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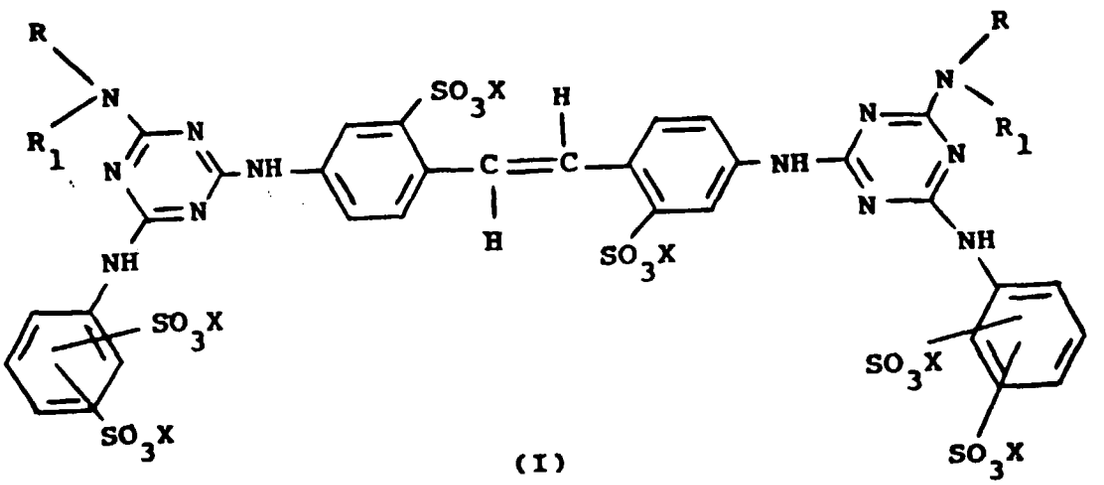
(54) A method for whitening a detergent composition

(57) The use of brighteners of formula



(I)

wherein R and R_1, which can be the same or different from each other, are each -H, CH_3, $-CH_2CH_3$, $-CH_2-CH_2OH$; X is the cation of sodium, potassium, ammonium, an amine or an alkanolamine residue, in the brightener of some kinds of detergent products.

The presence of the brighteners of formula (I) satisfactorily solves the problem of increasing the whiteness degree of the paste, or, in the case of a powder detergent, of the granules obtained after atomization.

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Description

The present invention relates to the use of a highly hydrophilic stilbene-type brightener for increasing the white degree of finished detergent products in the form of pastes or of slurry intermediates. More in particular, the scope of the added brightener is to brighten up the white color of the detergent pastes as to cover the unaesthetic brownish, greyish or yellowish color given by the natural coloration of the raw materials.

State of the art

The use of optical brighteners in detergents is well known in the art. But their use is mainly linked to the effect which the optical brighteners have on the surfaces washed with the detergent. In fact, during the washing action, the optical brightener tends to be adsorbed on the surface and to coat it more or less completely. Through the brightener absorbing action of the UV fraction of sun-light and of the subsequent emission in the visible spectrum (a well-known mechanism, see for example Kirk-Othmer Encyclopedia of Chemical Technology - Vol. 4 page 222) an evident increase of whiteness degree of the substrate is obtained.

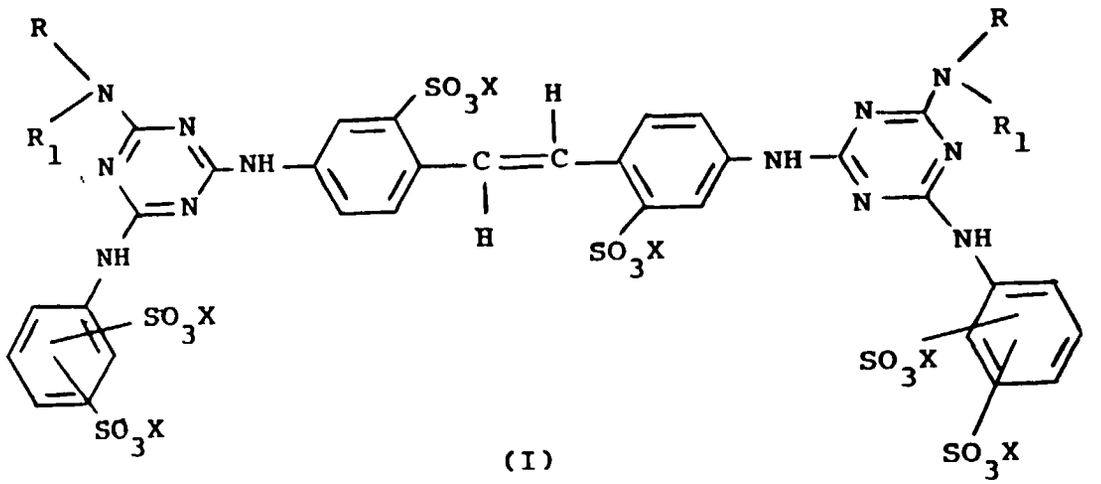
The optical brightener however does not carries on its action only when it is adsorbed on a solid, but also when it is in an aqueous solution. For this reason a secondary effect of its use relates to the possibility of whitening the detergent itself. In other words, the optical brightener is also useful as white coloring for the detergent. Said established use in the market has simply aesthetic reasons bound to the fact that consumers associate the candour of the detergent to a high washing capability. This necessity promoted the use of optical brighteners in enhancing the fluorescence of the detergent itself. A classic example are brighteners, such as biphenyl-4,4'-bis(styryl-2-sulfonic) acid sodium salts, which is used in small amounts but is very expensive.

Therefore, there is the aim to introduce optical stilbene-type brighteners which are highly hydrosoluble in order to bleach detergent powders or pastes or intermediate slurries.

Abstract of the invention

It has now been found that highly hydrosoluble stilbene-type optical brighteners, up to now used in the paper and textile industrial field, are surprisingly effective in the whitening of detergent products.

Therefore, it is an object of the present invention, a method for whitening, namely for increasing the degree of whiteness, of abrasive creams, detergent pastes, powdery detergents and soaps, said method comprising the addition of from 0.0001% to 1% by weight, calculated on the detergent composition, of one or more compounds of formula (I)



(I)

wherein R and R_1, which can be the same or different from each other, are -H, $-CH_3$, $-CH_2CH_3$, $-CH_2-CH_2OH$ and X is a sodium, potassium or ammonium cation, an amine or an alkanolamine group.

Detergent compositions having an improved degree of white, containing one or more compounds of formula (I), are a further object of the present invention.

These and other objects of the present invention will be shown in detail in some preferred embodiments also by means of examples.

Detailed disclosure of the invention

The compounds of formula (I) are known in the chemical literature and are commercially available or can be prepared according to known processes.

The following compounds are particularly preferred:

- hexasodium salt of 2,2'-[1,2-ethenediyl-bis[(3-sulfo-4,1-phenylene)imino-[6-[bis(2-hydroxyethyl)amino-1,3,5-triazin-4,2-diyl]imino]]bis 1,4-benzenedisulfonic acid (CAS 68971-49-3);
- hexasodium salt of 2,2'-[1,2-ethenediyl-bis[(3-sulfo-4,1-phenylene)imino-[6-(2-diethylamino)-1,3,5-triazin-4,2-diyl]imino]]bis 1,4-benzene-disulfonic acid (CAS 41098-56-0);
- tetrasodium salt of 2,2'-[1,2-ethenediyl-bis[5-[[4-[bis(2-hydroxyethyl)amino]-6-[(4-sulfophenyl)amino]-1,3,5-triazin-4,2-yl]amino]bis 1,4-benzenedisulfonic acid (CAS 16470-24-9).

These compounds have been well known and used since long time in different technical fields such as paper and textile industry.

The salts of said substances are very soluble in water and in water-glycols mixtures and tend to remain easily in solution during washing operations. Accordingly, they do not compete with other kinds of optical brighteners in the adsorbption on any type of surface. They do not disturb the practically experienced systems of optical brightener for textile detergency, nor tend to deposit on hard surfaces nor on the skin.

Nevertheless, their peculiarity stands in their high capacity of emitting in the visible spectrum so that extremely small amounts of these substances in solution confer to the whole environment a high whiteness degree. Moreover, they result perfectly compatible with the more common ingredients used in detergent industry and are stable to temperature variations.

According to the present invention, the optical brighteners of formula (I) are added during the formulation process of the detergent product, preferably at the end of the formulation.

The process according to the present invention also applies to a formulated detergent well-known in the market, thus improving its white degree.

The compositions according to the present invention containing one or more compounds of formula (I) are for example abrasive creams, detergent pastes, powder detergents (comprising those obtained by atomization) and soaps.

These compositions are prepared with conventional ingredients and techniques well known to the ordinary person skilled in the art.

In a preferred embodiment, a liquid detergent composition according to the present invention comprises:

up to 70% by weight of surfactants selected from the group consisting of ionic, non ionic, soaps and their mixtures;
from 0.0001% to 1%, preferably from 0.001% to 0.5%, by weight of one or more optical brighteners of formula (I);
well-known organic adjuvants, such as optical brighteners frequently used for brightening washed tissues such as for example 4,4-bis{[(4-anilino)-6-(di-N-2-hydroxyethyl)amino-1,3,5-triazin-2-yl]amino}stilbene-2,2'disulfonic acid and 4-bis{[4-anilino)-6-morpholino-1,3,5-triazin-2-yl]amino}stilbene-2,2'-disulfonic acid.

In the case of laundry detergent, said optical brightener can be efficaciously combined with more hydrophobic optical brighteners of the same family which vice versa show more markedly the brightener action on the fibre. The use of optical brighteners of the same chemical stilbene-triazine family allows a reduction of the number and the type of impurities present in the final product. Moreover, since the brightener action of the powder is devoted to a specific optical brightener which does not interact with the other, a reduction of the total amount of optical brightener present in the formulation is achieved.

In the case of abrasive pastes, the use of an optical brightener allows the effective whitening of the formulation, said whitening being obtainable with difficulty by means of a selection of the abrasive powder.

The following examples further illustrate the invention. Unless differently indicated, all the percentages are by weight.

Example 1

An abrasive cream was prepared with the following composition:

Non-ionic surfactant (alkyl-ethoxylated alcohol C14 E07)	2%
anionic surfactant (sodium lauryl-sulfate)	1%
Suspending agent (acryl-vinyl copolymer Polygel W30(R) by 3V SIGMA)	0.5%
Abrasive powder (calcium carbonate)	40%
Water	up to 100
pH	9-10

The formulation was prepared by firstly dissolving the surfactants in water, then the polymer. After neutralization with soda and adjusting pH to the defined value, the abrasive powder was added slowly. A cream with a viscosity comprised between 2000 and 5000 cps was obtained.

To the base formulation a 0.06% of hexasodium salt of 2,2'-[1,2-ethenediyl-bis[(3-sulfo-4,1-phenylene)imino-[6-[bis(2-hydroxyethyl)amino-1,3,5-triazin-4,2-diyl]imino]]bis 1,4-benzene disulfonic acid was added (in particular a 0.5% of an aqueous solution with extinction coefficient of 75 was used).

Example 2

An abrasive cream identical to the one of Example 1 was prepared.

To the base formulation a 0.06% of hexasodium salt of 2,2'-[1,2-ethenediyl-bis[(3-sulfo-4,1-phenylene)imino[6-(2-diethylamino)-1,3,5-triazin-4,2-diyl]imino]]bis 1,4-benzenedisulfonic acid (in particular a 0.5% of an aqueous solution with extinction coefficient of 75 was used) was added.

Example 3

An abrasive cream identical to the one of Example 1 was prepared.

To the base formulation a 0.06% of tetrasodium salt of 2,2'-[1,2-ethenediyl-bis[5-[[4-[bis(2-hydroxyethyl)amino]-6-[(4-sulfophenyl)amino]-1,3,5-triazin-4,2-yl]amino]bis-1,4-benzenedisulfonic acid (in particular a 0.3% of an aqueous solution with extinction coefficient of 120 was used) was added.

The increase of white degree between the formulation with and without optical brightener according to the present invention is evident with naked eye. An instrumental evaluation through a spectrophotometer for surfaces (Elrepho 2000 by Zeiss) gave the following results:

Brightener	White Degree CIE	White Degree Berger	Gloss ISO R457	Yellowing ISO
None	64,12	64,27	74,36	5,79
Example 1	91,80	89,36	82,17	-4,59
Example 2	79,95	78,38	78,83	-0.12
Example 3	67,78	71,10	77,99	3,51

It can be seen that the increase of white obtained in the cream is relevant taking into account that also the yellowing degree is strongly lowered.

Example 4

A similar evaluation of the efficacy of the process of the invention was made on finished abrasive creams present on the European market. The composition of the creams was not determined. Creams are indicated with their Trade Names.

The hexasodium salt of 2,2'-[1,2-ethenediyl-bis[(3-sulfo-4,1-phenylene)imino-[6-[bis(2-hydroxyethyl)amino-1,3,5-triazin-4,2-diyl]imino]]bis 1,4-benzenedisulfonic acid was used.

The brightener was added in the amount above defined and this time the addition was made after formulation. The

following table reports that all the pastes gained whiteness/brighteness:
White degree according to Berger with and without optical brightener.

Optical brightener	None	with
Real Casa (R)	32.73	52.40
CIF (R)	35.71	63.89
SMAC (R)	17.39	53.98
HOB Brite (R)	43.17	56.66
Cream Surface Wipe (R)	24.68	37.45
Cream Cleaner (R)	32.24	44.66
Ceramic Hob Cleaner (R)	26.12	40.37
Flash (R)	-1.46	16.94
Ajax Cream (R)	-25.30	-8.59

The results demonstrate the general applicability of the process according to the present invention, independently of the type and composition of the detergent product.

Example 5

A detergent paste was prepared having the following composition:

Anionic surfactant (alkyl-ethoxysulfate C14 E02 S04, 28% solution)	40%
Anionic surfactant (sodium lauryl-sulfate)	10%
Chelating agent (sodium tripolyphosphate)	25%
Water	up to 100
pH	9-10

The solution of the surfactants was made under slight heating of the paste.

To the base formulation a 0.06% of hexasodium salt of 2,2'-[1,2-ethenediyl-bis[(3-sulfo-4,1-phenylene)imino[6-[bis(2-hydroxyethyl)amino-1,3,5-triazin-4,2-diyl]imino]]bis 1,4-benzenedisulfonic acid was added (in particular a 0.5% of an aqueous solution with extinction coefficient of 75 was used).

Example 6

A detergent paste identical to the one of Example 5 was prepared.

To the base formulation a 0.06% of hexasodium salt of 2,2'-[1,2-ethenediyl-bis[(3-sulfo-4,1-phenylene)imino-[6-(2-diethylamino)-1,3,5-triazin-4,2-diyl]imino]]bis 1,4-benzenedisulfonic acid was added (in particular a 0.5% of an aqueous solution with extinction coefficient of 75 was used).

Example 7

A detergent paste identical to the one of Example 5 was prepared.

To the base formulation a 0.06% of tetrasodium salt of 2,2'-[1,2-ethenediyl-bis[5-[[4-[bis(2-hydroxyethyl)amino]-6-[(4-sulfophenyl)amino]-1,3,5-triazin-4,2-yl]amino]bis-1,4-benzenedisulfonic acid was added (in particular a 0.3% of a solution aqueous with extinction coefficient of 120 was used).

The increase of the white degree between the formulations with and without the optical brightener according to the invention is evident with naked eye. An instrumental evaluation by means of a spectrophotometer for surfaces (Elrepho

2000 by Zeiss) gave the following results:

Brightener	White Degree CIE	White Degree Berger	Gloss ISO R457	Yellowing ISO
None	71.11	71.55	72.81	0.86
Example 5	100.13	102.00	85.80	-10.70
Example 6	87.57	88.01	82.10	-1.69
Example 7	77.10	79.93	75.21	-2.17

It can be seen that the increase of white obtained in the cream is relevant taking into account that also the yellowing degree is strongly lowered.

Example 8 - Bleaching of slurry for powder detergents.

A slurry for detergent was prepared having the following composition:

Anionic surfactant (alkyl-ethoxysulfate C14 E02 S04, 28% solution)	31%
Anionic surfactant (sodium lauryl-sulfate)	7.7%
Chelating agent (sodium tripolyphosphate)	19%
Sodium perborate	12%
Tetracetylethylenediamine	4%
Zeolites	8%
Water	up to 100
pH	9-10

To the base formulation a 0.06% of hexasodium salt of 2,2'-[1,2-ethenediyl-bis[(3-sulfo-4,1-phenylene)imino-[6-[bis(2-hydroxyethyl)amino-1,3,5-triazin-4,2-diyl]imino]]bis 1,4-benzene disulfonic acid (in particular a 0.5% of a solution aqueous with extinction coefficient of 75 was used).

Example 9

A slurry identical to the one of Example 8 was prepared.

To the formulation a 0.06% of hexasodium salt of 2,2'-[1,2-ethenediyl-bis[(3-sulfo-4,1-phenylene)imino-[6-(2-diethylamino)-1,3,5-triazin-4,2-diyl]imino]]bis 1,4-benzenedisulfonic acid was added (in particular a 0.5% of an aqueous solution with extinction coefficient of 75 was used).

Example 10

A slurry identical to the one of Example 8 was prepared.

To the formulation a 0.06% of tetrasodium salt of 2,2'-[1,2-ethenediyl-bis[5-[[4-[bis(2-hydroxyethyl)amino]-6-[(4-sulfophenyl)amino]-1,3,5-triazin-4,2-yl]amino]bis-1,4-benzenedisulfonic acid was added (in particular a 0.3% of a solution aqueous with extinction coefficient of 120 was used).

The results are still satisfying as indicated in following table, both before and after drying:

Brightener	White Degree CIE	White Degree Berger	Gloss ISO R457	Yellowing ISO
Before Drying				
None	85.81	84.70	87.13	1.14
Example 8	127.28	131.73	103.91	-16.18
Example 9	125.40	122.63	90.31	-22.31
Example 10	107.67	107.74	86.35	-15.81
After drying				
None	82.31	81.23	84.00	2.05
Example 8	124.02	139.31	109.01	-11.50
Example 9	123.31	129.47	106.99	-12.21
Example 10	123.84	129.61	107.66	-11.73

Example 11 - Brightener Paste for Soaps

A soap was prepared having the following composition:

Fatty acids of natural origin (animal fat, of coconut and palm oil)	70%
Glycerin	10%
Stearic acid	3,0%
Sodium chloride	2,0%
EDTA	0.2%
BHT	0.01%
Water	up to 100
pH	8

After evaporation of the soap, by heating the mixture, three distinct samples were prepared:

Sample B: unchanged soap;
Sample R: soap added with 0.5% of Titanium oxide as reference brightener agent;
Sample O: soap added with 0.06% of hexasodium salt of 2,2'-[1,2-ethenediyl-bis[(3-sulfo-4,1-phenylene)imino-[6-[bis(2-hydroxyethyl)amino-1,3,5-triazin-4,2-diyl]imino]]bis 1,4-benzene disulfonic acid (in particular a 0.5% of an aqueous solution with extinction coefficient of 75 was used).

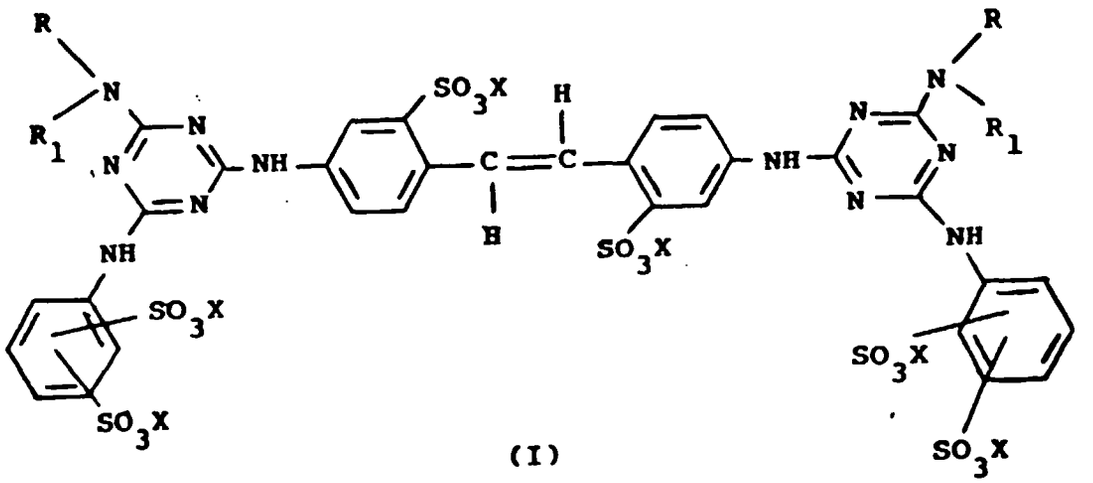
Sample	White Degree Berger
R	88.20
B	78.81
O	95.19

It can be seen that the addition of the optical brightener according to the present invention favours the whitening of

the paste much more than a conventional agent such as titanium oxide.

Claims

1. A process for increasing the degree of white of a detergent composition, said process comprising the addition of an amount ranging from 0.0001% to 1% by weight of the composition of one or more compounds of formula (I),



(I)

wherein R and R_1, which can be the same or different, are each -H, $-CH_3$, $-CH_2CH_3$, $-CH_2-CH_2OH$ and X is a sodium, potassium or ammonium cation, an amine or an alkanolamine.

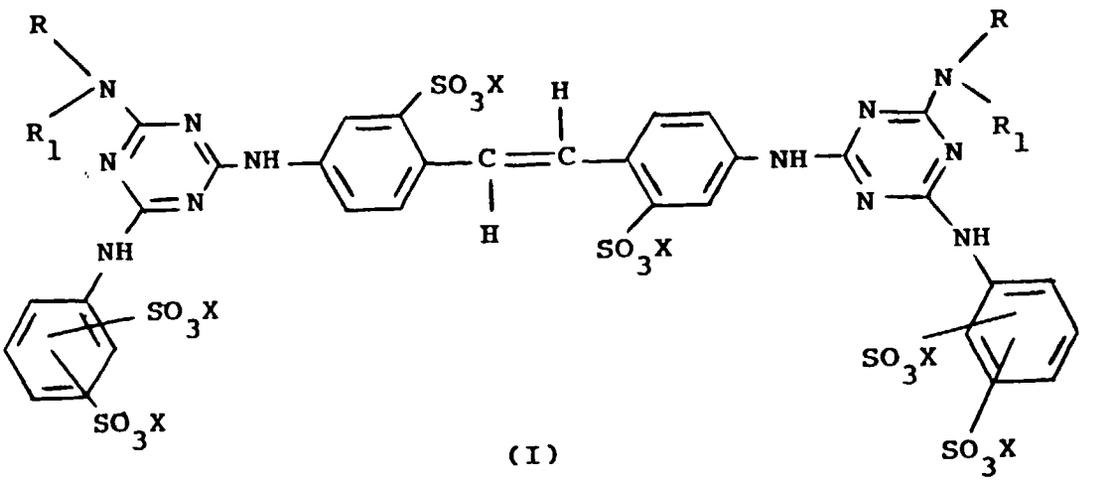
2. A process according to claim 1, wherein said composition is selected from the group consisting of from abrasive cream, detergent paste, powder detergent, soap and slurry.

3. A process according to claim 1, wherein said compound of formula (I) is hexasodium salt of 2,2'-[1,2-ethenediyl-bis[(3-sulfo-4,1-phenylene)imino-[6-[bis(2-hydroxyethyl)amino-1,3,5-triazin-4,2-diyl]imino]]bis 1,4-benzene disulfonic acid

4. A process according to claim 1, wherein said compound of formula (I) is hexasodium salt of 2,2'-[1,2-ethenediyl-bis[(3-sulfo-4,1-phenylene)imino-[6-(2- diethylamino)-1,3,5-triazin-4,2-diyl]imino]]bis 1,4-benzenedisulfonic acid

5. A process according to claim 1, wherein said compound of formula (I) is tetrasodium salt of 2,2'-[1,2-ethenediyl-bis[5-[[4-[bis(2-hydroxyethyl)amino]-6-[(4-sulfophenyl)amino]-1,3,5-triazin-4,2-yl]amino]bis-1,4-benzenedisulfonic acid

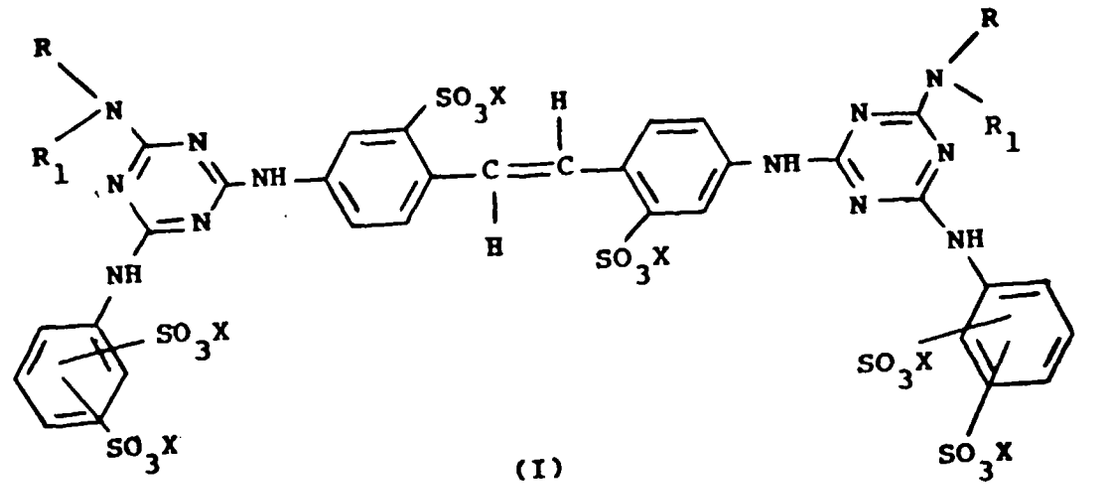
6. A process for increasing the degree of white of a laundry detergent, said process comprising the addition of an amount ranging from 0.0001% to 1% by weight of the composition of a mixture of two or more compounds of formula (I),



(I)

wherein R and R_1, which can be the same or different, are each -H, $-CH_3$, $-CH_2CH_3$, $-CH_2-CH_2OH$ and X is a sodium, potassium or ammonium cation, an amine or an alkanolamine, said mixture of compounds of formula (I) being formed by hydrophilic and hydrophobic compounds.

7. A detergent composition having improved degree of white comprising from 0.0001% to 1% by weight of the composition of one or more compounds of formula (I)



(I)

wherein R and R_1, which can be the same or different, are each -H, $-CH_3$, $-CH_2CH_3$, $-CH_2-CH_2OH$ and X is a sodium, potassium or ammonium cation, an amine or an alkanolamine.

8. A composition according to claim 7, selected from the group consisting of abrasive cream, detergent paste, powdery detergent soap and slurry.

9. A composition according to claim 7, wherein said compound of formula (I) is hexasodium salt of 2,2'-[1,2-ethenediyl-bis[(3-sulfo-4,1-phenylene)imino-[6-[bis(2-hydroxyethyl)amino-1,3,5-triazin-4,2-diyl]imino]]bis 1,4-benzene disulfonic acid.

10. A composition according to claim 7, wherein said compound of formula (I) is hexasodium salt of 2,2'-[1,2-ethenediyl-bis[(3-sulfo-4,1-phenylene)imino-[6-(2-diethylamino)-1,3,5-triazin-4,2-diyl]imino]]bis 1,4-benzenedisulfonic acid.

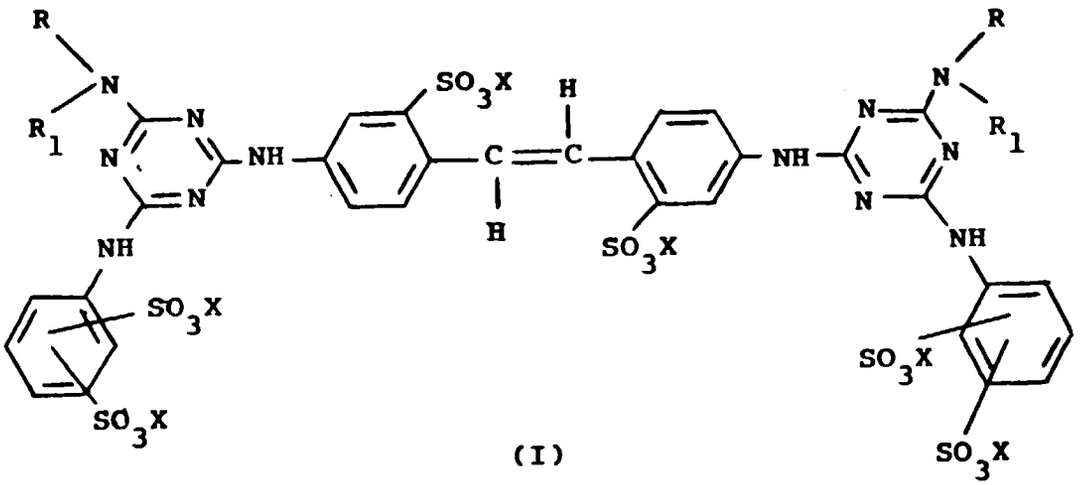
11. A composition according to claim 7, wherein said compound of formula (I) is the tetrasodium salt of 2,2'-[1,2-ethenediyl-bis[5-[[4-[bis(2-hydroxyethyl)amino]-6-[(4-sulfophenyl)amino]-1,3,5-triazin-4,2-yl]amino]bis-1,4-benzenedi-

sulfonic acid.

12. A liquid detergent composition according to claim 7, comprising:

up to 70% by weight of surfactants selected from the group consisting of ionic, non ionic, soaps e their mixtures;
from 0.0001% to 1%, preferably from 0.001% to 0.5% by weight of one or more optical brighteners of formula (I);
well-known organic adjuvants, such as optical brighteners frequently used for whitening washed tissues.

13. A laundry detergent having improved degree of white comprising from 0.0001% to 1% by weight of the composition of a mixture of compounds of formula (I)



(I)

wherein R and R_1, which can be the same or different, are each -H, $-CH_3$, $-CH_2CH_3$, $-CH_2-CH_2OH$ and X is a sodium, potassium or ammonium cation, an amine or an alkanolamine, said mixture of compounds of formula (I) being formed by hydrophilic and hydrophobic compounds.