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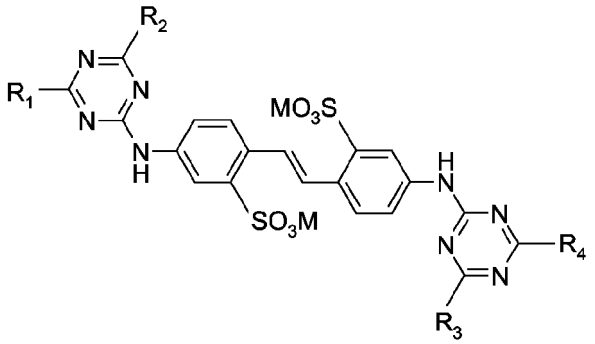
Remarks:
Claim 11.... is deemed to be abandoned due to non-payment of the claims fee (Rule 45 (3) EPC).

(54) **Fluorescent Whitening Compositions**

(57) The present invention relates to a composition for the fluorescent whitening of paper comprising
a) a bis-triazinylamino stilbene of the formula



(1),

in which
R_1, R_2, R_3 and R_4 each, independently, represent $-NH_2$, $-OC_1$-C_4alkyl, -Oaryl, $-NHC_1$-C_4alkyl, $-N(C_1$-C_4alkyl$)_2$, -N (C_1-C_4alkyl)(C_1-C_4hydroxyalkyl), $-NHC_1$-C_4hydroxyalkyl, $-N(C_1$-C_4hydroxyalkyl$)_2$, or-NHaryl, whereby aryl is phenyl, which may be unsubstituted or substituted by one or two sulphonic acid groups, -COOH, $-COOC_1$-C_4alkyl, $-CONH_2$, $-CONHC_1$-C_4alkyl or by $-CON(C_1$-C_4alkyl$)_2$, a morpholino, piperidino or pyrrolidino residue, $-SC_1$-C_4alkyl or aryl, or an amino acid or amino acid amide residue from which a hydrogen atom has been abstracted from the amino group and M represents hydrogen, an alkaline or alkaline earth metal, ammonium or ammonium that is mono-, di-, tri- or tetrasubstituted by C_1-C_4alkyl or C_2-C_4hydroxyalkyl or
a distyryl biphenyl fluorescent whitening agent (FWA) of the formula

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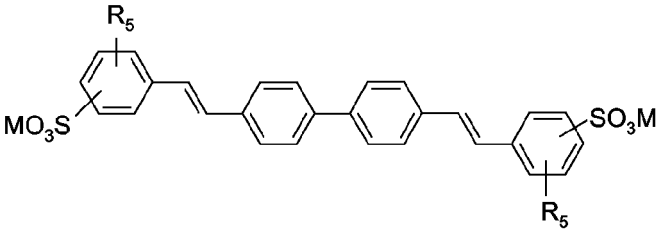


(2),

in which
R_5 represents hydrogen, chlorine or C_1-C_4alkoxy and
M is as defined above, or mixtures of (1) and (2),
b) water and, optionally,
c) one or more auxiliaries, characterized in that the pH of the composition lies within the range of from 10 to 13, size or film press liquors and coating colours containing the composition and use and process for application of the composition to paper.

Description

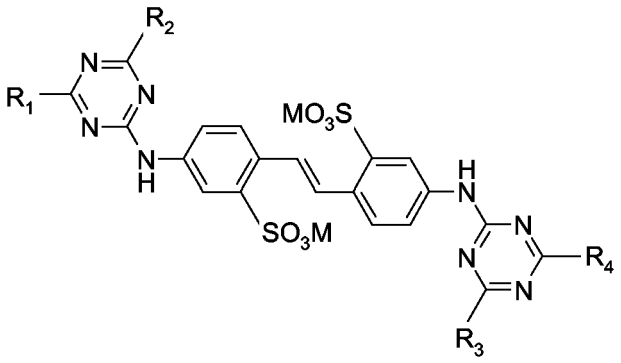
[0001] The present invention relates to a composition for the fluorescent whitening of paper, size or film press liquors and coating colours containing the composition and use and process for application of the composition to paper.

[0002] Present day white papers demand an ever-increasing efficiency in the utilization of fluorescent whitening agents (FWA's) for their production. Since, to a large extent, the choice of FWA is governed by economic aspects, it is essential that the conditions for the application of such compounds to the paper ensure that a maximum efficiency in the whitening power of the FWA is attained.

[0003] Coatings containing FWA's are traditionally applied from either size or film press liquors or coating colours, the pH value of which lie in the neutral or slightly alkaline region of between 7.0 and 9.5. However, it has now been found that an increase in the pH value results in higher degrees of whiteness when FWA's are applied to paper by such coating techniques.

[0004] Consequently, in a first aspect, the invention relates to a composition for fluorescent whitening of paper comprising

a) a bis-triazinylamino stilbene of the formula



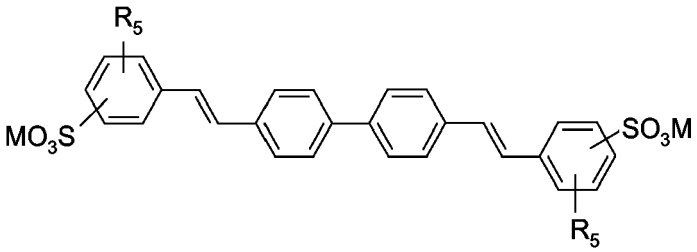
(1),

in which

R_1, R_2, R_3 and R_4 each, independently, represent $-NH_2$, $-OC_1$-C_4alkyl, -Oaryl, $-NHC_1$-C_4alkyl, $-N(C_1$-C_4alkyl$)_2$, $-N(C_1$-C_4alkyl$)(C_1$-C_4hydroxyalkyl), $-NHC_1$-C_4hydroxyalkyl, $-N(C_1$-C_4hydroxyalkyl$)_2$, or -NHaryl, whereby aryl is phenyl, which may be unsubstituted or substituted by one or two sulphonic acid groups, -COOH, $-COOC_1$-C_4alkyl, $-CONH_2$, $-CONHC_1$-C_4alkyl or by $-CON(C_1$-C_4alkyl$)_2$, a morpholino, piperidino or pyrrolidino residue, $-SC_1$-C_4alkyl or aryl, or an amino acid or amino acid amide residue from which a hydrogen atom has been abstracted from the amino group and

M represents hydrogen, an alkaline or alkaline earth metal, ammonium or ammonium that is mono-, di-, tri- or tetrasubstituted by C_1-C_4alkyl or C_2-C_4hydroxyalkyl or

a distyryl biphenyl fluorescent whitening agent (FWA) of the formula



(2),

in which

R_5 represents hydrogen, chlorine or C_1-C_4alkoxy and

M is as defined above, or mixtures of (1) and (2),

b) water and, optionally,

c) one or more auxiliaries, characterized in that the pH of the composition lies within the range of from 10 to 13, preferably from 11 to 13.

[0005] In order to adjust the pH of the composition to the desired range of between 10 and 13, any suitable base may be employed. However, such bases are preferably water-soluble inorganic bases, especially alkali metal hydroxides, in particular lithium, potassium and sodium hydroxides, whereby aqueous sodium hydroxide solution is most preferred.

[0006] In a further preferred aspect, the FWA used in the composition, component a) is a compound of formula (1), in which each

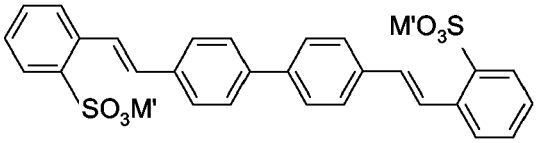
R_1 and R_3 group and each R_2 and R_4 group are identical and each pair, independently, represents $-NH_2$, $-NHC_1$-C_4alkyl, $-N(C_1$-C_4alkyl$)_2$, $-N(C_1$-C_4alkyl$)(C_1$-C_4hydroxyalkyl), $-NHC_1$-C_4hydroxyalkyl, $-N(C_1$-C_4hydroxyalkyl$)_2$, or -NHaryl, whereby aryl is phenyl, which may be unsubstituted or substituted by one or two sulphonic acid groups, a morpholino residue, or an amino acid or amino acid amide residue from which a hydrogen atom has been abstracted from the amino group and M represents hydrogen or an alkali metal ion.

[0007] Preferred amino acid or amino acid amide residue from which a hydrogen atom has been removed are those derived from glycine, alanine, serine, cysteine, phenylalanine, tyrosine (4-hydroxyphenylalanine), diiodotyrosine, tryptophan (β-indolylalanine), histidine ((β-imidazolylalanine), α-aminobutyric acid, methionine, valine (α-aminoisovaleric acid), norvaline, leucine (α-aminoisocaproic acid), isoleucine (α-amino-β-methylvaleric acid), norleucine (α-amino-n-caproic acid), arginine, ornithine (α,δ-diaminovaleric acid), lysine (α,ε-diaminocaproic acid), aspartic acid (aminosuccinic acid), glutamic acid (α-aminoglutaric acid), threonine, hydroxyglutamic acid and taurine, as well as mixtures and optical isomers thereof, glycine and aspartic acid being especially preferred.

A further preferred example of an amino acid from which an amino acid residue may be derived is iminodiacetic acid or the mono- or diacid amide thereof, whilst a suitable amino acid amide is 2-hydroxyethylaminopropionamide.

[0008] Most preferred compounds of formula (1) are those in which R_1 and R_3 both represent $-NHC_1$-C_4hydroxyalkyl, $-N(C_1$-C_4hydroxyalkyl$)_2$, or-NHaryl, whereby aryl is phenyl, which may be unsubstituted or substituted by one or two sulphonic acid groups, R_2 and R_4 represent $-NHC_1$-C_4hydroxyalkyl, $-N(C_1$-C_4hydroxyalkyl$)_2$ or an aspartic acid, an iminodiacetic acid or a 2-hydroxyethylamino-propionamide residue and M represents hydrogen or sodium, the compounds 4,4'-bis-[4,6-bis-(2-hydroxyethylamino)-triazin-2-yl-amino]stilbene-2,2'disulphonic acid and 4,4'-bis-[4-anilino-6-(2-hydroxydiethylamino)-triazin-2-yl-amino]stilbene-2,2'disulphonic acid being especially preferred.

[0009] Preferred distyryl biphenyl fluorescent whitening agents as component a) of the composition, are those selected from the compounds of formulae



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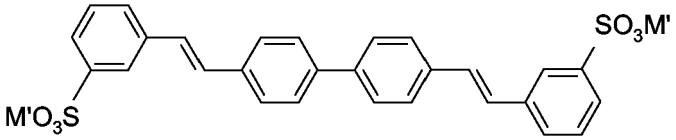

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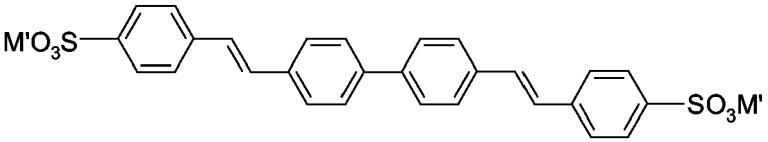
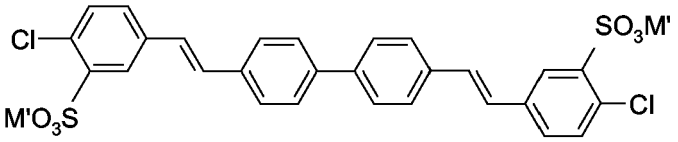


(5)

and



(6),

in which

M' represents hydrogen, lithium, potassium or sodium, whereby the 2,2'-disulphonic acid derivatives of formula (3) are most preferred.

[0010] Within the scope of the definitions of the substituents in the compounds of formulae (1) and (2), C_1-C_4alkyl radicals are branched or unbranched and are, for example, methyl, ethyl, propyl, isopropyl or n-, sec- or tert-butyl; they may be unsubstituted or substituted by halogen, for example fluorine, chlorine or bromine. C_1-C_4alkoxy is, for example, methoxy, ethoxy, propoxy, isopropoxy or n-butoxy whilst C_2-C_4hydroxyalkyl is, for example, hydroxyethyl, hydroxypropyl or hydroxybutyl.

[0011] The fluorescent whitening agents of formulae (1) and (2) are known compounds or may be prepared by known methods.

[0012] The content of fluorescent whitening agent in the composition may vary over large ranges. However, typically, the content of compounds of formulae (1) and/or (2) is between 5 and 40, preferably, between 10 and 30 and, most preferably, 15 to 25% by weight, based on the total weight of the composition.

[0013] When used for the fluorescent whitening of paper, the composition of the invention may be applied to the substrate by means of a size or film press or in the form of a coating composition. Thus, in a second aspect, the invention relates to the use of the composition of the invention for the fluorescent whitening of paper in the size press or film press or in a coating composition.

[0014] Where the application is performed by means of a size press or film press, the composition of the invention may be initially prepared by mechanical mixing of the components, adjustment of the pH to the desired value of between 10 and 13 by addition of a suitable base and then adding the desired quantity of the composition to the size press or film press liquor, prior to application to the paper. Thus, in a third aspect, the invention relates to a size press or film press liquor composition, useful for the fluorescent whitening of paper, comprising

a) 0.01 to 20%, preferably, 1 to 10% by weight of the fluorescent whitening composition of the invention;
b) 1 to 20%, preferably 2 to 15% and most preferably 7 to 12% by weight of one or more binders, for example anionic starch;
c) 0 to 10% by weight of pigment and/or further auxiliaries and
d) water to 100%.

[0015] Alternatively, the size press or film press liquor may be prepared in situ by addition of one or more of the FWA's to the liquor bath and then adjusting the pH of the composition in the size press or film press to the desired value of between 10 and 13 by addition of a suitable base. Thus, in a fourth aspect, the invention relates to a size press or film press liquor composition, useful for the fluorescent whitening of paper, comprising

a) 0.001 to 2% by weight of the fluorescent whitening agent of formula (1) and/or formula (2), as defined above;
b) 1 to 20% by weight of one or more binders;
c) 0 to 10% by weight of pigment and/or further auxiliaries and
d) water to 100%, characterized in that the pH value of the composition is maintained at a value of between 10 and 13, preferably between 11 and 13, during the application of the composition to the paper.

[0016] As a further alternative, the compositions of the invention may be applied to paper in the form of a coating colour, whereby the composition may be applied to the substrate by coating using any type of coating equipment such as a blade coater, roll coater etc.

[0017] The amount of the composition for use according to the invention employed in the paper coating composition depends on the desired whitening effect; but usually corresponds to an amount containing from 0.01 to 5% by weight of the fluorescent whitening agent

[0018] The paper coating compositions generally have a solids content of from 20 to 80% by weight, preferably from 25 to 70% by weight.

[0019] In a fifth aspect, the invention relates to a paper coating colour composition comprising, in addition to 0.01 to 20 parts by weight of the composition disclosed above, per 100 parts of inorganic pigment,

(i) from 3 to 25 parts by weight of binder and co-binder,
(ii) 0 to 1 part by weight of rheology modifier,
(iii) 0 to 2 parts by weight of wet-strength agent and
(iv) 0 to 5 parts by weight of a further fluorescent whitening agent and/or shading colourant and/or further auxiliaries.

[0020] The whitening compositions according to the invention are excellently suitable for whitening the optionally pigmented coating compositions customarily used in the textile, paint, adhesives, plastics, wood and paper industries. Such coating compositions comprise, as binders (co-binders), plastics dispersions based on copolymers of butadiene and styrene, of naphthalene sulphonic acids and formaldehyde, of polyethylene and polypropylene oxides, of acrylonitrile, butadiene and styrene, of acrylic acid esters, of ethylene and vinyl chloride and of ethylene and vinyl acetate, or homopolymers, such as polyvinyl chloride, polyvinylidene chloride, polyethylene, polyvinyl acetate, polyvinyl alcohol, or polyurethane.

[0021] If desirable, the coating colour composition may, in addition to the whitening composition, contain further fluorescent whitening agents and/or shading dyes or pigments.

[0022] For the purpose of pigmenting the coating colour compositions there are generally employed aluminium silicates, such as China clay or kaolin, and also barium sulphate, satin white, silicon dioxide, titanium dioxide or calcium compounds. These are described by way of example in J.P. Casey "Pulp and Paper; Chemistry and Chemical Technology", 2nd Ed. Vol. III; p. 1648-1649 and in Mc Graw-Hill "Pulp and Paper Manufacture", 2nd Ed. Vol. II, p. 497 and in EP-A-0 003 568.

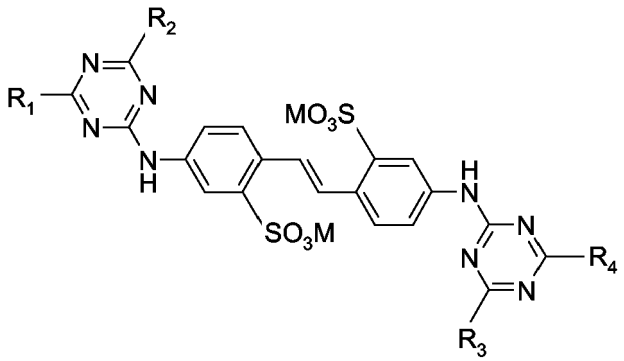
[0023] The whitening compositions according to the invention may be used especially for the coating of paper, including ink-jet and photographic paper, wood, foils, textiles, non-woven materials and suitable building materials. Special preference is given to use on paper and cardboard and on photographic and ink-jet papers.

[0024] The coating colour composition or size press or film press liquor composition may contain, as further auxiliaries, binders, agents for improving rheology and printability, fixing agents, wet-strength agents, antifoams and/or biocides. Examples of binders are polyvinyl alcohols, polyvinyl acetate, acrylic ester/styrene co-polymers, carboxylated styrene/butadiene copolymers, polyvinyl pyrrolidone, oxidized starch, carboxymethyl cellulose and other water-soluble cellulose derivatives, whilst, for example, polyacrylamides and co-polymers thereof may serve to improve rheology and printability.

[0025] Use of the paper coating colour composition or the size press or film press liquor composition, as disclosed above, for the fluorescent whitening of paper, constitutes a sixth aspect of the invention.

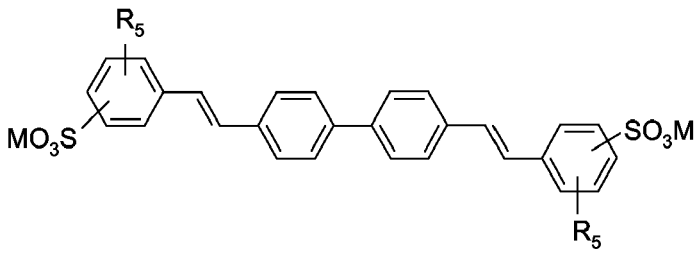
[0026] In a seventh aspect, the invention relates to a process for the fluorescent whitening of paper by applying to the paper a composition comprising

a) a bis-triazinylamino stilbene of the formula



(1),

in which the definitions and preferences of R_1, R_2, R_3, R_4 each and M are as given above or a distyryl biphenyl fluorescent whitening agent (FWA) of the formula



(2),

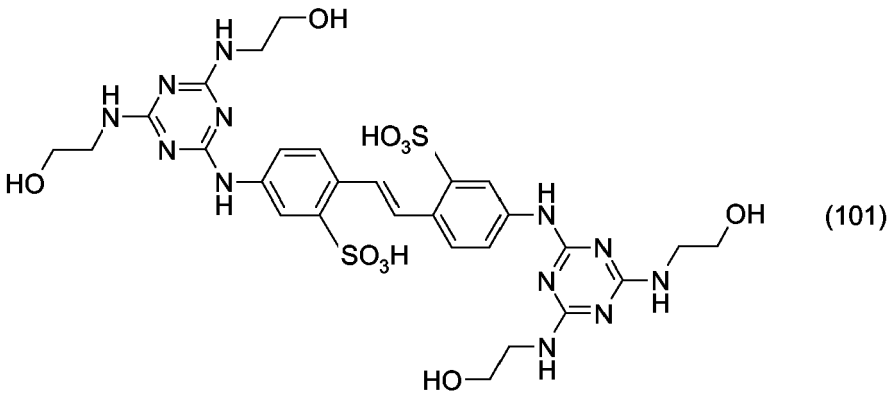
in which R_5 and M and their preferences are as previously defined or mixtures of (1) and (2),
b) water and, optionally,
c) one or more auxiliaries, characterized in that the pH of the composition is adjusted to a value of from 10 to 13, preferably from 11 to 13, prior to or during the application of the composition to the paper.

[0027] In a final aspect, the invention relates to paper, which has been treated with a composition as disclosed above, a size press or film press liquor composition or a paper coating colour composition as disclosed above or according to the above process, whereby coatings or coverings so obtained have, in addition to a high degree of fastness to light, an excellent degree of whiteness.

[0028] The following Examples illustrate the invention, without intending to be restrictive in nature; parts and percentages are by weight unless otherwise stated.

A. Preparation of Compositions

[0029] Solutions containing 20.2% of the compound of formula



(101)

are prepared by dissolving the compound in water and the pH of the respective solutions adjusted to values of 9.3, 10.5, 11.0, 11.5, 12.0 and 12.5 by addition of 4N aqueous sodium hydroxide solution.

B. Size Press Application

[0030] To 100g of an aqueous solution containing 8.0g of anionic potato starch (Perfectamyl® A4692), sufficient of the above solutions are added such that the size press baths contain 0.5, 1.0, 2.0, 3.0, 4.0, 6.0 and 8.0g of the fluorescent whitening agent (FWA)/kg of paper. This solution is applied to a neutral sized, wood- and FWA-free base paper having a weight of 80g/m^2 by means of a Mathis size press running at 2m/min and a pressure of 2500kpascal, whereby the pick-up corresponds to 20-25$\pm$0.5%.

[0031] After drying in hot air at 80°C for 5 minutes, the degrees of whiteness, W_{CIE} of the resulting sheets are measured using a Datacolor Elrepho 3000 spectrophotometer. In order to compare the efficiencies of the compositions, the quantities of FWA required to attain a degree of whiteness of 105 (g of FWA/kg of whitened paper) are calculated. The results are collated in the following Table 1:

Table 1

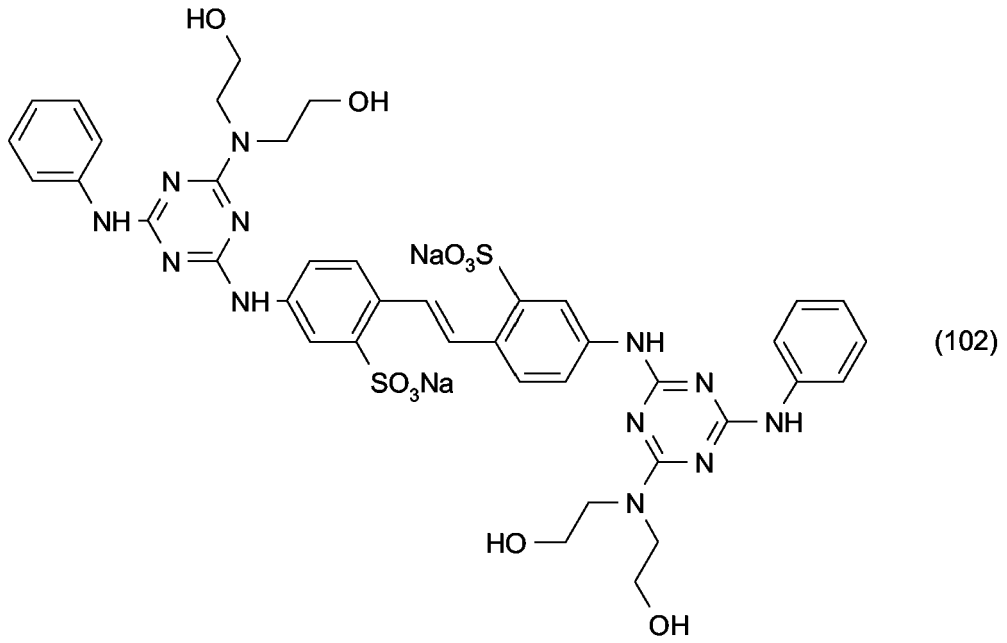
Example No.	ph of Composition	FWA for W_{CIE}	105/Abs[1] 105/Rel[2]
1	12.5	2.45	84
2	12.0	2.66	91
3	11.5	2.57	88
4	11.0	2.56	88
5	9.3	2.91	100
[1] g of FWA (100% active substance)/kg whitened paper required [2]Relative amount of FWA required			

[0032] As is apparent from the above results, compositions of higher pH values result in substantially higher efficiency of the FWA.

C. Coating Application

[0033] In order to simulate an ink jet paper coating, but eliminating factors such as penetration into the paper and varying degrees of whiteness of the uncoated base papers, the composition of the invention was applied to plastic foils in the form of a paper coating composition.

[0034] A 22% aqueous solution of the compound of formula



(102)

is diluted to 1 % with water and the pH adjusted to 11.8 by addition of aqueous sodium hydroxide solution. For comparative purposes, a further sample is diluted with water to 1%, whereby the resulting solution has a pH value of 9.1.

[0035] A formulation suitable for preparing ink jet papers is prepared by the addition of 5.0 g of the poly-DADMAC (diallyl dimethyl ammonium chloride) Catiofast® LF Harz DA (40% solution), 100 g of Gasil® M35 powder (silicon dioxide) and 120 g of the polyvinyl alcohol Mowiol® 4-98 (25% solution) to 365 g of water. Sufficient amounts of the solutions of compound (102) are added such that the coating colour contains 4.0 and 8.0g of the fluorescent whitening agent (FWA) /kg of coating, i.e. 0.4 and 0.8% respectively. The coatings are then applied with a K Control 202 Erichsen coater equipped with rod #3 to Imperial Drafting Film 50 double matt plastic foils at a speed of 6m/min. The coated substrates are subsequently passed once through an infrared dryer heated to 185°C at a speed of 5-10 m/min to provide a dry coat weight of $5.4 \pm 0.2 g/m^2$. The degrees of whiteness, W_{CIE} of the resulting sheets are measured using a Datacolor Elrepho 450x spectrophotometer and appear in Table 2 below.

Table 2

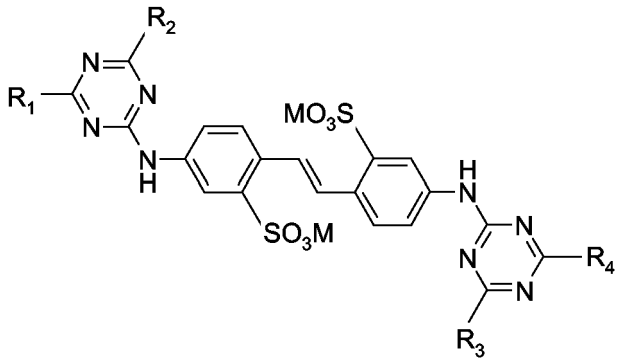
Example No	pH of Composition	Whiteness at 0.4%	Whiteness at 0,8%
6	11.8	92.1	101.2
7	9.1	88.4	90.0

[0036] As is apparent from the above results, compositions of higher pH values result in substantially higher efficiency of the FWA.

Claims

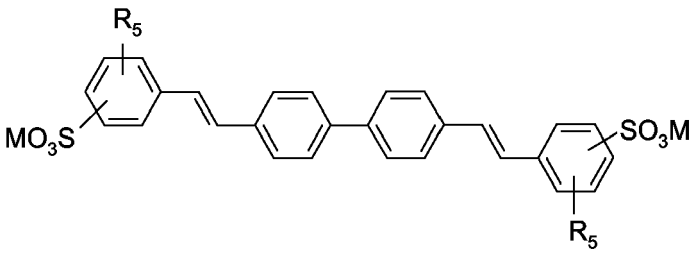
1. A composition for fluorescent whitening of paper comprising

a) a bis-triazinylamino stilbene of the formula



(1),

in which
R_1, R_2, R_3 and R_4 each, independently, represent $-NH_2$, $-OC_1$-C_4alkyl, -Oaryl, $-NHC_1$-C_4alkyl, $-N(C_1$-C_4alkyl$)_2$, $-N(C_1$-C_4alkyl$)(C_1$-C_4hydroxyalkyl), $-NHC_1$-C_4hydroxyalkyl, $-N(C_1$-C_4hydroxyalkyl$)_2$, or -NHaryl, whereby aryl is phenyl, which may be unsubstituted or substituted by one or two sulphonic acid groups, -COOH, $-COOC_1$-C_4alkyl, $-CONH_2$, $-CONHC_1$-C_4alkyl or by $-CON(C_1$-C_4alkyl$)_2$, a morpholino, piperidino or pyrrolidino residue, $-SC_1$-C_4alkyl or aryl, or an amino acid or amino acid amide residue from which a hydrogen atom has been abstracted from the amino group and
M represents hydrogen, an alkaline or alkaline earth metal, ammonium or ammonium that is mono-, di-, tri- or tetrasubstituted by C_1-C_4alkyl or C_2-C_4hydroxyalkyl or a distyryl biphenyl fluorescent whitening agent (FWA) of the formula



(2),

in which
R_5 represents hydrogen, chlorine or C_1-C_4alkoxy and
M is as defined above, or mixtures of (1) and (2),
b) water and, optionally,
c) one or more auxiliaries, **characterized in that** the pH of the composition lies within the range of from 10 to 13.

2. A composition according to claim 1, wherein the pH value of the composition is adjusted to between 10 and 13 by addition of an alkali metal hydroxide.

3. A composition according to claim 1 or claim 2, wherein the fluorescent whitening agent, component a) of the composition, is a compound of formula (1) in which each
R_1 and R_3 group and each
R_2 and R_4 group are identical and each pair, independently, represents $-NH_2$, $-NHC_1$-C_4alkyl, $-N(C_1$-C_4alkyl$)_2$, $-N(C_1$-C_4alkyl$)(C_1$-C_4hydroxyalkyl), $-NHC_1$-C_4hydroxyalkyl, $-N(C_1$-C_4hydroxyalkyl$)_2$, or -NHaryl, whereby aryl is phenyl, which may be unsubstituted or substituted by one or two sulphonic acid groups, a morpholino residue, or an amino acid or amino acid amide residue from which a hydrogen atom has been abstracted from the amino group and M represents hydrogen or an alkali metal ion.

4. A composition according to any one of claims 1 to 3, wherein the content of compounds of formulae (1) and/or (2) is between 5 and 40% by weight, based on the total weight of the composition.

5. Use of the composition according to any one of claims 1 to 4, for the fluorescent whitening of paper in the size press or film press or in a coating colour composition.

6. A size press or film press liquor composition, useful for the fluorescent whitening of paper, comprising

a) 0.01 to 20% by weight of the fluorescent whitening composition, according to any one of claims 1 to 4;
b) 1 to 20% by weight of one or more binders;
c) 0 to 10% by weight of pigment and/or further auxiliaries and
d) water to 100%.

7. A size press or film press liquor composition, useful for the fluorescent whitening of paper, comprising

a) 0.001 to 2% by weight of the fluorescent whitening agent of formula (1) and/or formula (2), according to of claim 1;
b) 1 to 20% by weight of one or more binders;
c) 0 to 10% by weight of pigment and/or further auxiliaries and
d) water to 100%, **characterized in that** the pH value of the composition is maintained at a value of between 10 and 13 during the application of the composition to the paper.

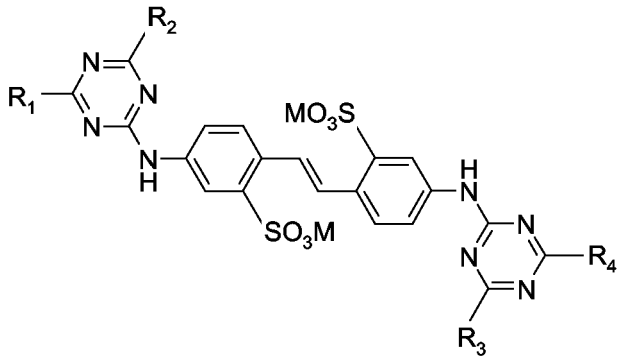
8. A paper coating colour composition comprising, in addition to 0.01 to 20 parts by weight of the composition according to any one of claims 1 to 4, per 100 parts of inorganic pigment,

i) from 3 to 25 parts by weight of binder and co-binder,
ii) 0 to 1 part by weight of rheology modifier,
iii) 0 to 2 parts by weight of wet-strength agent and
iv) 0 to 5 parts by weight of a further fluorescent whitening agent and/or shading colourant and/or further auxiliaries.

9. Use of the paper coating composition according to claim 8 or the size press or film press liquor composition according to claim 6 or claim 7, for the fluorescent whitening of paper.

10. A process for the fluorescent whitening of paper by applying to the paper a composition comprising

a) a bis-triazinylamino stilbene of the formula

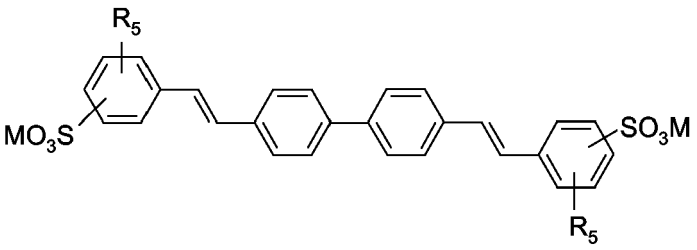


(1),

in which

R_1, R_2, R_3 and R_4 each, independently, represent $-NH_2$, $-OC_1$-C_4alkyl, -Oaryl, $-NHC_1$-C_4alkyl, $-N(C_1$-C_4alkyl$)_2$, $-N(C_1$-C_4alkyl$)(C_1$-C_4hydroxyalkyl), $-NHC_1$-C_4hydroxyalkyl, $-N(C_1$-C_4hydroxyalkyl$)_2$, or -NHaryl, whereby aryl is phenyl, which may be unsubstituted or substituted by one or two sulphonic acid groups, -COOH, $-COOC_1$-C_4alkyl, $-CONH_2$, $-CONHC_1$-C_4alkyl or by $-CON(C_1$-C_4alkyl$)_2$, a morpholino, piperidino or pyrrolidino residue, $-SC_1$-C_4alkyl or aryl, or an amino acid or amino acid amide residue from which a hydrogen atom has been abstracted from the amino group and

M represents hydrogen, an alkaline or alkaline earth metal, ammonium or ammonium that is mono-, di-, tri- or tetrasubstituted by C_1-C_4alkyl or C_2-C_4hydroxyalkyl or a distyryl biphenyl fluorescent whitening agent (FWA) of the formula



(2),

in which

R_5 represents hydrogen, chlorine or C_1-C_4alkoxy and

M is as defined above, or mixtures of (1) and (2),

b) water and, optionally,

c) one or more auxiliaries, **characterized in that** the pH of the composition is adjusted to a value of from 10 to 13 prior to or during the application of the composition to the paper.

11. Paper, which has been treated with a composition according to claim 1, a size press or film press liquor composition according to claim 6 or claim 7, a paper coating composition according to claim 8 or according to the process of claim 10.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 11 7354

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	19 February 2007	Settele, Ulrika

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