueous preparation of salt component (b) is added, followed by the addition of an aqueous preparation of the fluorescent whitening agent component (a), preferably adjusted in pH value, and the other components.

[0026] The composition of the invention can be used for whitening paper, in particular for surface treatment of paper, e.g. in a size press.

[0027] The process of the invention for whitening paper is carried out according to known processes, preferably using a size press, and is subject to no restrictions. The paper used is not critical and may be any cellulose sheet.

[0028] Paper obtained by the process of the invention exhibits, in addition to improved printing performance, improved whiteness, and is in particular suitable for inkjet printing applications.

[0029] The whiteness of the papers produced can be characterized by the CIE whiteness. Different fluorescent whitening agents can be compared to each other with respect to the saturation behavior when determined according to CIE whiteness. In other words, if a larger amount of fluorescent whitening agent is used and no further increase in whiteness is found, there is a saturation behavior and there may even be adverse effects on the whiteness when using higher amounts. The effect of saturation is also referred to as greening. The greening limit, i.e. the point at which increasing amounts of fluorescent whitening agent used results in virtually no further increase in whiteness, can be derived, for example, from the a^* - b^* diagram, where a^* and b^* are the color coordinates in the CIE- $L^*a^*b^*$ system.

[0030] The following example illustrates the invention and shows preferred embodiments, without limiting the scope of protection.

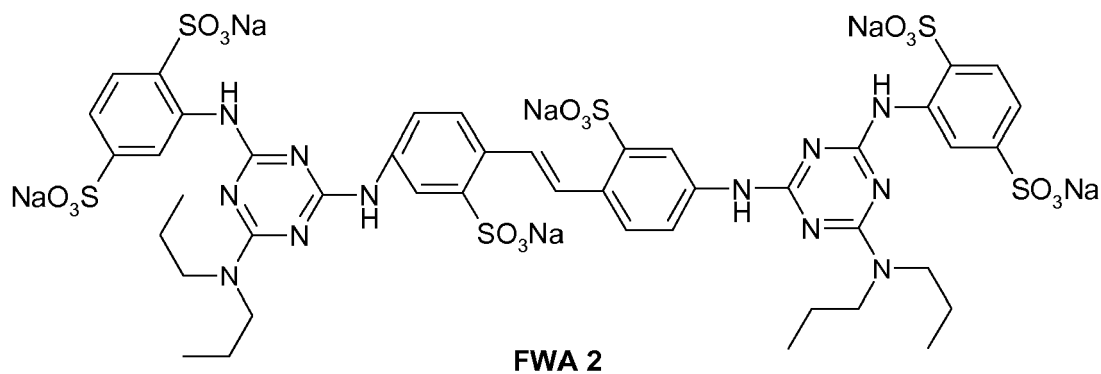
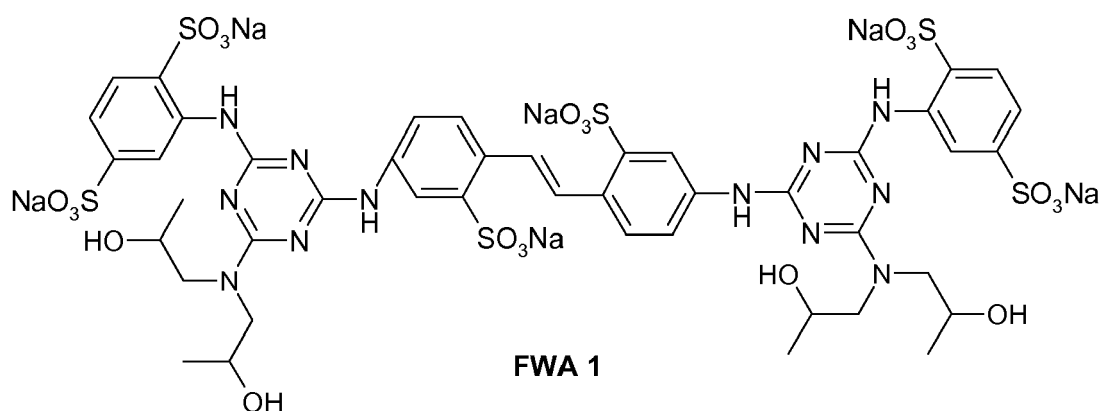
Example

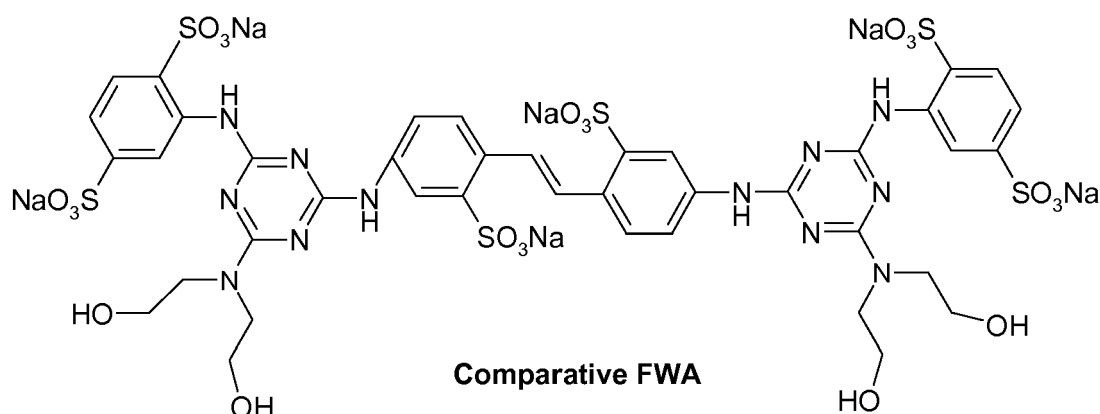
[0031] The whitening performance of different fluorescent whitening agents in the presence of calcium chloride was studied using the following test procedure for size press application.

[0032] First, a 15% starch solution of neutral oxidatively degraded potato starch (Perfectamyl 4692) and a 50% calcium chloride solution were prepared. The paper used was a 80 g/m² basepaper, which was a machine paper, internally sized (Cobb equals to 110 g/m²) and slightly whitened with fluorescent whitening agent to have the following optical characteristics: CIE -104.89; L^* = 93.92; a^* = 1.21; b^* = -4.34.

[0033] The fluorescent whitening agent was weighed in a glass, and 13.33 g of 15% starch solution was added. Then, 50% calcium chloride solution was weighed in, and the solution was filled up with water to 20 g, so that the tests were carried out in a 10% starch solution. After stirring for a short time the solution was applied on one side of the basepaper by a semiautomatic lab coater with a Rakel (No. 2) which should simulate a film press application. 1.7 g/m² of dry starch was applied on that basepaper. After the drawing the paper was directly dried on a drying cylinder at about 100°C. After climatization over night the prepared side of the papers were measured with a Datacolor spectrometer (ISO2469) by determining CIE, L*, a* and b*, the light source used based on ISO2469 standard.

[0034] The amounts used of fluorescent whitening agent per 100g starch preparation were as indicated in Table 1 below. The amount of calcium chloride was 2g for each fluorescent whitening agent. The following fluorescent whitening agents were used:





[0035] The results obtained are summarized in Table 1.

Table 1

FWA	Amount (wt%) in starch preparation	CIE whiteness	L*	a*	b*
FWA 1	0.8	127.41	93.92	2.14	-9.32
	1.6	133.13	94.13	2.15	-10.50
	2.4	135.06	94.27	1.98	-10.87
FWA2	0.8	125.94	93.87	2.11	-9.01
	1.6	131.64	94.03	2.20	-10.21
	2.4	133.86	94.17	2.11	-10.65
Comparative FWA	0.8	126.13	93.98	1.80	-9.01
	1.6	129.95	94.19	1.54	-9.76
	2.4	130.81	94.37	1.22	-9.87

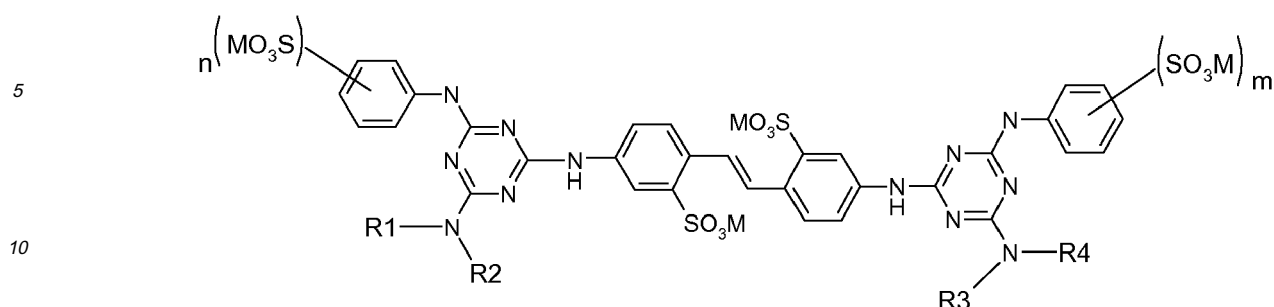
[0036] As may be taken from Table 1, FWA 1 and FWA 2 containing certain aliphatic amine groups, namely of diisopropanolamine or dipropylamine, in combination with dimethanilic acid, showed for almost all concentrations of fluorescent whitening agent used an improvement in whiteness in the presence of calcium chloride compared to the comparative FWA which does not contain that specific combination of groups. For further illustration, the results of Table 1 are also shown in Fig. 1.

[0037] The above experimental data show that the use of bis-triazinylamino-stilbene fluorescent whitening agent compounds with a specific combination of terminal groups according to the invention results in paper of improved whiteness in the presence of a salt of a bivalent cation, such as calcium chloride.

Claims

1. A composition suitable for surface treatment of paper, wherein the composition contains

(a) at least one fluorescent whitening agent of the formula (I)



15 wherein n and m are, independently of each other, an integer of 1, 2, or 3; R₁, R₂, R₃ and R₄ represent, independently of each other, hydrogen, C₁ - C₄ alkyl, C₂-C₄ alkoxyalkyl, C₂-C₄ cyanoalkyl, or C₂-C₄ hydroxyalkyl; or R₁ and R₂ or R₃ and R₄ independently of each other together with N atom form morpholine, piperidine or pyrrolidine ring;

20 wherein at least one of R₁, R₂, R₃ and R₄ contains at least 3 carbon atoms; M represents hydrogen, or one equivalent of a cation, in particular Li, Na, K, Ca, Mg, ammonium, or ammonium which is mono-, di-, tri- or tetra-substituted by C₁ - C₄ alkyl or C₂-C₄ hydroxyalkyl;

(b) at least one salt of a bivalent cation;

(c) at least one carrier; and

(d) water.

- 25 2. The composition of claim 1, wherein n and m each are 2, and the -SO₃M groups are in 2,5-position.
3. The composition of claim 1 or 2, wherein R₁, R₂, R₃ and R₄ are, independently of each other, propyl, cyanoethyl, or hydroxypropyl.
- 30 4. The composition of any of claims 1 to 3, wherein n and m are 2, and R₁, R₂, R₃ and R₄ are propyl.
5. The composition of any of claims 1 to 3, wherein n and m are 2, and R₁, R₂, R₃ and R₄ are hydroxypropyl, in particular hydroxyisopropyl.
- 35 6. The composition of any of claims 1 to 3, wherein n and m are 2, R₁ and R₃ are hydroxypropyl, in particular hydroxyisopropyl, and R₂ and R₄ are cyanoethyl.
7. The composition of any of the preceding claims, wherein M is Na or K.
- 40 8. The composition of any of the preceding claims, wherein the salt of component (b) is calcium chloride.
9. The composition of any of the preceding claims, wherein the carrier of component (c) is selected from carboxymethylcellulose, polyvinyl alcohol, starch, and mixtures thereof.
- 45 10. The composition of claim 9, wherein the carrier is starch.
11. The composition of any of the preceding claims, wherein the composition contains component (a) in an amount of 0.02 to 3 weight-%, component (b) in an amount of 0.2 to 8 weight-%, and component (c) in an amount of 3 to 20 weight-%, each based on 100 weight-% of the composition.
- 50 12. The composition of any of the preceding claims, wherein the composition is a size press liquor which optionally contains a sizing agent.
13. A process for whitening paper, wherein a cellulose sheet is brought into contact with a composition as defined in any of the preceding claims.
- 55 14. The process of claim 13, wherein the contacting is conducted in a size press.

15. A paper obtainable by the process according to claim 13 or 14.

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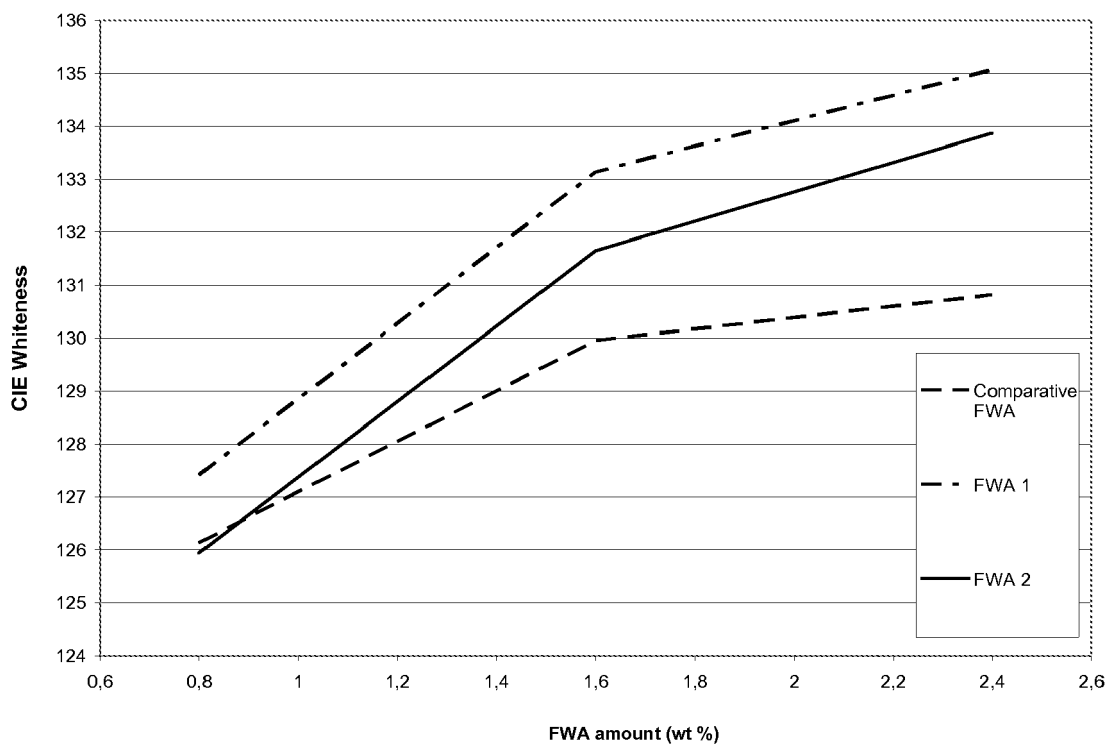
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Fig. 1





EUROPEAN SEARCH REPORT

Application Number
EP 10 17 1451

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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Y	* page 2, paragraph 1 - page 4, paragraph 19 * * claims 1-15 *	1-15	
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A,D	US 6 207 258 B1 (VARNELL DANIEL F [US]) 27 March 2001 (2001-03-27) * column 1, lines 10-16 * * column 3, line 58 - column 4, line 3 * * column 5, lines 25-29 * * column 9, line 61 - column 10, line 9 * * column 10, lines 41-47 *	1-15	TECHNICAL FIELDS SEARCHED (IPC) D21H
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 19 January 2011	Examiner Beins, Ulrika
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 L : document cited for other reasons & : member of the same patent family, corresponding document			

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EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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