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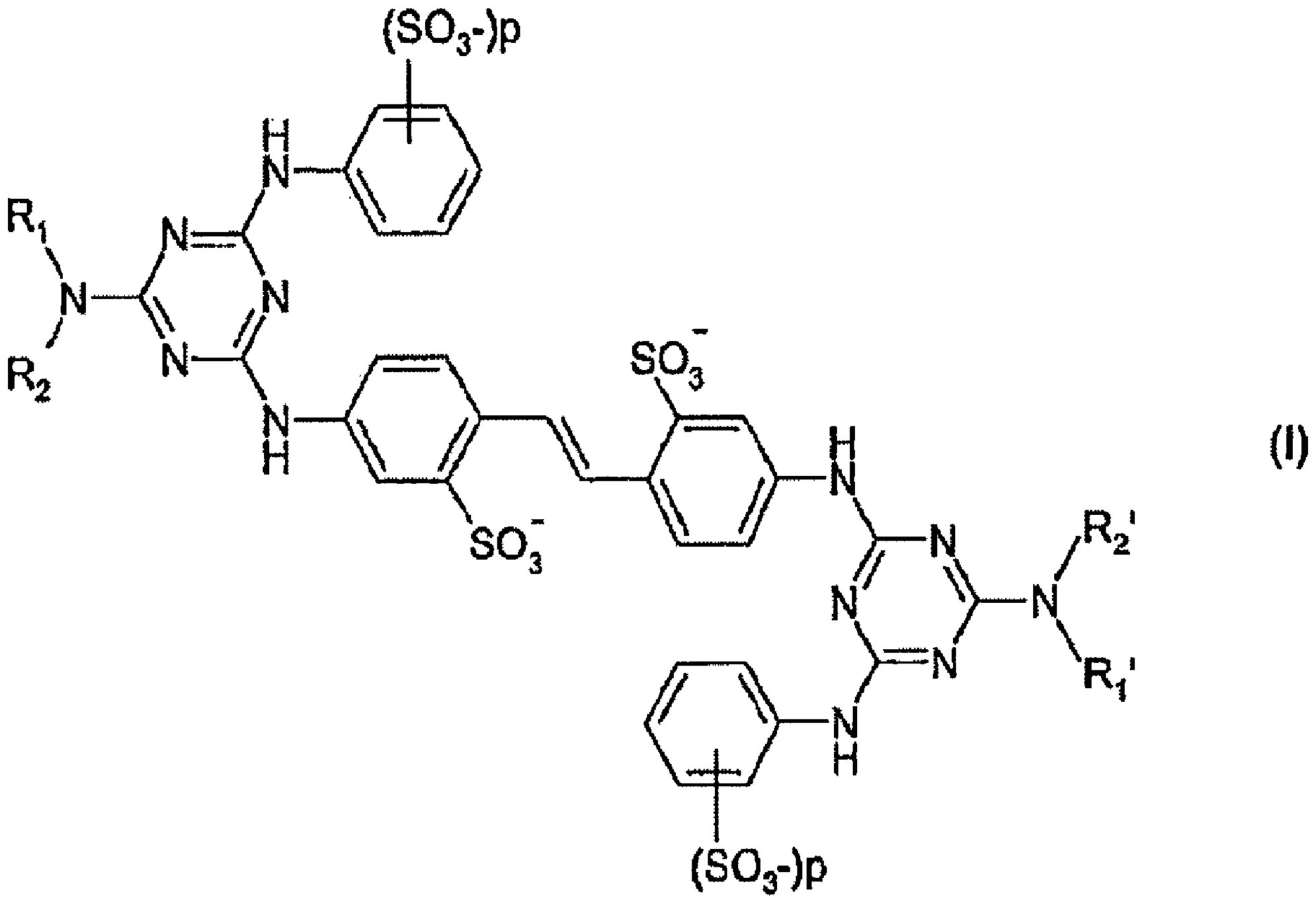
(54) **Titre : COMPOSITIONS AQUEUSES DE BLANCHIMENT ET DE NUANCAGE DANS LES APPLICATIONS DE REVETEMENTS**
(54) **Title: AQUEOUS COMPOSITIONS FOR WHITENING AND SHADING IN COATING APPLICATIONS**



(I)

(57) **Abrégé/Abstract:**
Aqueous coating composition for optical brightening and shading of substrates comprising (a) at least one optical brightener of formula (I) in which the anionic charge on the brightener is balanced by a cationic charge composed of one or more identical or different cations selected from the group consisting of hydrogen, an alkali metal cation, alkaline earth metal, ammonium, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched alkyl radical, ammonium which is mono-, di-, tri-

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(57) **Abrégé(suite)/Abstract(continued):**

or tetrasubstituted by a C_1-C_4 linear or branched hydroxyalkyi radical, ammonium which is, di-, tri- or tetrasubstituted by a mixture of C_1-C_4 linear or branched alkylradical and linear or branched hydroxyalkyi radical or mixtures of said compounds, R_1 and R_1' may be the same or different, and each is hydrogen, C_1-C_4 linear or branched alkyl, C_2-C_4 linear or branched hydroxyalkyi, $CH_2CO_2^-$, $CH_2CH_2CONH_2$or CH_2CH_2CN, R_2 and R_2'may be the same or different, and each is C_1-C_4 linear or branched alkyl, C_2-C_4 linear or branched hydroxyalkyl, $CH_2CO_2^-$, $CH(CO_2^-)CH_2CO_2^-$, $CH(CO_2^-)CH_2CH_2CO_2^-$, $CH_2CH_2SO_3^-$, $CH_2CH_2CO_2^-$, $CH_2CH(CH_3)CO_2^-$, benzyl, or R_1 and R_2 and/or R_1' and R_2', together with the neighboring nitrogen atom signify a morpholine ring and p is 0, 1 or 2, (b) at least one shading dye of formula (II) in which R_3 signifies H, methyl or ethyl, R_4 signifies paramethoxyphenyl, methyl or ethyl, M signifies a cation selected from the group consisting of hydrogen, an alkali metal cation, alkaline earth metal, ammonium, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched alkyl radical, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched hydroxyalkyl radical, ammonium which is, di-, tri- or tetrasubstituted by a mixture of C_1-C_4 linear or branched alkylradical and linear or branched hydroxyalkyl radical or mixtures of said compounds, (c) at least one white pigment, (d) at least one primary binder, (e) optionally one or more secondary binders and (f) water.

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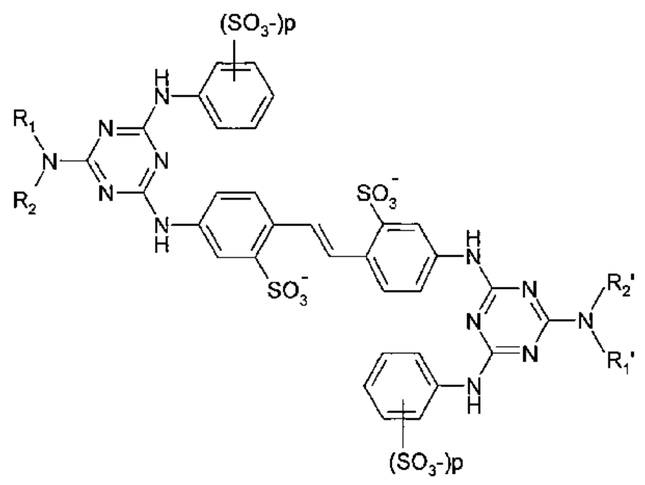
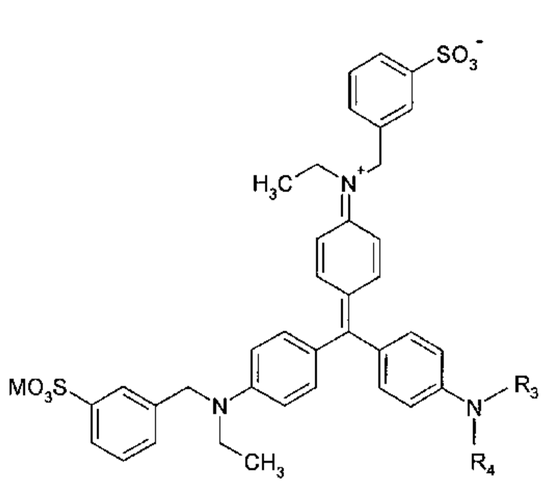
(54) **Title**: AQUEOUS COMPOSITIONS FOR WHITENING AND SHADING IN COATING APPLICATIONS



(I)



(II)

(57) **Abstract**: Aqueous coating composition for optical brightening and shading of substrates comprising (a) at least one optical brightener of formula (I) in which the anionic charge on the brightener is balanced by a cationic charge composed of one or more identical or different cations selected from the group consisting of hydrogen, an alkali metal cation, alkaline earth metal, ammonium, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched alkyl radical, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched hydroxyalkyi radical, ammonium which is, di-, tri- or tetrasubstituted by a mixture of C_1-C_4 linear or branched alkylradical and linear or branched hydroxyalkyi radical or mixtures of said compounds, R_1 and R_1' may be the same or different, and each is hydrogen, C_1-C_4 linear or branched alkyl, C2-C4 linear or branched hydroxyalkyi, $CH_2CO_2^-$, $CH_2CH_2CONH_2$or CH_2CH_2CN, R_2 and R_2'may be the same or different, and each is C_1-C_4 linear or branched alkyl, C_2-C_4 linear or branched hydroxyalkyl, $CH_2CO_2^-$, $CH(CO_2^-)CH_2CO_2^-$, $CH(CO_2^-)CH_2CH_2CO_2^-$, $CH_2CH_2SO_3^-$, $CH_2CH_2CO_2^-$, $CH_2CH(CH_3)CO_2^-$, benzyl, or R_1 and R_2 and/or R_1' and R_2', together with the neighboring nitrogen atom signify a morpholine ring and p is 0, 1 or 2, (b) at least one shading dye of formula (II) in which R_3 signifies H, methyl or ethyl, R_4 signifies paramethoxyphenyl, methyl or ethyl, M signifies a cation selected from the group consisting of hydrogen, an alkali metal cation, alkaline earth metal, ammonium, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched alkyl radical, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched hydroxyalkyl radical, ammonium which is, di-, tri- or tetrasubstituted by a mixture of C_1-C_4 linear or branched alkylradical and linear or branched hydroxyalkyl radical or mixtures of said compounds, (c) at least one white pigment, (d) at least one primary binder, (e) optionally one or more secondary binders and (f) water.

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Aqueous Compositions for whitening and shading in Coating Applications

The instant invention relates to aqueous coating compositions comprising derivatives of diaminostilbene optical brightener, shading dyes, white pigments, primary binders, and optionally secondary binders which can be used to provide coated substrates of high whiteness and brightness.

Background of the Invention

It is well known that the whiteness and thereby the attractiveness of coated papers can be improved by the addition of optical brighteners and shading dyes to the coating composition.

WO 0218705 A1 however teaches that the use of shading dyes, while having a positive effect on whiteness, has a negative impact on brightness. The solution to this problem is to add additional optical brightener, the advantage claimed in WO 0218705 A1 being characterized by the use of a mixture comprising at least one direct dye (exemplified by C.I. Direct Violet 35) or pigment (exemplified by C.I. Pigment Violet 23) and at least one optical brightener.

In order to satisfy the demand for coated papers of higher whiteness and brightness, there is a need for more efficient shading compositions.

Surprisingly, we have now discovered certain shading dyes which have a strongly positive effect on whiteness while having little or no effect on brightness, and which can be used in coating compositions comprising optical brighteners, white pigments, primary binders, and optionally secondary binders in order to enable the papermaker to reach high levels of whiteness and brightness.

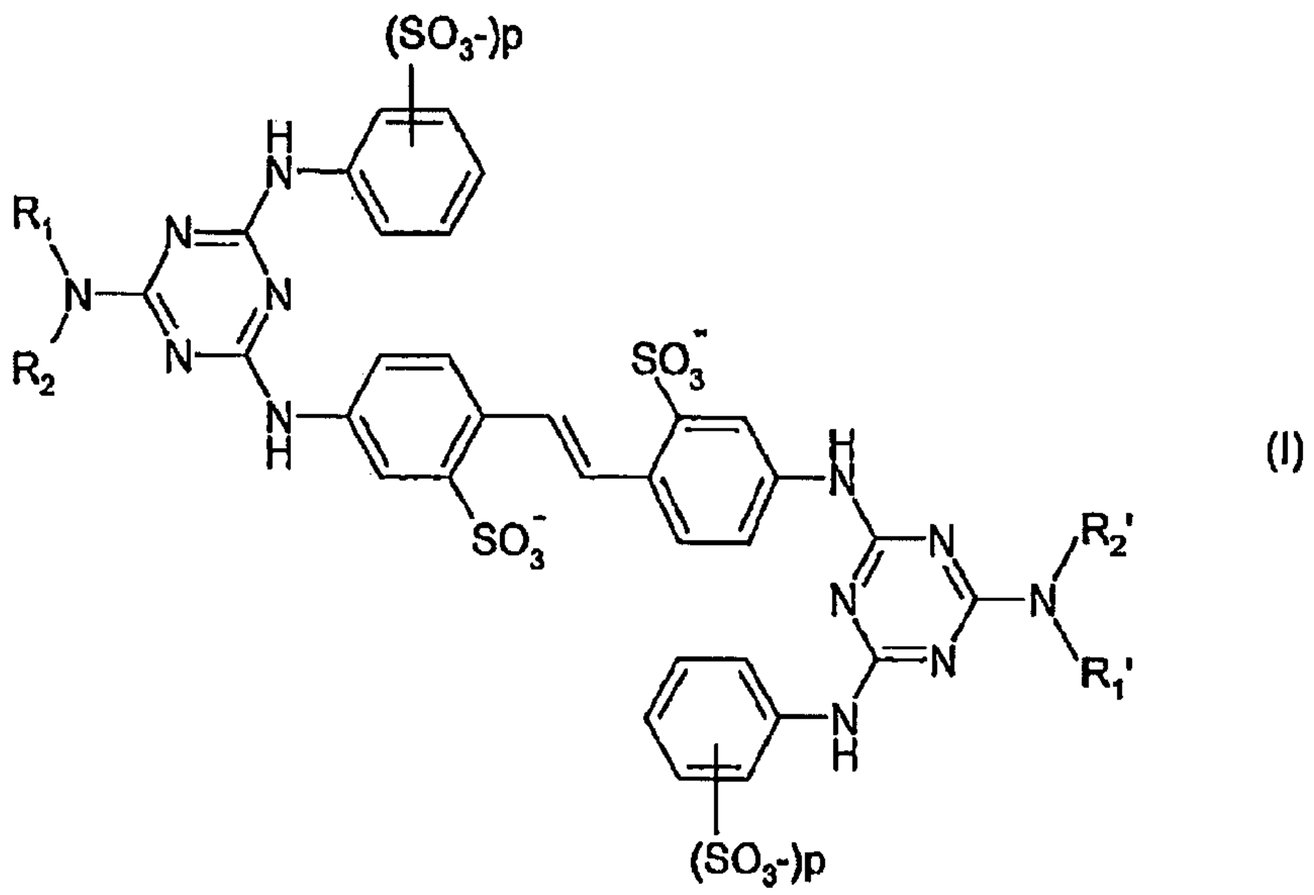
Therefore, the goal of the present invention is to provide aqueous coated compositions containing derivatives of diaminostilbene optical brightener, certain shading dyes, white pigments, primary binders, and optionally secondary binders,

which afford enhanced high whiteness levels while avoiding the disadvantages characterized by the use of shading dyes (loss of brightness) or pigments (lower whiteness build) recognized as being state-of-the-art.

Summary of the Invention

In one aspect, there is provided an aqueous coating composition for optical brightening and shading of substrates comprising

(a) at least one optical brightener of formula (I)

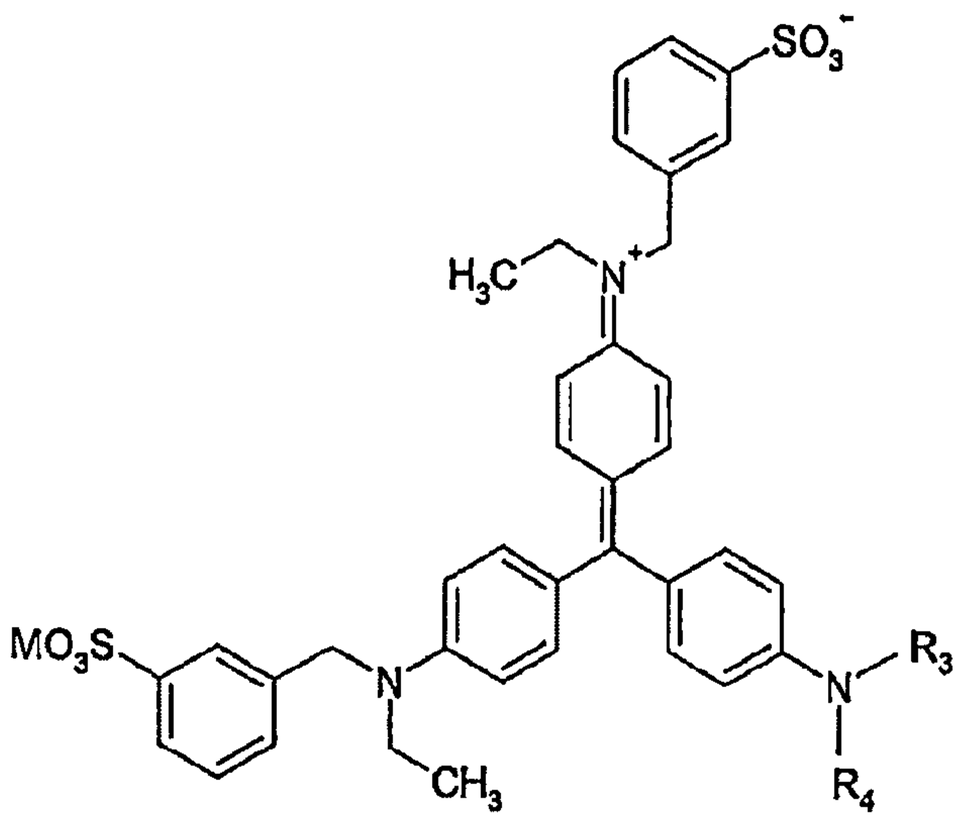


(I)

in which the anionic charge on the brightener is balanced by a cationic charge composed of one or more identical or different cations selected from the group consisting of hydrogen, an alkali metal cation, alkaline earth metal, ammonium, ammonium which is mono-, di-, tri- or tetra substituted by a C_1-C_4 linear or branched alkyl radical, ammonium which is mono-, di-, tri- or tetra substituted by a C_1-C_4 linear or branched hydroxyalkyl radical, ammonium which is, di-, tri- or tetrasubstituted by a mixture of C_1-C_4 linear or branched alkylradical and linear or branched hydroxyalkyl radical or mixtures of said

compounds, R_1 and R_1' may be the same or different, and each is hydrogen, C_1-C_4 linear or branched alkyl, C_2-C_4 linear or branched hydroxyalkyl, $CH_2CO_2^-$, $CH_2CH_2CONH_2$ or CH_2CH_2CN, R_2 and R_2' may be the same or different, and each is C_1-C_4 linear or branched alkyl, C_2-C_4 linear or branched hydroxyalkyl, $CH_2CO_2^-$, $CH(CO_2^-)CH_2CO_2^-$, $CH(CO_2^-)CH_2CH_2CO_2^-$, $CH_2CH_2SO_3^-$, $CH_2CH_2CO_2^-$, $CH_2CH(CH_3)CO_2^-$, benzyl, or R_1 and R_2 and/or R_1' and R_2', together with the neighboring nitrogen atom, signify a morpholine ring and p is 0, 1 or 2,

(b) at least one shading dye of formula (II)



(II)

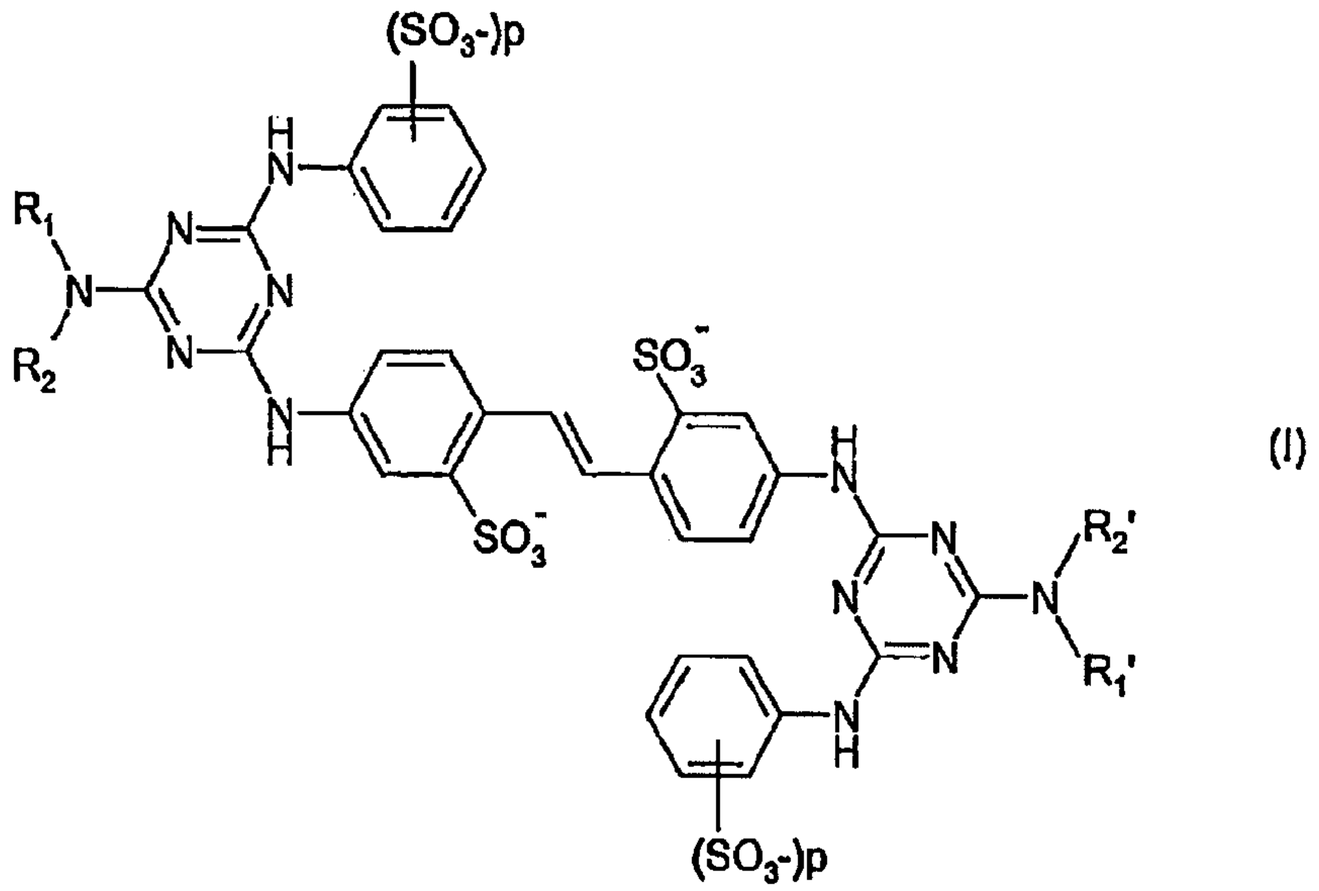
in which R_3 signifies H, methyl or ethyl, R_4 signifies paramethoxyphenyl, methyl or ethyl, M signifies a cation selected from the group consisting of hydrogen, an alkali metal cation, alkaline earth metal, ammonium, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched alkyl radical, ammonium which is mono-, di-, tri- or tetra substituted by a C_1-C_4 linear or branched hydroxyalkyl radical, ammonium which is, di-, tri- or tetrasubstituted by a mixture of C_1-C_4 linear or branched alkylradical and linear or branched hydroxyalkyl radical or mixtures of said compounds, (c) at least one white pigment, (d) at least one primary binder, (e) optionally one or more secondary binders and (f) water.

In another aspect, there is provided use of the aqueous coating composition as described herein for shading and whitening of paper substrates.

Description of the Invention

The present invention therefore provides aqueous coating compositions for optical brightening and shading of substrates, preferably paper, comprising

(a) at least one optical brightener of formula (I)



(I)

in which

the anionic charge on the brightener is balanced by a cationic charge composed of one or more identical or different cations selected from the group consisting of hydrogen, an alkali metal cation, alkaline earth metal, ammonium, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched alkyl radical, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched hydroxyalkyl radical, ammonium which is, di-, tri- or tetrasubstituted by a mixture of C_1-C_4 linear or branched alkylradical and linear or branched hydroxyalkyl radical or mixtures of said compounds,

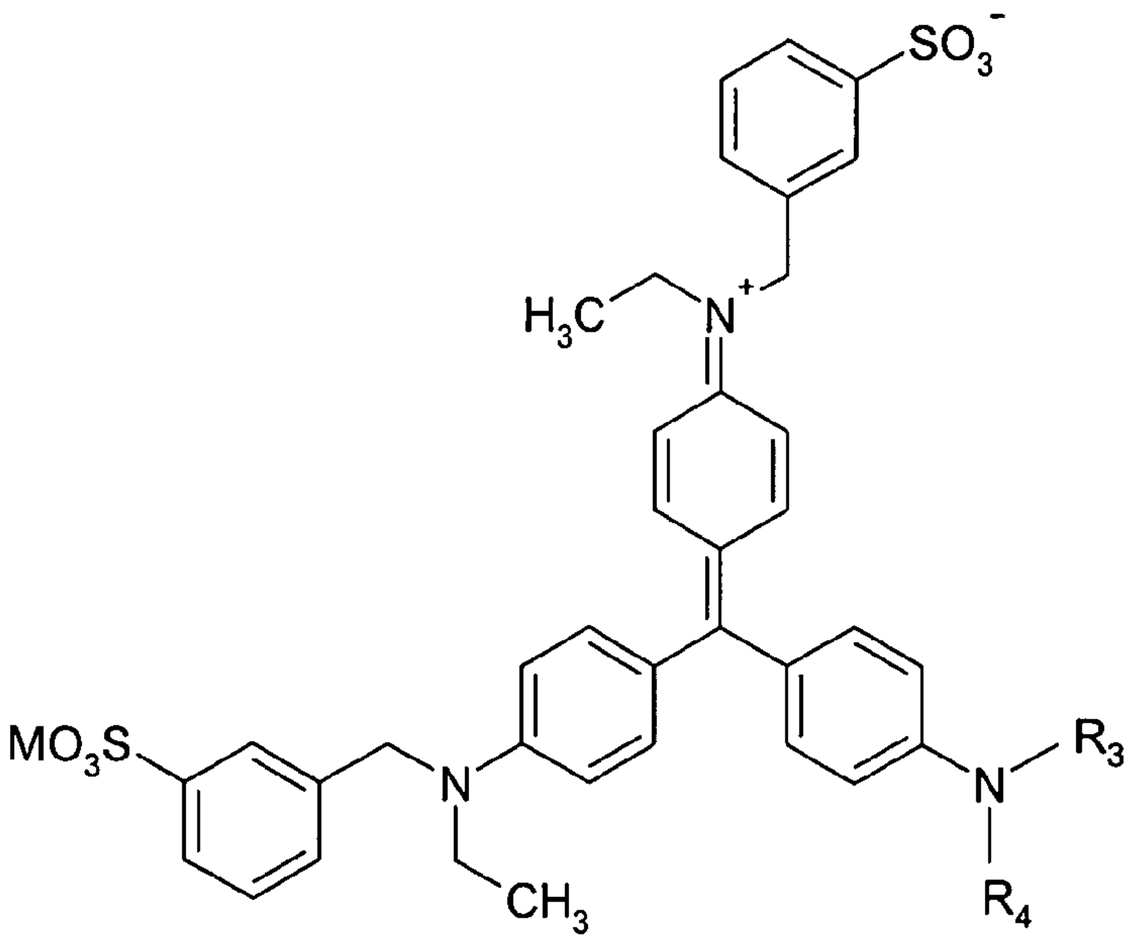
R_1 and R_1' may be the same or different, and each is hydrogen, C_1-C_4 linear or branched alkyl, C_2-C_4 linear or branched hydroxyalkyl, $CH_2CO_2^-$, $CH_2CH_2CONH_2$ or CH_2CH_2CN,

R_2 and R_2' may be the same or different, and each is C_1-C_4 linear or branched alkyl, C_2-C_4 linear or branched hydroxyalkyl, $CH_2CO_2^-$, $CH(CO_2^-)CH_2CO_2^-$, $CH(CO_2^-)CH_2CH_2CO_2^-$, $CH_2CH_2SO_3^-$, $CH_2CH_2CO_2^-$, $CH_2CH(CH_3)CO_2^-$, benzyl, or

R_1 and R_2 and/or R_1' and R_2', together with the neighboring nitrogen atom signify a morpholine ring and

p is 0, 1 or 2,

(b) at least one shading dye of formula (II)



(II)

in which

R_3 signifies H, methyl or ethyl,

R_4 signifies paramethoxyphenyl, methyl or ethyl,

M signifies a cation selected from the group consisting of hydrogen, an alkali metal cation, alkaline earth metal, ammonium, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched alkyl radical, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or

branched hydroxyalkyl radical, ammonium which is, di-, tri- or tetrasubstituted by a mixture of C_1-C_4 linear or branched alkylradical and linear or branched hydroxyalkyl radical or mixtures of said compounds,

(c) at least one white pigment,

(d) at least one primary binder,

(e) optionally one or more secondary binders and

(f) water.

In compounds of formula (I) for which p is 1, the SO_3^- group is preferably in the 4-position of the phenyl group.
In compounds of formula (I) for which p is 2, the SO_3^- groups are preferably in the 2,5-positions of the phenyl group.

Preferred compounds of formula (I) are those in which
the anionic charge on the brightener is balanced by a cationic charge composed of one or more identical or different cations selected from the group consisting of hydrogen, an alkali metal cation, alkaline earth metal, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched hydroxyalkyl radical, ammonium which is, di-, tri- or tetrasubstituted by a mixture of C_1-C_4 linear or branched alkylradical and linear or branched hydroxyalkyl radical or mixtures of said compounds,

R_1 and R_1' may be the same or different, and each is hydrogen, C_1-C_4 linear or branched alkyl, C_2-C_4 linear or branched hydroxyalkyl, $CH_2CO_2^-$, $CH_2CH_2CONH_2$ or CH_2CH_2CN,

R_2 and R_2' may be the same or different, and each is C_1-C_4 linear or branched alkyl, C_2-C_4 linear or branched hydroxyalkyl, $CH_2CO_2^-$, $CH(CO_2^-)CH_2CO_2^-$ or $CH_2CH_2SO_3^-$ and

p is 0, 1 or 2.

More preferred compounds of formula (I) are those in which
the anionic charge on the brightener is balanced by a cationic charge composed of one or more identical or different cations selected from the group consisting of Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched hydroxyalkyl radical, ammonium which is, di-, tri- or tetrasubstituted by a mixture of C_1-C_4 linear or branched alkylradical and linear or branched hydroxyalkyl radical or mixtures of said compounds,

R_1 and R_1' may be the same or different, and each is hydrogen, methyl, ethyl, propyl, α-methylpropyl, β-methylpropyl, β-hydroxyethyl, β-hydroxypropyl, $CH_2CO_2^-$, $CH_2CH_2CONH_2$ or CH_2CH_2CN,

R_2 and R_2' may be the same or different, and each is methyl, ethyl, propyl, α-methylpropyl, β-methylpropyl, β-hydroxyethyl, β-hydroxypropyl, $CH_2CO_2^-$, $CH(CO_2^-)CH_2CO_2^-$ or $CH_2CH_2SO_3^-$ and

p is 0, 1 or 2.

Especially preferred compounds of formula (I) are those in which
the anionic charge on the brightener is balanced by a cationic charge composed of one or more identical or different cations selected from the group consisting of Na^+, K^+, triethanolammonium, N-hydroxyethyl-N,N-dimethylammonium, N-hydroxyethyl-N,N-diethylammonium or mixtures of said compounds,

R_1 and R_1' may be the same or different, and each is hydrogen, ethyl, propyl, β-hydroxyethyl, β-hydroxypropyl, $CH_2CO_2^-$, or CH_2CH_2CN,

R_2 and R_2' may be the same or different, and each is ethyl, propyl, β-hydroxyethyl, β-hydroxypropyl, $CH_2CO_2^-$, $CH(CO_2^-)CH_2CO_2^-$ or $CH_2CH_2SO_3^-$ and

p is 1 or 2.

Compound of formula (I) is used in an amount typically of from 0.01 to 5 % by weight, preferably in the range of from 0.05 to 3 % by weight, the % by weight being based on the total weight of dry white pigment.

Preferred compounds of formula (II) are those in which

R_3 signifies H, methyl or ethyl,

R_4 signifies paramethoxyphenyl, methyl or ethyl,

M signifies a cation selected from the group consisting of hydrogen, an alkali metal cation, alkaline earth metal, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched hydroxyalkyl radical, ammonium which is, di-, tri- or tetrasubstituted by a mixture of C_1-C_4 linear or branched alkylradical and linear or branched hydroxyalkyl radical or mixtures of said compounds.

More preferred compounds of formula (II) are those in which

R_3 signifies methyl or ethyl,

R_4 signifies methyl or ethyl,

M signifies a cation selected from the group consisting of Li^+, Na^+, K^+, ½ Ca^{2+}, ½ Mg^{2+}, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched hydroxyalkyl radical, ammonium which is, di-, tri- or tetrasubstituted by a mixture of C_1-C_4 linear or branched alkylradical and linear or branched hydroxyalkyl radical or mixtures of said compounds.

Especially preferred compounds of formula (II) are those in which

R_3 signifies methyl,

R_4 signifies methyl,

M signifies a cation selected from the group consisting of Na^+, K^+, triethanolammonium, N-hydroxyethyl-N,N-dimethylammonium, N-hydroxyethyl-N,N-diethylammonium or mixtures of said compounds.

Compound of formula (II) is used in an amount typically of from 0.00001 to 0.01 % by weight, preferably in the range of form 0.00005 to 0.005 % by weight, the % by weight being based on the total weight of dry white pigment.

Although it is possible to produce coating compositions that are free from white pigments, the best white substrates for printing are made using opaque coating compositions comprise from 10 to 70 % by weight of white pigments, preferably of from 40 to 60 % by weight of white pigments, the % by weight being based on the

total weight of the coating composition. Such white pigments are generally inorganic pigments, e.g., aluminium silicates (kaolin, otherwise known as china clay), calcium carbonate (chalk), titanium dioxide, aluminium hydroxide, barium carbonate, barium sulphate, or calcium sulphate (gypsum). Preferably a mixture of from 10 to 20 % by weight of clay and of from 30 to 40 % by weight of chalk is used as white pigments, the % by weight being based on the total weight of the coating composition.

The binders may be any of those commonly used in the paper industry for the production of coating compositions and may consist of a single binder or of a mixture of primary and secondary binders.

The sole or primary binder is preferably a synthetic latex, typically a styrene-butadiene, vinyl acetate, styrene acrylic, vinyl acrylic or ethylene vinyl acetate polymer. The preferred primary binder is a latex binder.

The sole or primary binder is used in an amount typically in the range of form 2 to 25 % by weight, preferably of from 4 to 20 % by weight, the % by weight being based on the total weight of white pigment.

The secondary binder which may be optionally used may be, e.g., starch, carboxymethylcellulose, casein, soy polymers, polyvinyl alcohol or a mixture of any of the above. The preferred secondary binder which may be optionally used is a polyvinyl alcohol binder.

The polyvinyl alcohol which may be optionally used in the coating composition as secondary binder has preferably a degree of hydrolysis greater than or equal to 60 % and a Brookfield viscosity of from 2 to 80 mPa.s (4 % aqueous solution at 20 °C). More preferably, the polyvinyl alcohol has a degree of hydrolysis greater than or equal to 80 % and a Brookfield viscosity of from 2 to 40 mPa.s (4 % aqueous solution at 20 °C).

When optionally used, the secondary binder is used in an amount typically in the range of form 0.1 to 20 % by weight, preferably of from 0.2 to 8 % by weight, more preferably of from 0.3 to 6 % by weight, the % by weight being based on the total weight of white pigment.

The pH value of the coating composition is typically in the range of from 5 to 13, preferably of from 6 to 11, more preferably of from 7 to 10. Where it is necessary to adjust the pH of the coating composition, acids or bases may be employed. Examples of acids which may be employed include but are not restricted to hydrochloric acid, sulphuric acid, formic acid and acetic acid. Examples of bases which may be employed include but are not restricted to alkali metal and alkaline earth metal hydroxide or carbonates, ammonia or amines.

In addition to one or more compounds of formula (I), one or more compounds of formula (II), one or more white pigments, one or more binders, optionally one or more secondary binders and water, the coating composition may contain by-products formed during the preparation of compounds of formula (I) and compounds of formula (II) as well as other conventional paper additives. Examples of such additives are for example antifreezers, dispersing agents, synthetic or natural thickeners, carriers, defoamers, wax emulsions, dyes, inorganic salts, solubilizing aids, preservatives, complexing agents, biocides, cross-linkers, pigments, special resins etc.

The coating composition may be prepared by adding one or more compounds of formula (I) and one or more compounds of formula (II), to a preformed aqueous dispersion of one or more binders, optionally one or more secondary binders and one or more white pigments.

One or more compounds of formula (I) and one or more compounds of formula (II) can be added in any order or at the same time to the preformed aqueous dispersion of one or more binders, optionally one or more secondary binders and one or more white pigments.

One or more compounds of formula (I), one or more compounds of formula (II) and optionally one or more secondary binders can be added as solids or as preformed aqueous solutions to the preformed aqueous dispersion of one or more white pigments.

The present invention further provides a process for the optical brightening and tinting of paper substrates characterized in that an aqueous coating composition containing at least one optical brightener, at least one certain shading dye, at least one white pigment, at least one binder and optionally at least one secondary binder is used.

When used as a preformed aqueous solution, the concentration of compound of formula (I) in water is preferably of from 1 to 50 % by weight, more preferably of from 2 to 40 % by weight, even more preferably from 10 to 30 % by weight, the % by weight being based on the total weight of the preformed aqueous solution containing the compound of formula (I).

When used as a preformed aqueous solution, the concentration of compound of formula (II) in water is preferably of from 0.001 to 30 % by weight, more preferably of from 0.01 to 25 % by weight, even more preferably from 0.02 to 20 % by weight, the % by weight being based on the total weight of the preformed aqueous solution containing the compound of formula (II).

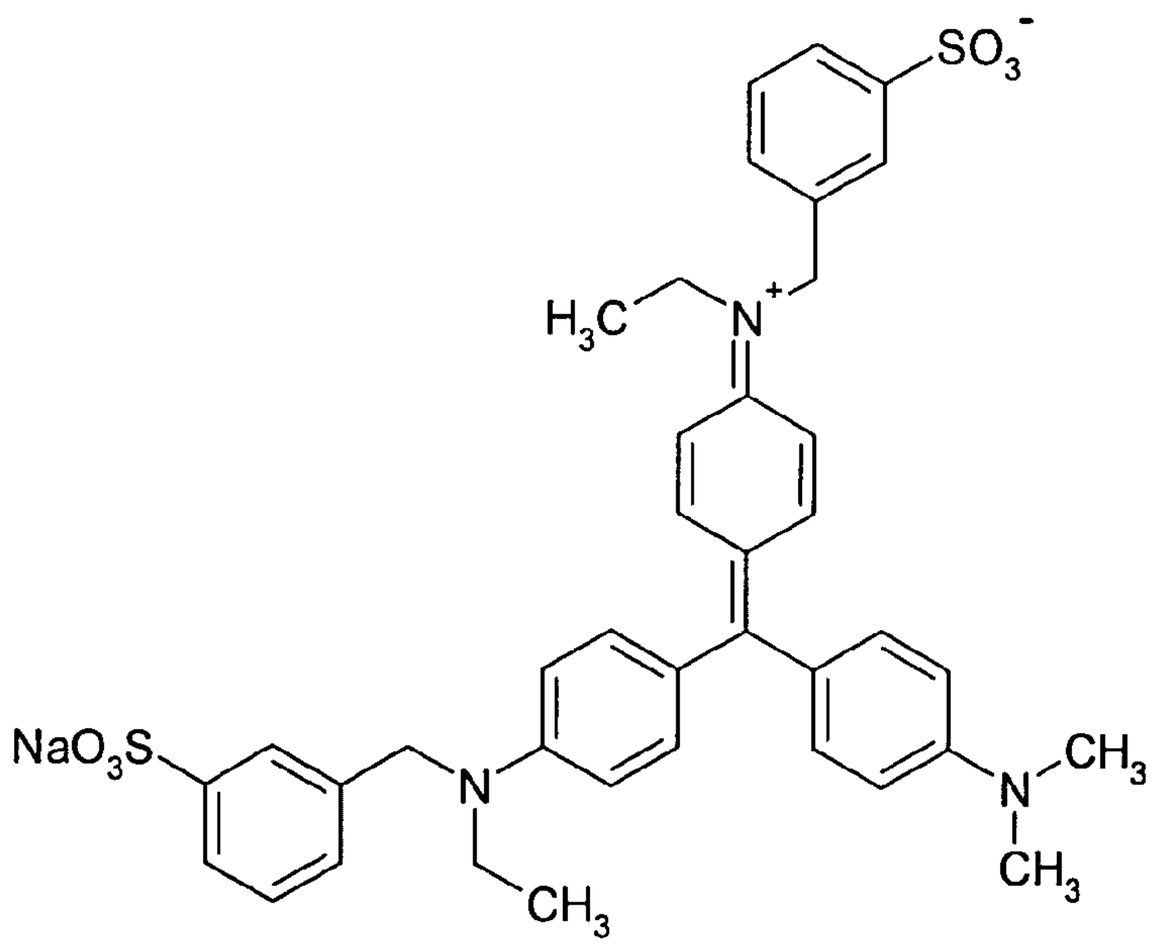
When used as a preformed aqueous solution, the concentration of secondary binders in water is preferably of from 1 to 50 % by weight, more preferably of from 2 to 40 % by weight, even more preferably from 5 to 30 % by weight, the % by weight being based on the total weight of the preformed aqueous solution containing the secondary binders.

The following examples shall demonstrate the instant invention in more details. In the present application, if not indicated otherwise, “parts” means “parts by weight” and “%” means “% by weight”.

Examples

Preparative Example 1

An aqueous shading solution (S1) containing compound of formula (1) is prepared by slowly adding 50 parts of compound of formula (1) to 450 parts of water at room temperature with efficient stirring. The obtained solution is stirred for 1 hour and filtered to remove any insoluble particles. The resulting shading solution (S1) has a pH in the range of from 6.0 to 7.0 and contains 10 % by weight of compound of formula (1), the % by weight being based on the total weight of the final aqueous shading solution (S1).

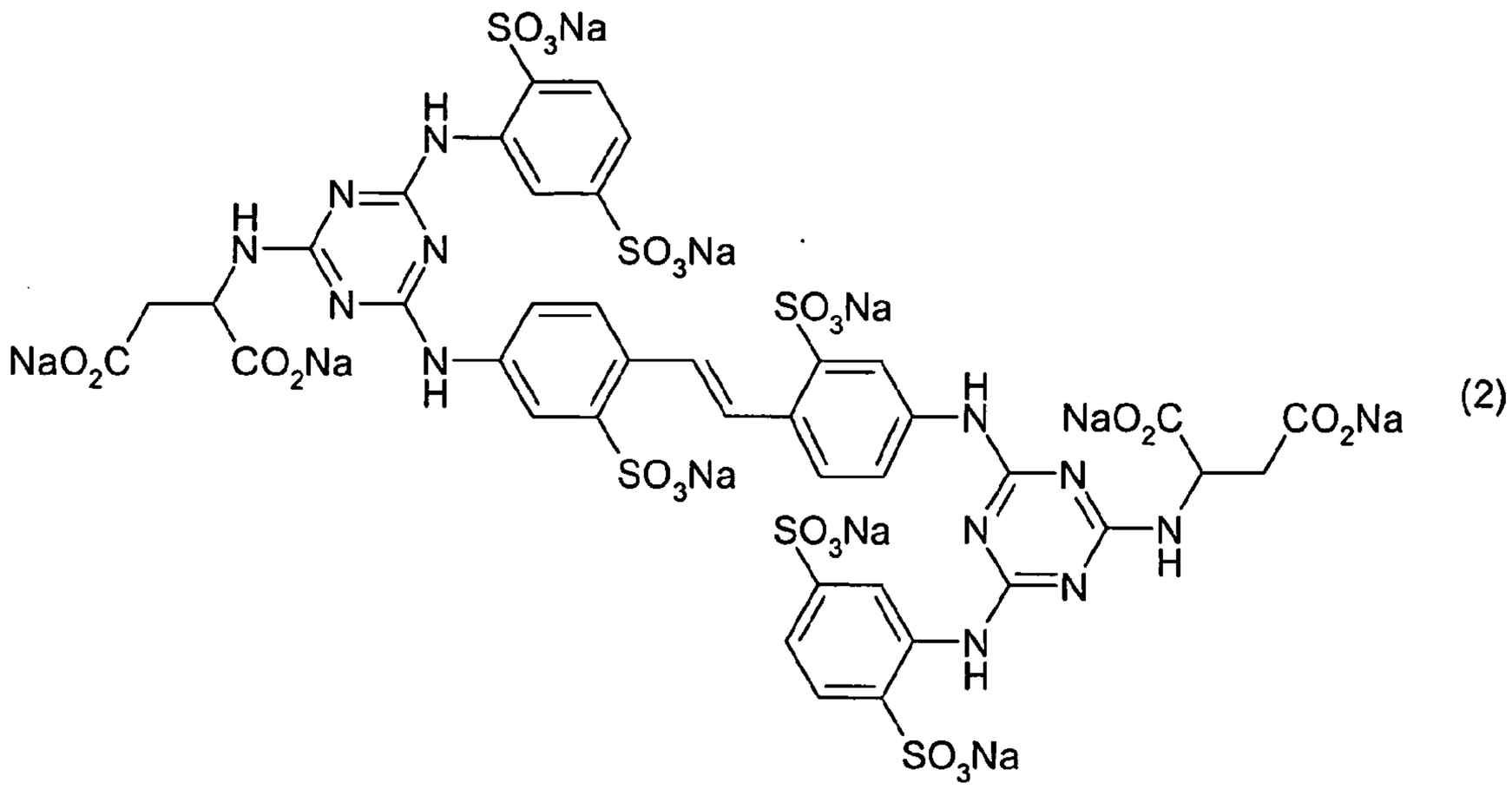


(1)

Application Example 1

A coating composition is prepared containing 70 parts chalk (commercially available under the trade name Hydrocarb 90 from OMYA), 30 parts clay (commercially available under the trade name Kaolin SPS from IMERYS), 42.8 parts water, 0.6 parts dispersing agent (a sodium salt of a polyacrylic acid commercially available under the trade name Polysalz S from BASF), 20 parts of 50 % latex (a styrene butadiene copolymer commercially available under the trade name DL 921 from Dow), 0.8 parts of a polyvinyl alcohol having a degree of

hydrolysis of 98 - 99 % and Brookfield viscosity of 4.0 - 5.0 mPa.s (4 % aqueous solution at 20 °C) and 0.5 parts of an aqueous solution of compound of formula (2) (approx. 18.0 % by weight of compound of formula (2), the % by weight being based on the total weight of the aqueous solution containing compound of formula (2)). The solids content of the coating composition is adjusted to approx. 65 % by the addition of water, and the pH is adjusted to 8 - 9 with sodium hydroxide.



(2)

Aqueous shading solution (S1) prepared according to preparative example 1 is diluted 1 part to 1000 parts with water.

The so-formed diluted aqueous solution is added to the stirred coating composition at a range of concentrations of from 0 to 20 % by weight (from 0 to 0.002 % by weight of compound of formula (1) based on dry solid), the % by weight being based on the total weight of the dry pigment.

The brightened and shaded coating composition is then applied to a commercial 75 gsm neutral-sized white paper base sheet using an automatic wire-wound bar applicator with a standard speed setting and a standard load on the bar. The coated paper is then dried for 5 minutes in a hot air flow. Afterwards the paper is allowed to condition and measured then for CIE Whiteness and brightness on a calibrated Minolta spectrophotometer. The results are shown in Table 1 and Table 2 respectively and clearly show that the instant invention provides a high level of

whiteness, while the loss of brightness at the highest addition level of shading dye is only 0.2 %.

Comparative Application Example 1a

Comparative application example 1a was conducted as in application example 1 with the sole difference that a 10 % by weight aqueous solution of C.I. Direct Violet 35 is used instead of the aqueous shading solution (S1), the % by weight being based on the total weight of the C.I. Direct Violet 35 aqueous solution.
CIE Whiteness and brightness are measured on a calibrated Minolta spectrophotometer. The results are shown in Table 1 and Table 2 respectively and clearly show that the use of a shading dye representing the state-of-the-art provides a lower whiteness level while accounting for a significant loss of brightness of up to 1.4 %.

Comparative Application Example 1b

Comparative application example 1b was conducted as in application example 1 with the sole difference that a 10 % by weight aqueous dispersion of C.I. Pigment Violet 23 is used instead of the aqueous shading solution (S1), the % by weight being based on the total weight of the C.I. Pigment Violet 23 aqueous dispersion.
CIE Whiteness and brightness are measured on a calibrated Minolta spectrophotometer. The results are shown in Table 1 and Table 2 respectively and clearly show that the use of a shading pigment representing the state-of-the-art provides significantly lower whiteness levels.

Table 1

Dye or pigment conc. (based on dry solid) [%]	Whiteness		
	Application Example 1	Comparative Application Example 1a	Comparative Application Example 1b
0	92.8	92.8	92.8
0.0005	94.1	94.1	93.4
0.001	95.7	94.9	94.4

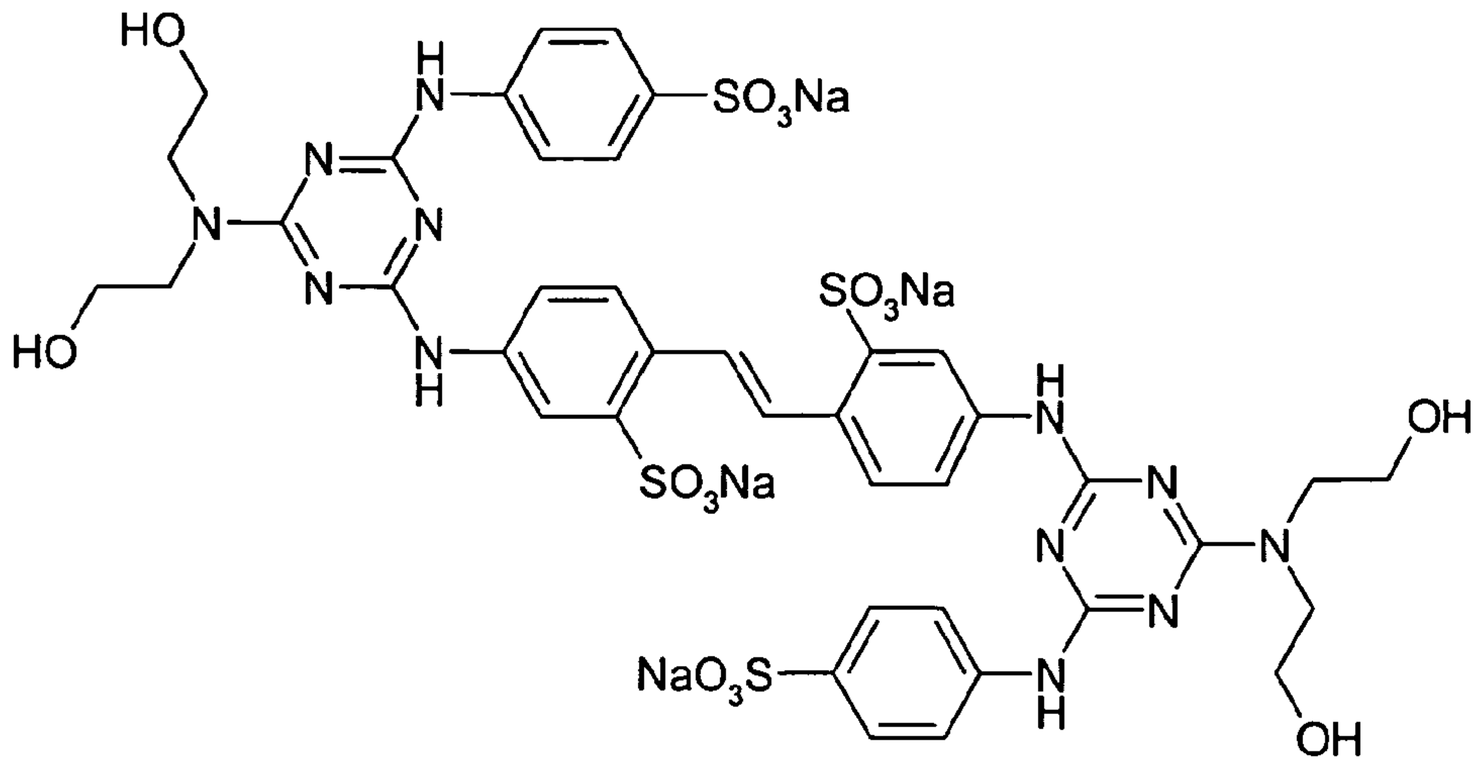
0.0015	97.2	95.9	95.5
0.002	98.5	96.3	96.1

Table 2

Dye or pigment conc. (based on dry solid) [%]	Brightness		
	Application Example 1	Comparative Application Example 1a	Comparative Application Example 1b
0	91.8	91.8	91.8
0.0005	91.7	91.6	91.5
0.001	91.8	91.4	91.8
0.0015	91.8	91.1	91.7
0.002	91.6	90.5	91.7

Application Example 2

A coating composition is prepared containing 70 parts chalk (commercially available under the trade name Hydrocarb 90 from OMYA), 30 parts clay (commercially available under the trade name Kaolin SPS from IMERYS), 42.8 parts water, 0.6 parts dispersing agent (a sodium salt of a polyacrylic acid commercially available under the trade name Polysalz S from BASF), 20 parts of 50 % latex (a styrene butadiene copolymer commercially available under the trade name DL 921 from Dow), 0.8 parts of a polyvinyl alcohol having a degree of hydrolysis of 98 - 99 % and a Brookfield viscosity of 4.0 - 5.0 mPa.s (4 % aqueous solution at 20 °C) and 0.5 parts of an aqueous solution of compound of formula (3) (approx. 25.2 % by weight of compound of formula (3), the % by weight being based on the total weight of the aqueous solution containing compound of formula (3)). The solids content of the coating composition is adjusted to approx. 65 % by the addition of water, and the pH is adjusted to 8-9 with sodium hydroxide.



(3)

Aqueous shading solution (S1) prepared according to preparative example 1 is diluted 1 part to 1000 parts with water.

The so-formed diluted aqueous solution is added to the stirred coating preparation at a range of concentrations of from 0 to 20 % by weight (from 0 to 0.002 % by weight of compound of formula (1) based on dry solid), the % by weight being based on the total weight of the dry pigment.

The brightened and shaded coating composition is then applied to a commercial 75 gsm neutral-sized white paper base sheet using an automatic wire-wound bar applicator with a standard speed setting and a standard load on the bar. The coated paper is then dried for 5 minutes in a hot air flow. Afterwards the paper is allowed to condition and measured then for CIE Whiteness and brightness on a calibrated Minolta spectrophotometer. The results are shown in Table 3 and Table 4 respectively and clearly show that the instant invention provides a high level of whiteness, while the loss of brightness at the highest addition level of shading dye is only 0.3 %.

Comparative Application Example 2a

Comparative application example 2a was conducted as in application example 2 with the sole difference that a 10 % by weight aqueous solution of C.I. Direct Violet 35 is used instead of the aqueous shading solution (S1), the % by weight being based on the total weight of the C.I. Direct Violet 35 aqueous solution.

CIE Whiteness and brightness are measured on a calibrated Minolta spectrophotometer. The results are shown in Table 3 and Table 4 respectively and clearly show that use of a shading dye representing the state-of-the-art provides a lower whiteness level while accounting for a significant loss of brightness of up to 2.2 %.

Comparative Application Example 2b

Comparative application example 2b was conducted as in application example 2 with the sole difference that a 10 % by weight aqueous dispersion of C.I. Pigment Violet 23 is used instead of the aqueous shading solution (S1), the % by weight being based on the total weight of the C.I. Pigment Violet 23 aqueous dispersion. CIE Whiteness and brightness are measured on a calibrated Minolta spectrophotometer. The results are shown in Table 3 and Table 4 respectively and clearly show that the use of a shading pigment representing the state-of-the-art provides significantly lower whiteness levels.

Table 3

Dye or pigment conc. (based on dry solid) [%]	Whiteness		
	Application Example 1	Comparative Application Example 1a	Comparative Application Example 1b
0	98.0	98.0	98.0
0.0005	99.6	97.9	98.9
0.001	100.6	98.0	99.8
0.0015	102.1	98.1	100.1
0.002	103.3	98.4	100.7

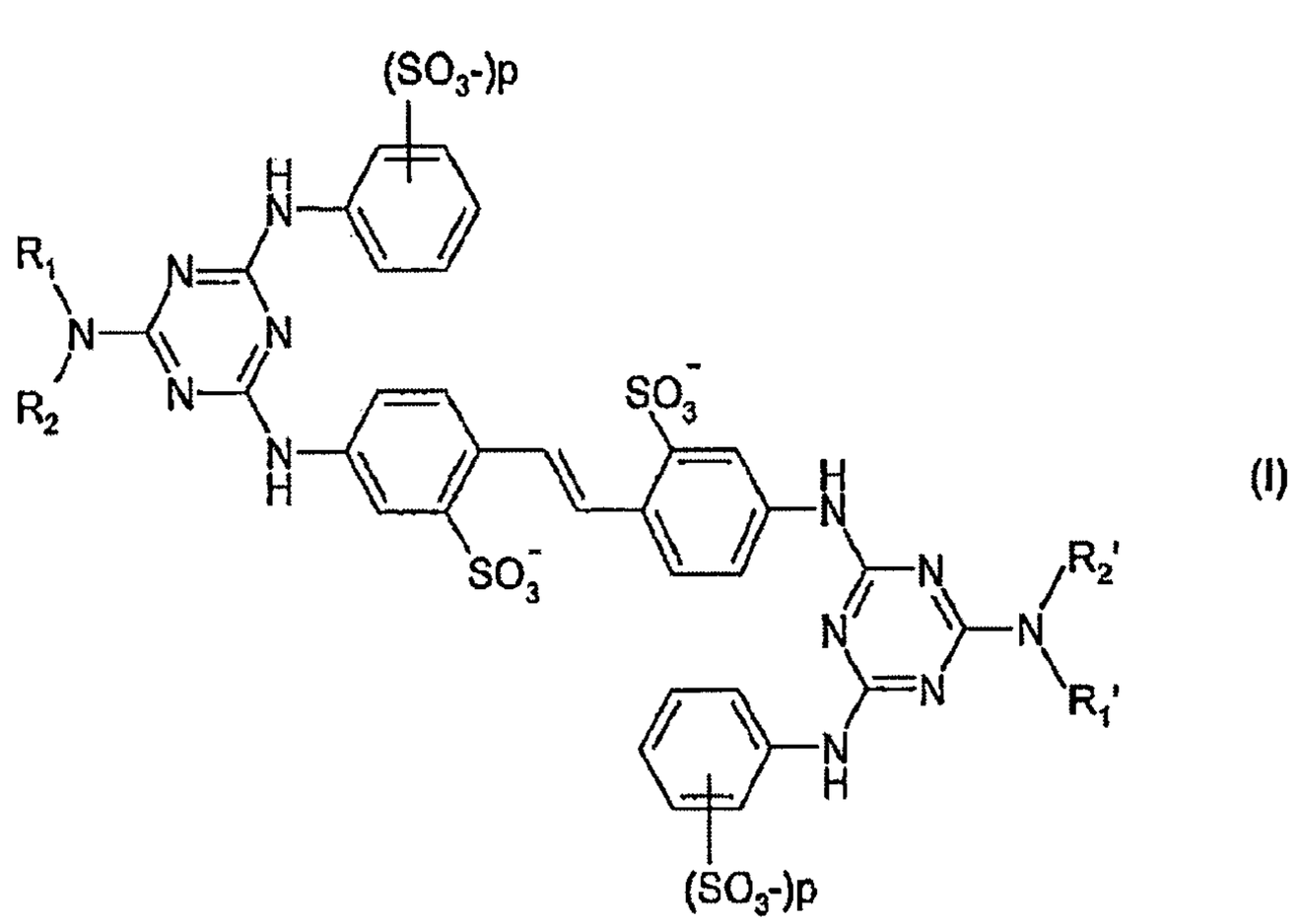
Table 4

Dye or pigment conc. (based on dry solid) [%]	Brightness		
	Application Example 1	Comparative Application Example 1a	Comparative Application Example 1b
0	93.5	93.5	93.5
0.0005	93.5	93.2	93.5
0.001	93.4	92.4	93.4
0.0015	93.3	91.9	93.3
0.002	93.2	91.4	93.2

CLAIMS:

1. Aqueous coating composition for optical brightening and shading of substrates comprising

(a) at least one optical brightener of formula (I)



(I)

in which

the anionic charge on the brightener is balanced by a cationic charge composed of one or more identical or different cations selected from the group consisting of hydrogen, an alkali metal cation, alkaline earth metal, ammonium, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched alkyl radical, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched hydroxyalkyl radical, ammonium which is, di-, tri- or tetrasubstituted by a mixture of C_1-C_4 linear or branched alkylradical and linear or branched hydroxyalkyl radical or mixtures of said compounds,

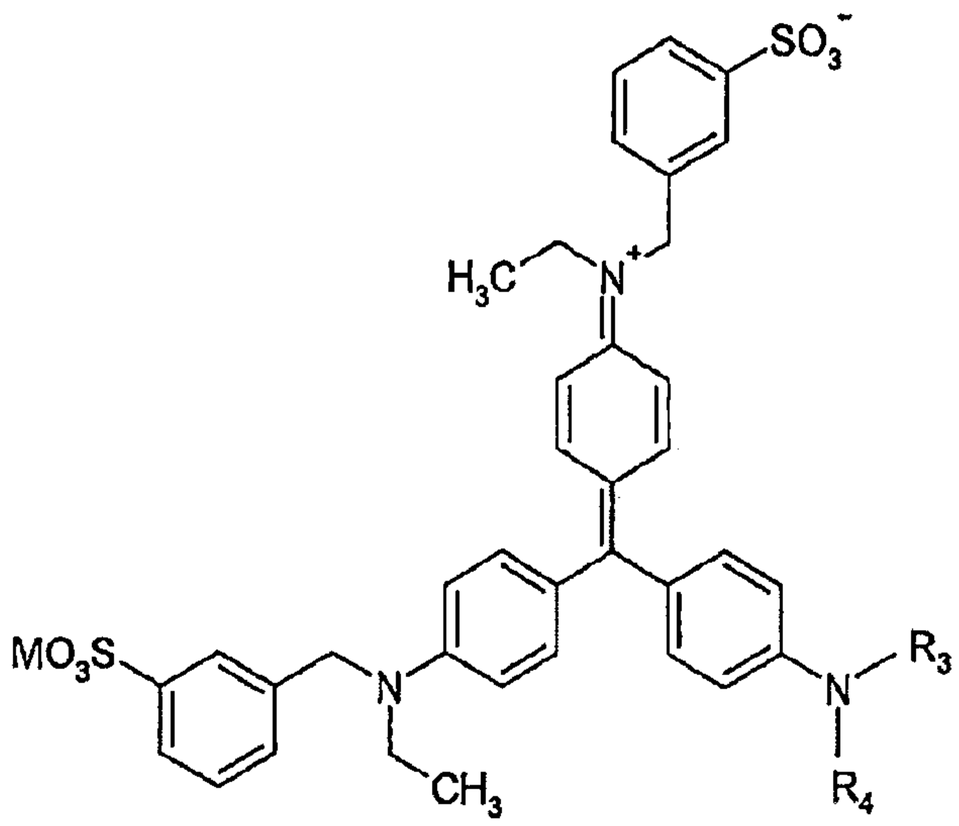
R_1 and R_1' may be the same or different, and each is hydrogen, C_1-C_4 linear or branched alkyl, C_2-C_4 linear or branched hydroxyalkyl, $CH_2CO_2^-$, $CH_2CH_2CONH_2$ or CH_2CH_2CN,

R_2 and R_2' may be the same or different, and each is C_1-C_4 linear or branched alkyl, C_2-C_4 linear or branched hydroxyalkyl, $CH_2CO_2^-$, $CH(CO_2^-)CH_2\ CO_2^-$, $CH(CO_2^-)CH_2CH_2CO_2^-$, $CH_2CH_2SO_3^-$, $CH_2CH_2CO_2^-$, $CH_2CH(CH_3)CO_2^-$, benzyl, or

R_1 and R_2 and/or R_1' and R_2', together with the neighboring nitrogen atom signify a morpholine ring and

p is 0, 1 or 2,

(b) at least one shading dye of formula (II)



(II)

in which

R_3 signifies H, methyl or ethyl,

R_4 signifies paramethoxyphenyl, methyl or ethyl,

M signifies a cation selected from the group consisting of hydrogen, an alkali metal cation, alkaline earth metal, ammonium, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched alkyl radical, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched hydroxyalkyl radical, ammonium which is, di-, tri- or tetrasubstituted by a mixture of C_1-C_4 linear or branched alkylradical and linear or branched hydroxyalkyl radical or mixtures of said compounds,

(c) at least one white pigment,

(d) at least one primary binder,

(e) optionally one or more secondary binders and

(f) water.

2. Aqueous coating composition according to claim 1, wherein in compounds of formula (I) for which p is 1, the SO_3^- group is in the 4-position of the phenyl group.

3. Aqueous coating composition according to claim 1 or 2, wherein in compounds of formula (I) for which p is 2, the SO_3^- groups are in the 2, 5-position of the phenyl group.

4. Aqueous coating composition according to any one of claims 1-3, wherein in compounds of formula (I) the anionic charge on the brightener is balanced by a cationic charge composed of one or more identical or different cations selected from the group consisting of hydrogen, an alkali metal cation, alkaline earth metal, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched hydroxyalkyl radical, ammonium which is, di-, tri- or tetrasubstituted by a mixture of C_1-C_4 linear or branched alkylradical and linear or branched hydroxyalkyl radical or mixtures of said compounds,

R_1 and R_1'	are the same or different, and each is hydrogen, C_1-C_4 linear or branched alkyl, C_2-C_4 linear or branched hydroxyalkyl, $CH_2CO_2^-$, $CH_2CH_2CONH_2$ or CH_2CH_2CN,
R_2 and R_2'	are the same or different, and each is C_1-C_4 linear or branched alkyl, C_2-C_4 linear or branched hydroxyalkyl, $CH_2CO_2^-$, $CH(CO_2^-)CH_2CO_2^-$ or $CH_2CH_2SO_3^-$ and
p	is 0, 1 or 2.

5. Aqueous coating composition according to any one of claims 1-4, wherein the compound of formula (I) is used in an amount of from 0.01 to 5 % by weight based on the total weight of dry white pigment.

6. Aqueous coating composition according to any one of claims 1-5, wherein in the compound of formula (II)

R_3 signifies H, methyl or ethyl,

R_4 signifies paramethoxyphenyl, methyl or ethyl,

M signifies a cation selected from the group consisting of hydrogen, an alkali metal cation, alkaline earth metal, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched hydroxyalkyl radical, ammonium which is, di-, tri- or tetrasubstituted by a mixture of C_1-C_4 linear or branched alkylradical and linear or branched hydroxyalkyl radical or mixtures of said compounds.

7. Aqueous coating composition according to any one of claims 1-6, wherein in the compound of formula (II)

R_3 signifies methyl or ethyl,

R_4 signifies methyl or ethyl,

M signifies a cation selected from the group consisting of Li^+, Na^+, K^+, ½ Ca^{2+}, ½ Mg^{2+}, ammonium which is mono-, di-, tri- or tetrasubstituted by a C_1-C_4 linear or branched hydroxyalkyl radical, ammonium which is, di-, tri- or tetrasubstituted by a mixture of C_1-C_4 linear or branched alkylradical and linear or branched hydroxyalkyl radical or mixtures of said compounds.

8. Aqueous coating composition according to any one of claims 1-7, wherein the compound of formula (II) is used in an amount from 0.00001 to 0.01 % by weight based on the total weight of dry white pigment.

9. Aqueous coating composition according to any one of claims 1-8, wherein the coating composition comprises 10 to 70 % by weight of white pigments based on the total weight of the coating composition.

10. Aqueous coating composition according to any one of claims 1-9, wherein the sole or primary binder is a synthetic latex, vinyl acetate, styrene acrylic, vinyl acrylic or ethylene vinyl acetate polymer.

11. Aqueous coating composition according to any one of claims 1-9 wherein the sole or primary binder is a styrene-butadiene.

12. Aqueous coating composition according to any one of claims 1-11, wherein the sole or primary binder is used in an amount in the range from 2 to 25 % by weight based on the total weight of white pigment.

13. Aqueous coating composition according to any one of claims 1-12, wherein the secondary binder is starch, carboxymethylcellulose, casein, soy polymers, polyvinyl alcohol or a mixture of any of the afore-mentioned.

14. Aqueous coating composition according to any one of claims 1-13, wherein polyvinyl alcohol is used as secondary binder.

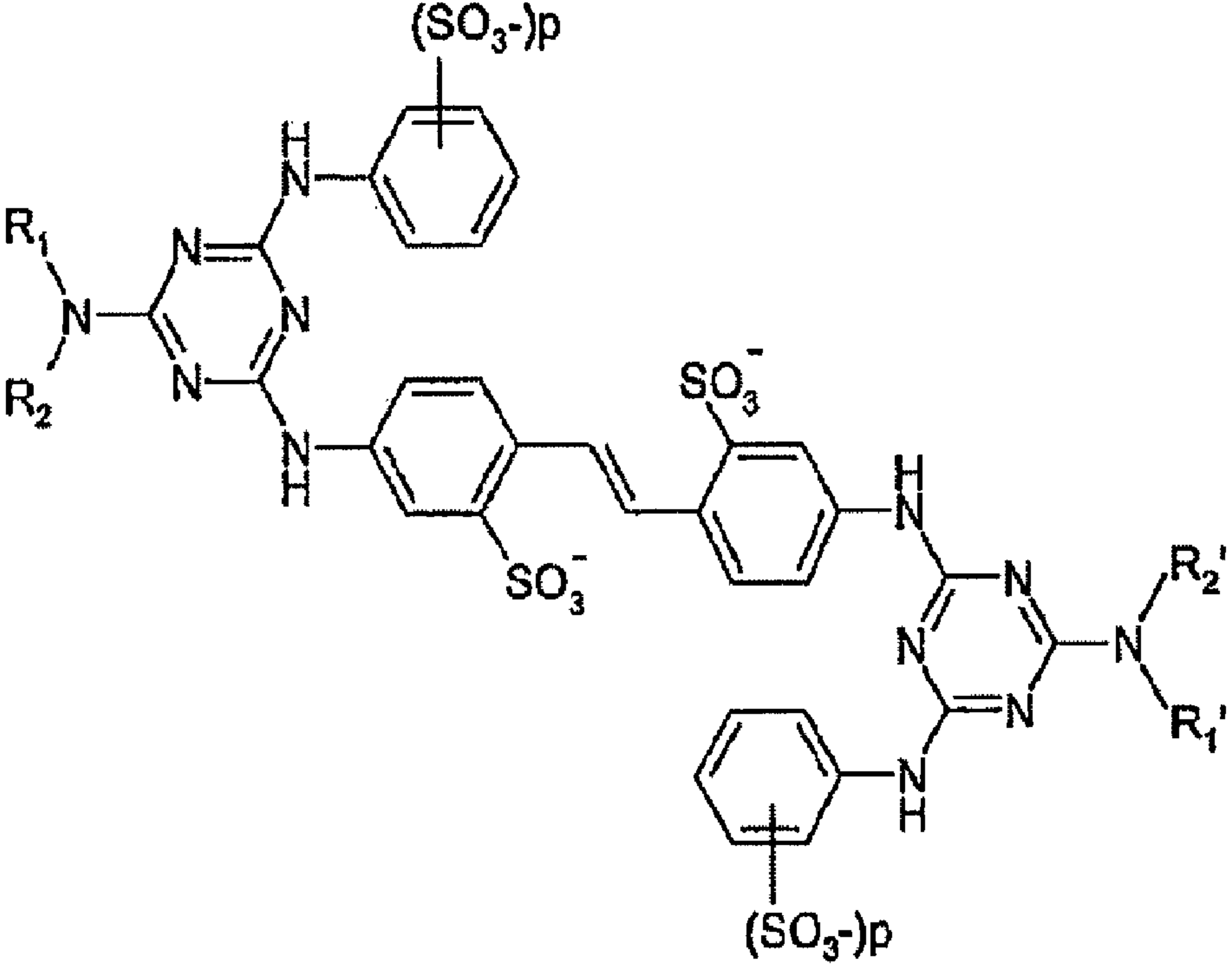
15. Aqueous coating composition according to claim 14, the polyvinyl alcohol has a degree of hydrolysis greater than or equal to 60 % and a Brookfield viscosity of from 2 to 80 mPa.s (4 % aqueous solution at 20 °C).

16. Aqueous coating composition according to any one of claims 1-15, wherein the secondary binder is used in an amount in the range from 0.1 to 20 % by weight based on the total weight of white pigment.

17. Aqueous coating composition according to any one of claims 1-16, wherein the pH value of the coating composition is in the range of from 5 to 13.

18. Use of the aqueous coating composition according to any one of claims 1-3 for shading and whitening of paper substrates.

19. Use according to claim 18, wherein the coating composition is used as a preformed solution comprising the compound of formula (I) in a concentration of 1 to 50 weight % and the compound of formula (II) in a concentration of 0.001 to 30 weight % based on the total weight of the preformed aqueous solution.



(I)