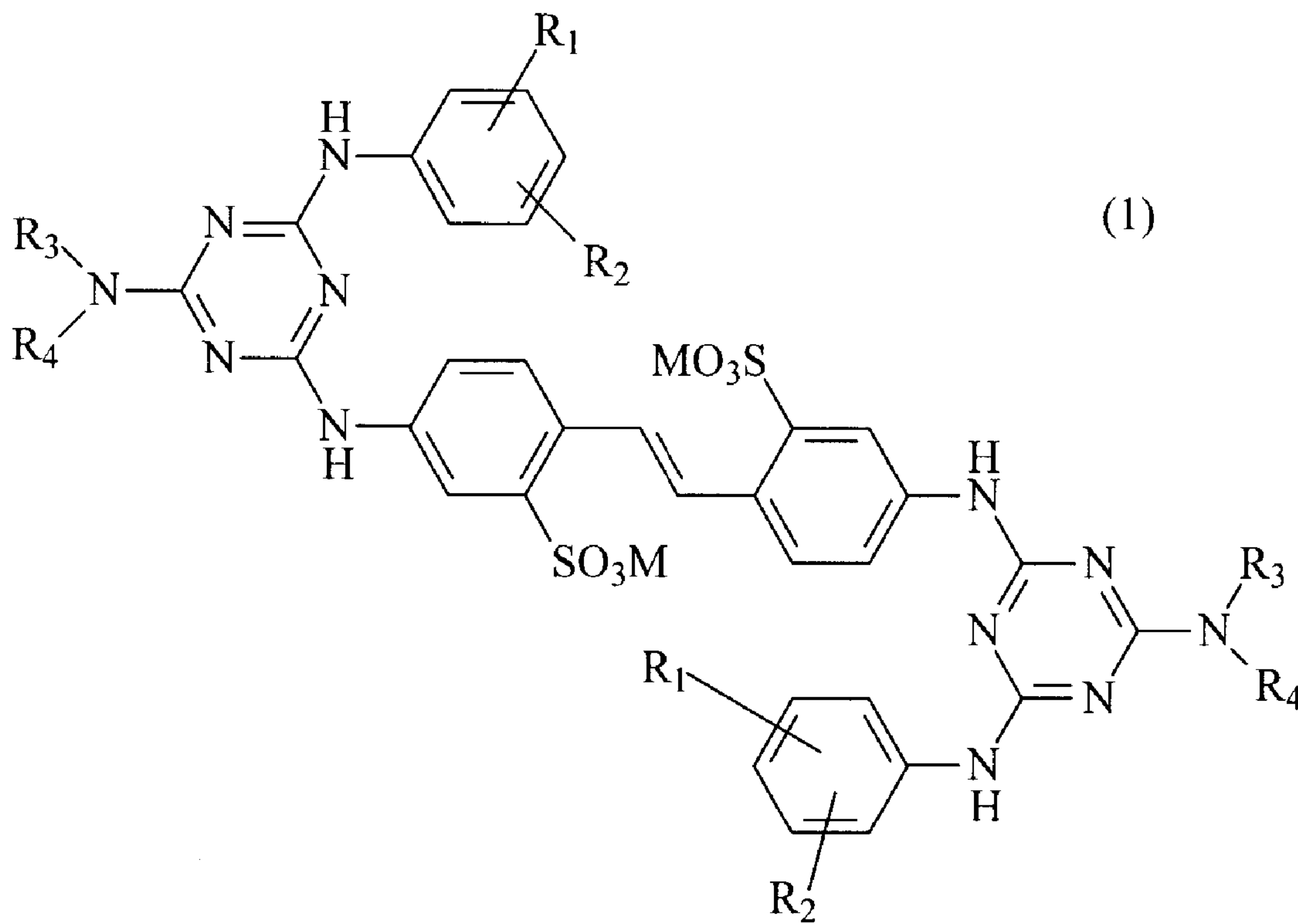




(86) Date de dépôt PCT/PCT Filing Date: 2009/03/12
 (87) Date publication PCT/PCT Publication Date: 2009/10/01
 (45) Date de délivrance/Issue Date: 2016/05/31
 (85) Entrée phase nationale/National Entry: 2010/09/24
 (86) N° demande PCT/PCT Application No.: EP 2009/052921
 (87) N° publication PCT/PCT Publication No.: 2009/118248
 (30) Priorités/Priorities: 2008/03/26 (EP08102906.8);
 2008/12/10 (EP08171223.4); 2008/12/12 (EP08171480.0)

(51) Cl.Int./Int.Cl. *D21H 17/66* (2006.01),
D21H 21/16 (2006.01), *D21H 21/30* (2006.01)
 (72) Inventeurs/Inventors:
 JACKSON, ANDREW CLIVE, CH;
 PUDDIPHATT, DAVID, CH;
 KLEIN, CEDRIC, FR
 (73) Propriétaire/Owner:
 CLARIANT FINANCE (BVI) LIMITED, VG
 (74) Agent: FETHERSTONHAUGH & CO.

(54) Titre : COMPOSITIONS D'AZURANT OPTIQUE AMELIOREES
 (54) Title: IMPROVED OPTICAL BRIGHTENING COMPOSITIONS



(57) Abrégé/Abstract:

A sizing composition for paper, characterised in that the sizing composition comprises (a) at least one optical brightener of formula (1), (b) a magnesium salt; and (c) a binding agent, which is selected from the group consisting of native starch, enzymatically modified starch and chemically modified starch; 0.1 to 15 parts of component (b) being present per part of component (a).

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
1 October 2009 (01.10.2009)(10) International Publication Number
WO 2009/118248 A3

(51) International Patent Classification:

D21H 17/66 (2006.01) **D21H 21/30** (2006.01)
D21H 21/16 (2006.01)

(21) International Application Number:

PCT/EP2009/052921

(22) International Filing Date:

12 March 2009 (12.03.2009)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

08102906.8 26 March 2008 (26.03.2008) EP
08171223.4 10 December 2008 (10.12.2008) EP
08171480.0 12 December 2008 (12.12.2008) EP(71) Applicant (for all designated States except US): **CLARIANT INTERNATIONAL LTD** [CH/CH];
Rothausstrasse 61, CH-4132 Muttenz 1 (CH).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **JACKSON, Andrew, Clive** [GB/CH]; Lange Rütli 6, CH-4142 Münchenstein BL (CH). **PUDDIPHATT, David** [TH/CH]; Unterer Moosweg 16, CH-4203 Grellingen (CH).(74) Agents: **MIKULECKY, Klaus** et al.; Clariant Produkte (Deutschland) GmbH, Group Intellectual Property, Am Unisys-Park 1, 65843 Sulzbach (DE).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

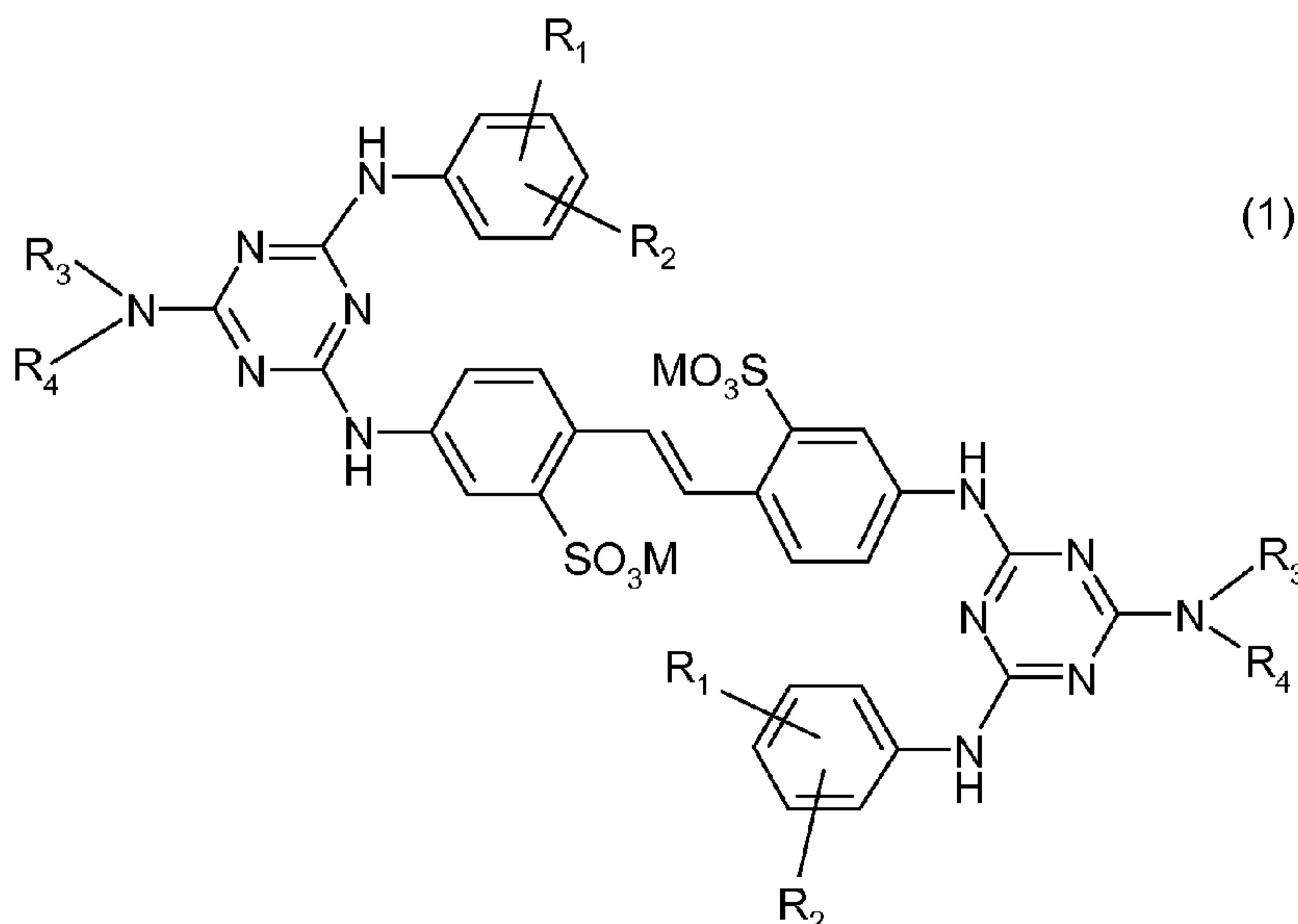
Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(88) Date of publication of the international search report:

19 November 2009

(54) Title: IMPROVED OPTICAL BRIGHTENING COMPOSITIONS



(57) Abstract: A sizing composition for paper, characterised in that the sizing composition comprises (a) at least one optical brightener of formula (1), (b) a magnesium salt; and (c) a binding agent, which is selected from the group consisting of native starch, enzymatically modified starch and chemically modified starch; 0.1 to 15 parts of component (b) being present per part of component (a).

IMPROVED OPTICAL BRIGHTENING COMPOSITIONS

The instant invention relates to compositions which provide superior optical brightening effects when applied to the surface of paper at the size-press.

5

BACKGROUND

A high level of whiteness is an important parameter for the end-user of paper products. The most important raw materials of the papermaking industry are cellulose, pulp and lignin which naturally absorb blue light and therefore are yellowish in color and impart a dull appearance to the paper. Optical brighteners are used in the papermaking industry to compensate for the absorption of blue light by absorbing UV-light with a maximum wavelength of 350 - 360 nm and converting it into visible blue light with a maximum wavelength of 440 nm.

15 In the manufacture of paper, optical brighteners may be added either at the wet end of the paper machine, or to the surface of paper, or at both points. In general, it is not possible to achieve the whiteness levels required of higher-quality papers by addition at the wet end alone.

20 A common method of adding optical brightener to the surface of paper is by application of an aqueous solution of the optical brightener at the size-press together with a sizing agent, typically a native starch or an enzymatically or chemically modified starch. A preformed sheet of paper is passed through a two-roll nip, the entering nip being flooded with sizing solution. The paper absorbs some of the solution, the remainder
25 being removed in the nip.

In addition to starch and optical brightener, the sizing solution can contain other chemicals designed to provide specific properties. These include defoamers, wax emulsions, dyes, pigments and inorganic salts.

30

In order to reach higher whiteness levels, considerable effort has been put into the development of new optical brighteners. See, for example, Japanese Kokai 62-106965, PCT Application WO 98/42685, US Patent 5,873,913 and European Patent 1,763,519.

35 GB 1 239 818 discloses hexasulphonated optical brighteners derived from triazinylaminostilbenes. Examples 1 to 6 disclose their sodium salts. Magnesium is only

31416-14

2

mentioned in a list of possible counterions for the hexasulphonated optical brighteners, starch as a component in a surface sizing composition is also only mentioned in a list of possible binding agents.

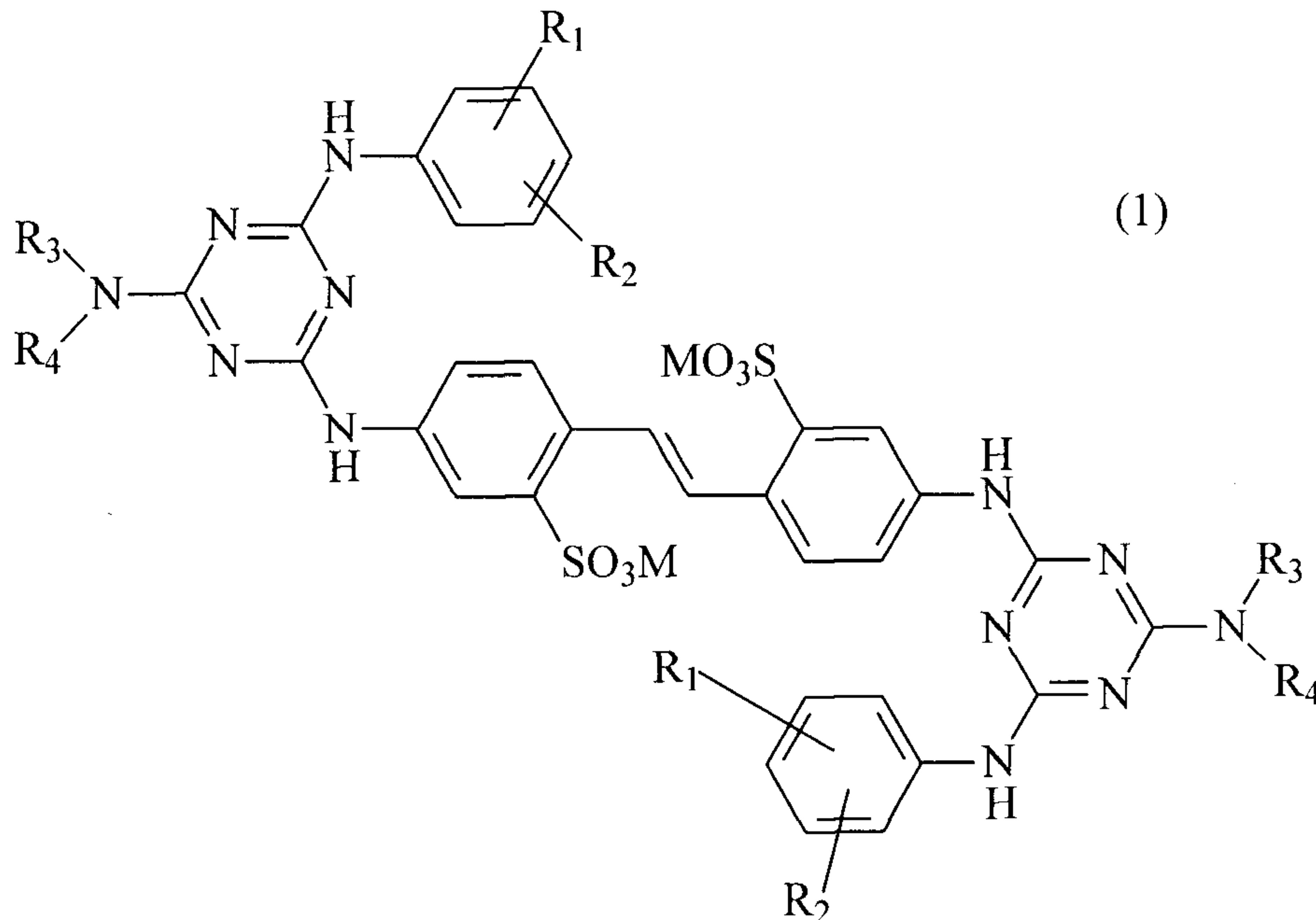
The demand remains for more efficient means of achieving high whiteness levels in
5 paper.

DESCRIPTION OF THE INVENTION

Surprisingly, we have found that optical brighteners of formula (1) when applied to the surface of paper in combination with magnesium salts in a starch sizing composition give enhanced whitening effects. Parts mean parts by weight in the following, if not
10 otherwise specified.

The present invention therefore relates to a sizing composition for paper, comprising:

(a) at least one optical brightener of formula (1):



wherein:

15 R_1 is H or a SO_3M ,

31416-14

3

R_2 is H or a SO_3M ,

R_3 is H, a C_{1-4} alkyl, a C_{2-3} hydroxyalkyl, a CH_2CO_2M , a $CH_2CH_2CONH_2$ or a CH_2CH_2CN ,

R_4 is a C_{1-4} alkyl, a C_{2-3} hydroxyalkyl, a CH_2CO_2M , a $CH(CO_2M)CH_2CO_2M$, a
5 $CH(CO_2M)CH_2CH_2CO_2M$ or benzyl, or

R_3 and R_4 together with the neighbouring nitrogen atom comprise a morpholine ring,
and

M is H, an alkali metal cation, ammonium, a mono-methyl-di- C_2 - C_3 -hydroxyalkyl
ammonium, a di-methyl-mono- C_2 - C_3 -hydroxyalkyl ammonium, an ammonium which
10 is mono-, di- or trisubstituted by a C_2 - C_3 hydroxyalkyl radical or mixtures thereof;

(b) a magnesium salt; and

(c) a binding agent selected from the group consisting of a native starch, an
enzymatically modified starch and a chemically modified starch;

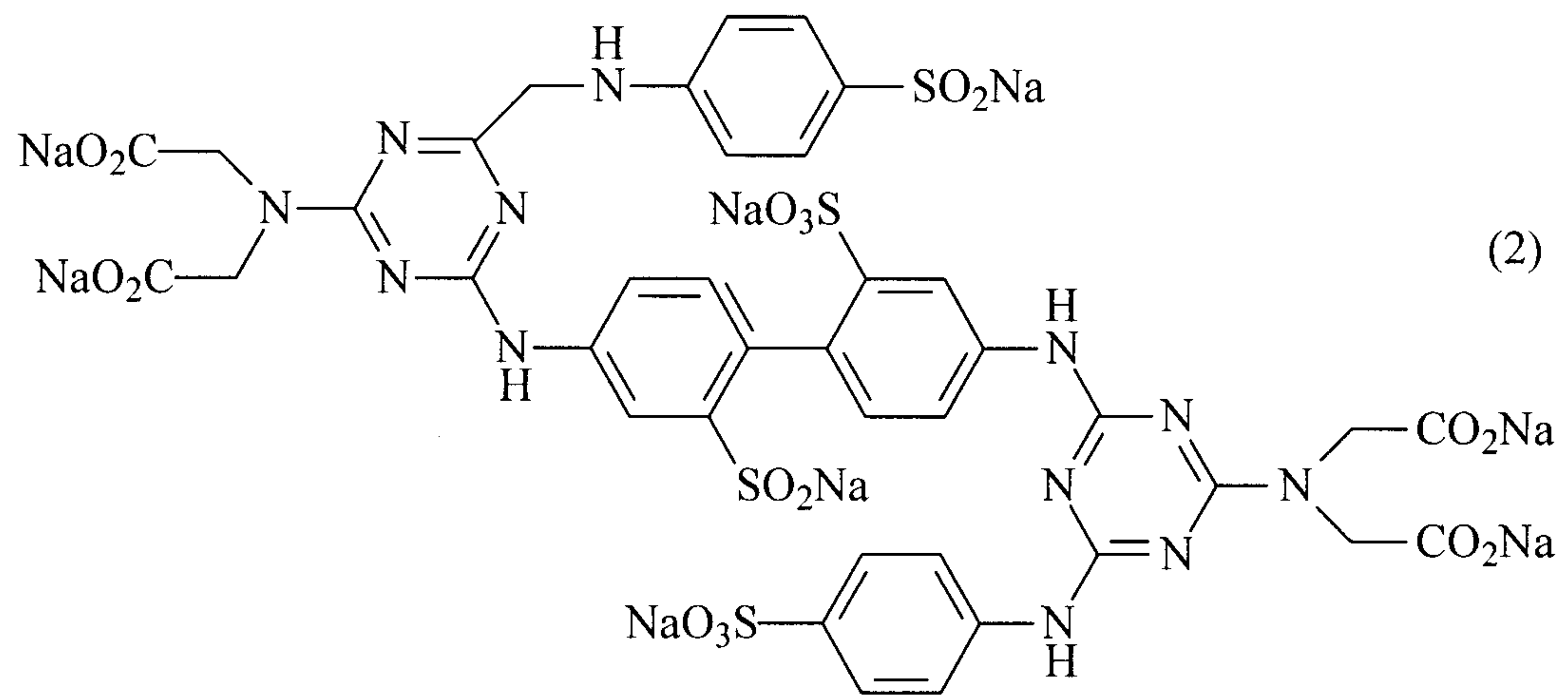
wherein 0.1 to 15 parts of the component (b) are present per part of the
15 component (a).

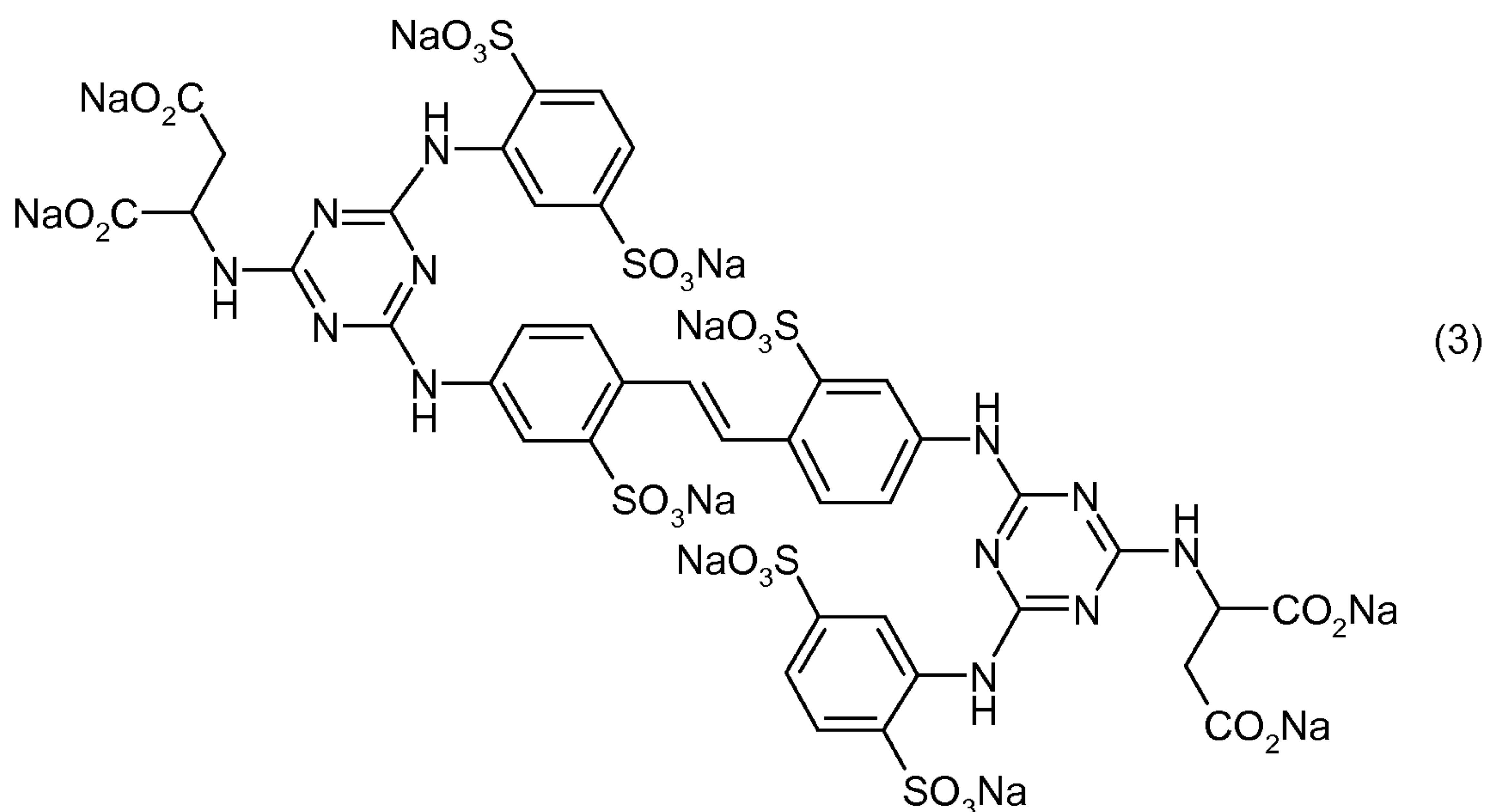
Preferred compounds of formula (1) are those in which R_3 represents hydrogen,
methyl, ethyl, n-propyl, isopropyl, β -hydroxyethyl, β -hydroxypropyl, CH_2CO_2M ,
 $CH_2CH_2CONH_2$ or CH_2CH_2CN and R_4 represents methyl, ethyl, n-propyl, isopropyl, 2-
butyl, β -hydroxyethyl, β -hydroxypropyl, CH_2CO_2M , $CH(CO_2M)CH_2CO_2M$,
20 $CH(CO_2M)CH_2CH_2CO_2M$ or benzyl.

Optical brighteners of formula (2) and (3) are specific examples for the optical
brighteners of formula (1), but the invention is not limited to these two specific
examples.

31416-14

3a





The magnesium salt can be, for example, magnesium acetate, magnesium bromide, magnesium chloride, magnesium formate, magnesium iodide, magnesium nitrate, magnesium sulphate or magnesium thiosulphate. Preferably, the magnesium salt is magnesium chloride, magnesium sulphate or magnesium thiosulphate. Most preferably, the magnesium salt is magnesium chloride.

Preferably, 0.15 to 10 parts of component (b) are present per part of component (a).
Most preferably, 0.4 to 5 parts of component (b) are present per part of component (a).

For the treatment of paper in the size-press, sizing compositions containing 0.2 to 30, preferably 1 to 15 grams per litre of the optical brightener, may be used. The sizing composition also contains a binding agent in a concentration of preferably 2 to 15% by weight, based on the total weight of the sizing composition. The pH is typically in the range 5-9, preferably 6-8.

The binding agent or size is selected from the group consisting of native starch, enzymatically modified starch and chemically modified starch. Modified starches are preferably oxidized starch, hydroxyethylated starch or acetylated starch. The native starch is preferably an anionic starch, a cationic starch, or an amphoteric starch. While the starch source may be any, preferably the starch sources are corn, wheat, potato, rice, tapioca or sago. One or more secondary binders may be present, preferably polyvinyl alcohol or carboxymethylcellulose.

31416-14

5

The present invention further relates to a process for optical brightening of paper comprising: (a) applying the sizing composition as defined herein, to the paper; and (b) drying the paper.

- 5 Preferably, a defoamer, a wax emulsion, a dye and/or a pigment is added to the sizing composition.

The following examples shall explain the instant invention in more details. If not indicated otherwise, "%" and "parts" are meant by weight.

10

EXAMPLE 1

Sizing compositions are prepared by adding an optical brightener of formula (2) in such an amount, that a range of final concentrations of from 2.5 to 12.5 g/l of optical brightener is achieved, to a stirred, aqueous solution of magnesium chloride (final
15 concentration is 8 g/l) and an anionic oxidized potato starch (Perfectamyl A4692 from AVEBE B.A.) (final concentration is 50 g/l) at 60°C.

The sizing solution is allowed to cool, then poured between the moving rollers of a laboratory size-press and applied to a commercial 75g/m² AKD (alkyl ketene dimer)
20 sized, bleached paper base sheet. The treated paper is dried for 5 minutes at 70°C in a flat bed drier. The dried paper is allowed to condition, then measured for CIE whiteness on a calibrated Elrepho spectrophotometer.

The Example is repeated both in the absence of magnesium chloride, i.e. only the
25 sodium salt of the optical brightener is present, and with the magnesium chloride replaced by an equivalent amount of calcium chloride.

The results are summarized in Table 1, and clearly demonstrate the advantage of using magnesium chloride over the use of calcium chloride and over the use only of the
30 sodium salt of the optical brightener in order to reach higher whiteness levels. The surprising nature of the invention is further illustrated by the observation that chloride salts of other divalent Group II metal ions, such as calcium chloride, even have a negative impact on the whitening effect of the optical brightener.

TABLE 1

Optical Brightener (2) (g/l of actives)	Magnesium Chloride (g/l)	Calcium Chloride (g/l)	CIE Whiteness
0	0	0	104.6
0	8	0	104.7
0	0	8	104.8
2.5	0	0	122.3
2.5	8	0	126.7
2.5	0	8	123.4
5.0	0	0	128.3
5.0	8	0	133.1
5.0	0	8	128.0
7.5	0	0	129.8
7.5	8	0	133.7
7.5	0	8	128.6
10.0	0	0	131.1
10.0	8	0	134.5
10.0	0	8	128.2
12.5	0	0	130.6
12.5	8	0	134.2
12.5	0	8	127.3

5 **EXAMPLE 2**

Sizing solutions are prepared by adding an optical brightener of formula (3) in such an amount, that a range of final concentrations of from 2.0 to 10.0 g/l of optical brightener is achieved, to a stirred, aqueous solution of magnesium chloride (final concentration is 8 g/l) and an anionic oxidized potato starch (Perfectamyl A4692 from AVEBE B.A.) (final concentration 50 g/l) at 60°C.

The sizing solution is allowed to cool, then poured between the moving rollers of a laboratory size-press and applied to a commercial 75g/m² AKD (alkyl ketene dimer) sized, bleached paper base sheet. The treated paper is dried for 5 minutes at 70°C in a

flat bed drier. The dried paper is allowed to condition, then measured for CIE whiteness on a calibrated Elrepho spectrophotometer.

The Example is repeated both in the absence of magnesium chloride, and with the
5 magnesium chloride replaced by an equivalent amount of calcium chloride.

The results are summarized in Table 2, and clearly demonstrate the advantage of
using magnesium chloride to reach higher whiteness levels in comparison to where the
optical brightener is present only as the sodium salt.

10

TABLE 2

Optical Brightener (3) (g/l of actives)	Magnesium Chloride (g/l)	Calcium Chloride (g/l)	CIE Whiteness
0	0	0	104.6
0	8	0	104.7
0	0	8	104.8
2.0	0	0	119.2
2.0	8	0	122.5
2.0	0	8	121.5
4.0	0	0	127.2
4.0	8	0	131.1
4.0	0	8	127.9
6.0	0	0	131.1
6.0	8	0	135.4
6.0	0	8	131.6
8.0	0	0	133.7
8.0	8	0	138.1
8.0	0	8	133.5
10.0	0	0	136.0
10.0	8	0	139.7
10.0	0	8	134.7

EXAMPLE 3

Sizing compositions are prepared by adding an optical brightener of formula (3) in such an amount, that a range of final concentrations of from 0 to 12.5 g/l of optical brightener is achieved, to stirred, aqueous solutions of magnesium chloride (final concentrations are 6.25 and 12.5g/l) and an anionic oxidized corn starch (final concentration 50 g/l) (Penford Starch 260) at 60°C. Each sizing solution is allowed to cool, then poured between the moving rollers of a laboratory size-press and applied to a commercial 75 g/m² AKD (alkyl ketene dimer) sized, bleached paper base sheet. The treated paper is dried for 5 minutes at 70°C in a flat bed drier.

10 The dried paper is allowed to condition, and then measured for CIE whiteness on a calibrated Auto Elrepho spectrophotometer. The results are shown in Table 3.

EXAMPLE 4

Sizing compositions are prepared by adding an optical brightener of formula (3) in such an amount, that a range of final concentrations of from 0 to 12.5 g/l of optical brightener is achieved, to stirred, aqueous solutions of magnesium thiosulphate hexahydrate (final concentrations are 10 and 20g/l) and an anionic oxidized corn starch (final concentration 50 g/l) (Penford Starch 260) at 60°C. The sizing solution is allowed to cool, then poured between the moving rollers of a laboratory size-press and applied to a commercial 75 g/m² AKD (alkyl ketene dimer) sized, bleached paper base sheet. The treated paper is dried for 5 minutes at 70°C in a flat bed drier.

20 The dried paper is allowed to condition, and then measured for CIE whiteness on a calibrated Auto Elrepho spectrophotometer. The results are shown in Table 3.

TABLE 3

Optical Brightener (3) (g/l of actives)	CIE Whiteness				
	no Mg salt, i.e. Na salt only	Magnesium salt added			
		Magnesium chloride (g/l) (example 3)		Magnesium thiosulphate hexahydrate (g/l) (example 4)	
		6.25	12.5	10.0	20.0
0	102.8	102.9	103.5	102.2	102.7
2.5	119.6	122.4	125.5	125.1	123.6
5.0	128.9	131.1	132.5	132.9	132.7
7.5	135.1	136.3	137.9	137.7	137.9
10.0	139.2	140.9	141.4	141.1	141.0
12.5	141.1	142.3	142.8	142.4	142.4

The results clearly demonstrate the advantage of using magnesium chloride or
5 magnesium thiosulphate to reach higher whiteness levels in comparison to where the
optical brightener is present only as the sodium salt.

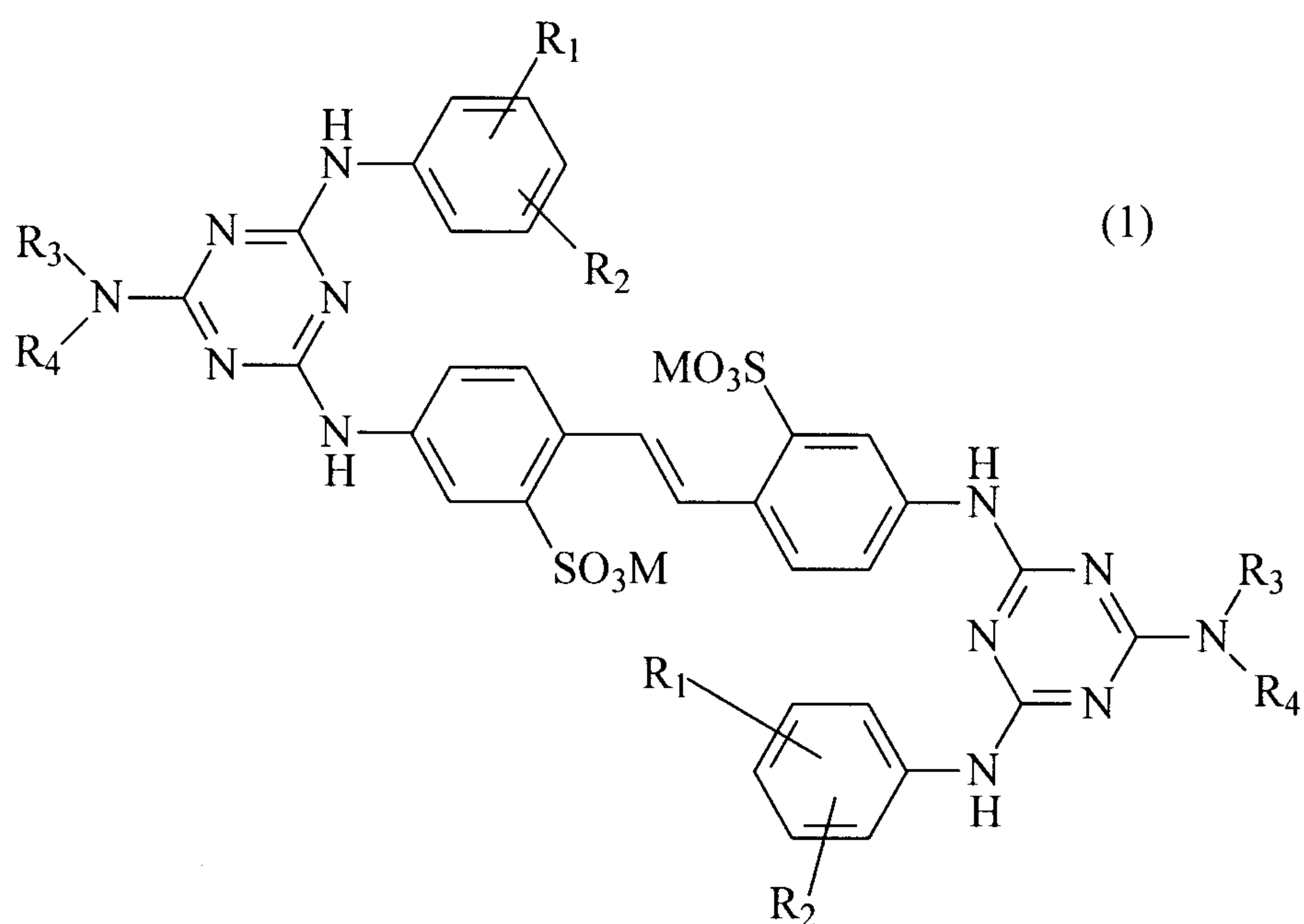
31416-14

10

CLAIMS:

1. A sizing composition for paper, comprising:

(a) at least one optical brightener of formula (1):



5 wherein:

R_1 is H or a SO_3M ,

R_2 is H or a SO_3M ,

R_3 is H, a C_{1-4} alkyl, a C_{2-3} hydroxyalkyl, a CH_2CO_2M , $CH_2CH_2CONH_2$ or CH_2CH_2CN ,

R_4 is a C_{1-4} alkyl, a C_{2-3} hydroxyalkyl, a CH_2CO_2M , a $CH(CO_2M)CH_2CO_2M$, a
 10 $CH(CO_2M)CH_2CH_2CO_2M$ or benzyl, or

R_3 and R_4 together with the neighbouring nitrogen atom comprise a morpholine ring,
 and

M is H, an alkali metal cation, ammonium, a mono-methyl-di- C_2 - C_3 -hydroxyalkyl

31416-14

11

ammonium, a di-methyl-mono-C₂-C₃-hydroxyalkyl ammonium, an ammonium which is mono-, di- or trisubstituted by a C₂-C₃ hydroxyalkyl radical or a mixture thereof;

(b) a magnesium salt; and

(c) a binding agent selected from the group consisting of a native starch, an
5 enzymatically modified starch and a chemically modified starch;

wherein 0.1 to 15 parts of the component (b) are present per part of the component (a).

2. The sizing composition according to claim 1, wherein R₃ is H, methyl, ethyl, n-propyl, isopropyl, β-hydroxyethyl, β-hydroxypropyl, a CH₂CO₂M,
10 CH₂CH₂CONH₂ or CH₂CH₂CN, and wherein R₄ is methyl, ethyl, n-propyl, isopropyl, 2-butyl, β-hydroxyethyl, β-hydroxypropyl, a CH₂CO₂M, a CH(CO₂M)CH₂CO₂M, a CH(CO₂M)CH₂CH₂CO₂M or benzyl.

3. The sizing composition according to claim 1 or 2, wherein 0.15 to 10 parts of the component (b) are present per part of the component (a).

15 4. The sizing composition according to claim 3, wherein 0.4 to 5 parts of the component (b) are present per part of the component (a).

5. The sizing composition according to any one of claims 1 to 4, wherein the component (b) is magnesium acetate, magnesium bromide, magnesium chloride, magnesium formate, magnesium iodide, magnesium nitrate, magnesium sulphate or
20 magnesium thiosulphate.

6. The sizing composition according to claim 5, wherein the component (b) is magnesium chloride.

7. The sizing composition according to claim 5, wherein the component (b) is magnesium thiosulphate.

31416-14

12

8. The sizing composition according to any one of claims 1 to 7, wherein the amount of the binding agent is from 2 to 15 % by weight, based on the total weight of the sizing composition.

9. A process for optical brightening of paper comprising:

5 (a) applying the sizing composition as defined in any one of claims 1 to 8, to the paper; and

(b) drying the paper.

10. The process according to claim 9, comprising the additional step of adding a defoamer, a wax emulsion, a dye and/or a pigment to the sizing

10 composition.

