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SPRUSON & FERGUSON

PATENTS ACT 1990

PATENT REQUEST: STANDARD PATENT

I/We, the Applicant(s)/Nominated Person(s) specified below, request I/We be granted a patent for the invention disclosed in the accompanying standard complete specification.

[70,71] Applicant(s)/Nominated Person(s): 689238

Ciba Specialty Chemicals Holding Inc
~~Ciba-Geigy AG, incorporated in Switzerland~~, of Klybeckstrasse 141, ~~4002 Basle~~, SWITZERLAND
CH – 4057 Basel

[54] Invention Title:

Fabric ~~Protective Use~~ detergents containing a Fluorescent whitening agent

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Ciba-Geigy AG

By: J. Spruson

Registered Patent Attorney

IRN: 300219

INSTR CODE: 52760

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Australia

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Notice Of Entitlement

I, John David O'Connor, of 31 Market Street, Sydney, New South Wales, 2000, Australia, Patent Attorney for the Applicant/Nominated Person in respect of an application entitled:

Protective Use

state the following:-

The Applicant/Nominated Person has entitlement from the actual inventors as follows:-

The Applicant/Nominated Person is the assignee of the actual inventors.

The Applicant/Nominated Person is the applicant of the basic application listed on the Patent Request.

The basic application listed on the Patent Request is the first application made in a Convention Country in respect of the invention.

Dated 10 May 1995

John David O'Connor

IRN: 300219

INSTR CODE: 52760

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(54) Title
FABRIC DETERGENTS CONTAINING A FLUORESCENT WHITENING AGENT

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(56) Prior Art Documents
US 5145991
US 5082578
AU 20005/95

(57)

Surprisingly, it has now been found that washing a textile fibre material with a detergent containing at least one particular fluorescent whitening agent which can also serve as a UV (ultra-violet) radiation absorber, namely one which absorbs radiation in the wavelength range 280-400 nm, imparts an excellent sun protection factor to the fibre material so washed.

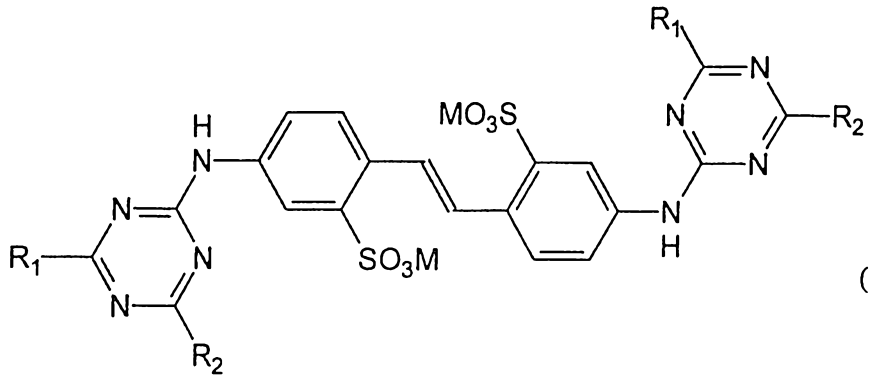
Claim

1. A process for improving the sun protection factor of textile fibre material comprising applying to the fibre material one or more fluorescent whitening agents which absorb radiation in the wavelength range 280-400 nm.

2. A process according to claim 1 in which the fluorescent whitening agent is applied by washing the textile fibre material with a detergent comprising at least one fluorescent whitening agent.

9. Process according to any of the preceding claims in which the fluorescent whitening agent used is one or more of those having one of the formulae:

.../2



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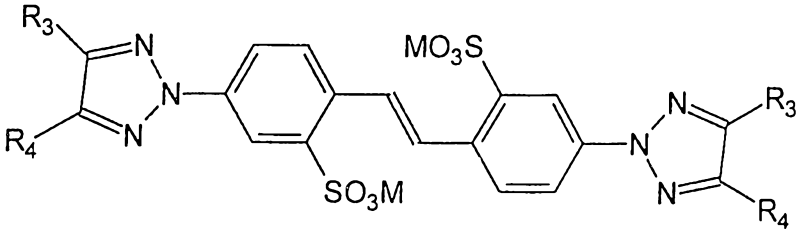

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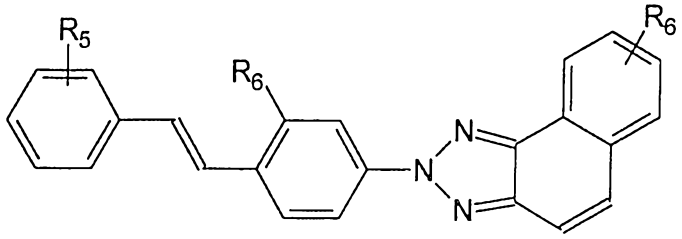

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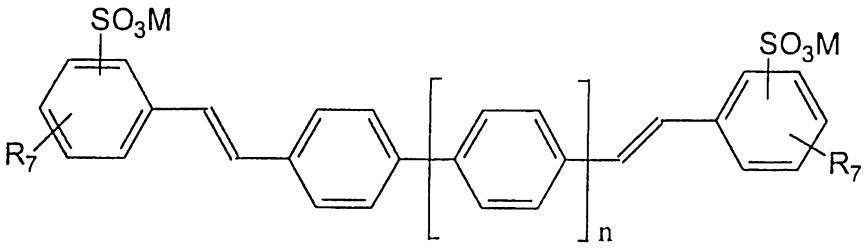

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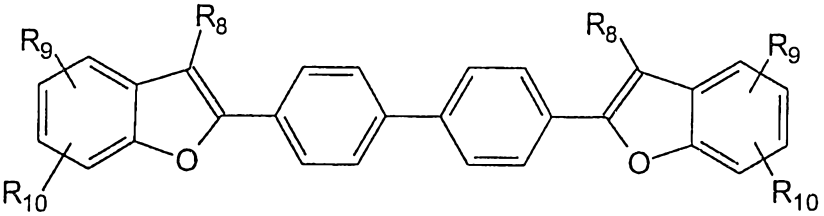

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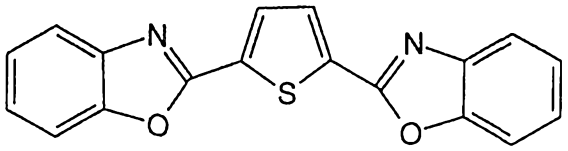

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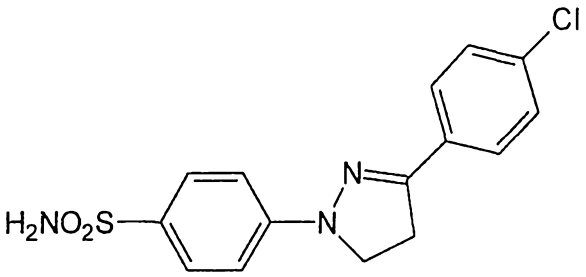

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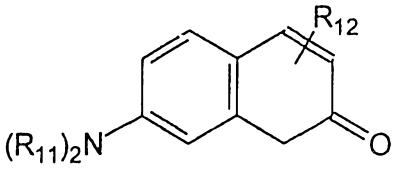
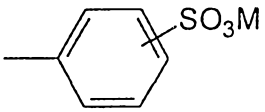


(8)

in which R_1 and R_2, independently, are OH, NH_2, O-C_1-C_4-alkyl, O-aryl, NH-C_1-C_4-alkyl, N(C_1-C_4-alkyl)$_2$, N(C_1-C_4-alkyl)(C_1-C_4-hydroxyalkyl), N(C_1-C_4-hydroxyalkyl)$_2$, NH-aryl, morpholino, S-C_1-C_4-alkyl, S-(aryl), Cl or OH; R_3 and R_4, independently, are H, C_1-C_4-alkyl, phenyl or a group of formula:



;

R_5 is H, Cl or SO_3M; R_6 is CN, SO_3M, S(C_1-C_4-alkyl)$_2$ or S(aryl)$_2$; R_7 is H, SO_3M, O-C_1-C_4-alkyl, CN, CI, COO-C_1-C_4-alkyl, or CON(C_1-C_4-alkyl)$_2$; R_8 is H, C_1-C_4-alkyl, Cl or SO_3M; R_9 and R_{10}, independently, are H, C_1-C_4-alkyl, SO_3M, Cl or O-C_1-C_4-alkyl; R_{11} is H or C_1-C_4-alkyl; R_{12} is H, C_1-C_4-alkyl, CN Cl, COO-C_1-C_4-alkyl, CON(C_1-C_4-alkyl)$_2$, aryl or O-aryl; M is H, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra-C_1-C_4-alkylammonium, mono-, di- or tri-C_1-C_4-hydroxyalkylammonium or ammonium that is di- or tri-substituted by a mixture of C_1-C_4-alkyl and C_1-C_4-hydroxyalkyl groups; and n is 0 or 1.

25. Detergent comprising at least one fluorescent whitening agent, which absorbs radiation in the wavelength range 280-400 nm, when used in a process according to any of claims 1 to 23.

26. Textile fibre material having an improved sun protection factor when treated according to a process claimed in any of claims 1 to 23.

~~Protective Use~~
Fabric detergents containing a Fluorescent whitening agent.

The present invention relates to the use of a detergent comprising at least one fluorescent whitening agent, which absorbs radiation in the wavelength range 280-400 nm, for the improvement of the sun protection factor (SPF) of textile fibre material washed with the detergent.

It is known that light radiation of wavelengths 280-400 nm permits tanning of the epidermis. Also known is that rays of wavelengths 280-320 nm (termed UV-B radiation), cause erythemas and skin burning which can inhibit skin tanning.

Radiation of wavelengths 320-400 nm (termed UV-A radiation) is known to induce skin tanning but can also cause skin damage, especially to sensitive skin which is exposed to sunlight for long periods. Examples of such damage include loss of skin elasticity and the appearance of wrinkles, promotion of the onset of erythemal reaction and the inducement of phototoxic or photoallergic reactions.

Any effective protection of the skin from the damaging effects of undue exposure to sunlight clearly needs to include means for absorbing both UV-A and UV-B components of sunlight before they reach the skin surface.

Traditionally, protection of exposed human skin against potential damage by the UV components in sunlight has been effected by directly applying to the skin a preparation containing a UV absorber. In areas of the world, e.g. Australia and America, which enjoy especially sunny climates, there has been a great increase in the awareness of the potential hazards of undue exposure to sunlight, compounded by fears of the consequences of alleged damage to the ozone layer. Some of the more distressing embodiments of skin damage caused by excessive, unprotected exposure to sunlight are development of melanomas or carcinomas on the skin.

One aspect of the desire to increase the level of skin protection against sunlight has been the consideration of additional measures, over and above the direct protection of the skin. For example, consideration has been given to the provision of protection to skin covered by clothing and thus not directly exposed to sunlight.

Most natural and synthetic textile materials are at least partially permeable to UV

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components of sunlight. Accordingly, the mere wearing of clothing does not necessarily provide skin beneath the clothing with adequate protection against damage by UV radiation. Although clothing containing a deeply coloured dye and/or having a tight weave texture may provide a reasonable level of protection to skin beneath it, such clothing is not practical in hot sunny climates, from the standpoint of the personal comfort of the wearer.

There is a need, therefore, to provide protection against UV radiation for skin which lies underneath clothing, including lightweight summer clothing, which is undyed or dyed only in pale shades. Depending on the nature of the dyestuff, skin covered by clothing dyed in some dark shades may also require protection against UV radiation.

Such lightweight summer clothing normally has a density of less than 200 g/m^2 and has a sun protection factor rating between 1.5 and 20, depending on the type of fibre from which the clothing is manufactured.

The SPF rating of a sun protectant (sun cream or clothing) may be defined as the multiple of the time taken for the average person wearing the sun protectant to suffer sun burning under average exposure to sun. For example, if an average person would normally suffer sun burn after 30 minutes under standard exposure conditions, a sun protectant having an SPF rating of 5 would extend the period of protection from 30 minutes to 2 hours and 30 minutes. For people living in especially sunny climates, where mean sun burn times are minimal, e.g. only 15 minutes for an average fair-skinned person at the hottest time of the day, SPF ratings of at least 20 are desired for lightweight clothing.

Surprisingly, it has now been found that washing a textile fibre material with a detergent containing at least one particular fluorescent whitening agent can also serve as a UV (ultra-violet) radiation absorber, namely one which absorbs radiation in the wavelength range 280-400 nm, imparts an excellent sun protection factor to the fibre material so washed.

Accordingly, the present invention provides a process for improving the sun protection factor (SPF) of a textile fibre material comprising applying to the fibre material one or more fluorescent whitening agents which absorb radiation in the wavelength range of 280-400 nm.

The process according to the present invention is preferably effected by washing the textile

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fibre material at least once with the detergent composition, preferably at a temperature ranging from 10 to 100°C., especially from 15 to 60°C.

The detergent composition used preferably comprises:
i) 5-90%, preferably 5-70% of an anionic surfactant and/or a nonionic surfactant;
ii) 5-70%, preferably 5-40% of a builder;
iii) 0-30%, preferably 1-12% of a peroxide;
iv) 0-10%, preferably 1-6% of a peroxide activator and/or 0-1%, preferably 0.1-3% of a bleaching catalyst;
v) 0.005-2%, preferably 0.01-1% of at least one fluorescent whitening agent which absorbs radiation in the wavelength range 280-400 nm; and
vi) 0.005-10%, preferably 0.1-5% of of one or more auxiliaries, each by weight, based on the total weight of the detergent.

The detergent may be formulated as a solid, as an aqueous liquid comprising 5-50, preferably 10-35% water or as a non-aqueous liquid detergent, containing not more than 5, preferably 0-1 wt.% of water, and based on a suspension of a builder in a non-ionic surfactant, as described, e.g., in GB-A-2158454.

The anionic surfactant component may be, e.g., a sulphate, sulphonate or carboxylate surfactant, or a mixture of these.

Preferred sulphates are alkyl sulphates having 12-22 carbon atoms in the alkyl radical, optionally in combination with alkyl ethoxy sulphates having 10-20 carbon atoms in the alkyl radical.

Preferred sulphonates include alkyl benzene sulphonates having 9-15 carbon atoms in the alkyl radical.

In each case, the cation is preferably an alkali metal, especially sodium.

Preferred carboxylates are alkali metal sarcosinates of formula $R\text{-}CO(R^1)CH_2COOM^1$ in which R is alkyl or alkenyl having 9-17 carbon atoms in the alkyl or alkenyl radical, R^1 is C_1-C_4 alkyl and M^1 is alkali metal.

The nonionic surfactant component may be, e.g., a condensate of ethylene oxide with a

C_9-C_{15} primary alcohol having 3-8 moles of ethylene oxide per mole.

The builder component may be an alkali metal phosphate, especially a tripolyphosphate; a carbonate or bicarbonate, especially the sodium salts thereof; a silicate; an aluminosilicate; a polycarboxylate; a polycarboxylic acid; an organic phosphonate; or an aminoalkylene poly (alkylene phosphonate); or a mixture of these.

Preferred silicates are crystalline layered sodium silicates of the formula $NaHSi_mO_{2m+1}.pH_2O$ or $Na_2Si_mO_{2m+1}.pH_2O$ in which m is a number from 1.9 to 4 and p is 0 to 20.

Preferred aluminosilicates are the commercially-available synthetic materials designated as Zeolites A, B, X, and HS, or mixtures of these. Zeolite A is preferred.

Preferred polycarboxylates include hydroxypolycarboxylates, in particular citrates, polyacrylates and their copolymers with maleic anhydride.

Preferred polycarboxylic acids include nitrilotriacetic acid and ethylene diamine tetra-acetic acid.

Preferred organic phosphonates or aminoalkylene poly (alkylene phosphonates) are alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates and diethylene triamine penta methylene phosphonates.

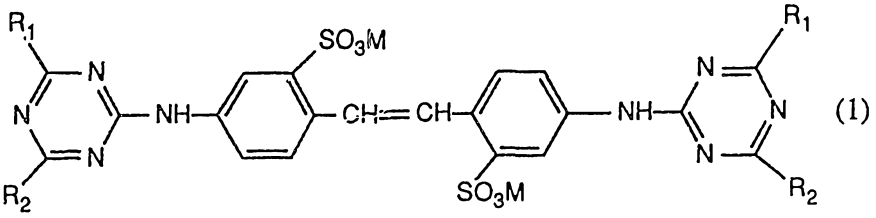
Any peroxide component may be any organic or inorganic peroxide compound, described in the literature or available on the market, which bleaches textiles at conventional washing temperatures, e.g. temperatures in the range of from 5°C. to 90°C. In particular, the organic peroxides are, for example, monoperoxides or polyperoxides having alkyl chains of at least 3, preferably 6 to 20, carbon atoms; in particular diperoxydicarboxylates having 6 to 12 C atoms, such as diperoxyperazelates, diperoxypersebacates, diperoxyphthalates and/or diperoxydodecanedioates, especially their corresponding free acids, are of interest. It is preferred, however, to employ very active inorganic peroxides, such as persulphate, perborate and/or percarbonate. It is, of course, also possible to employ mixtures of organic and/or inorganic peroxides. The peroxides, especially the inorganic peroxides, are preferably activated by the inclusion of an activator such as

tetraacetyl ethylenediamine or nonoyloxybenzene sulfonate. Bleaching catalysts which may be added include, e.g., enzymatic peroxide precursors and/or metal complexes. Preferred metal complexes are manganese or iron complexes such as manganese or iron phthalocyanines or the complexes described in EP-A-0 509 787.

The detergents used will usually contain one or more auxiliaries such as soil suspending agents, for example sodium carboxymethylcellulose; salts for adjusting the pH, for example alkali or alkaline earth metal silicates; foam regulators, for example soap; salts for adjusting the spray drying and granulating properties, for example sodium sulphate; perfumes; and also, if appropriate, antistatic and softening agents; such as smectite clays; enzymes, such as amylases; photobleaching agents; pigments; and/or shading agents. These constituents should, of course, be stable to any bleaching system employed.

Preferably a textile fibre material which is washed with the detergent according to the use of the present invention, contains 0.005 to 0.5%, especially 0.01 to 0.2% by weight of one or more fluorescent whitening agents which absorb radiation in the wavelength range 280-400 nm, based on the weight of the fibre material.

Preferred fluorescent whitening agents for use in the present invention are those having one of the formulae:



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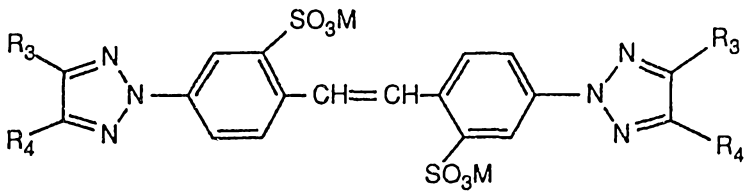

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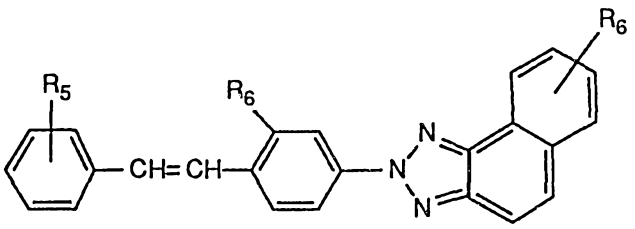

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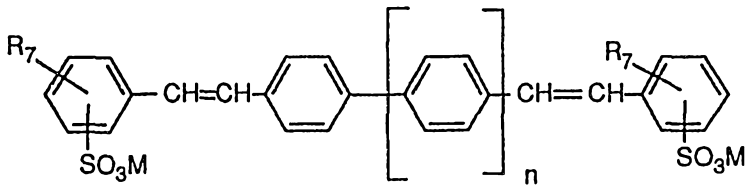

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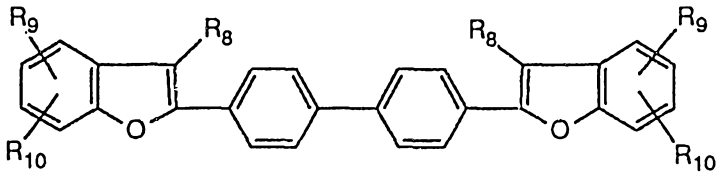

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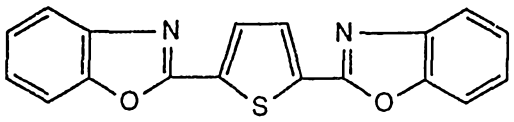

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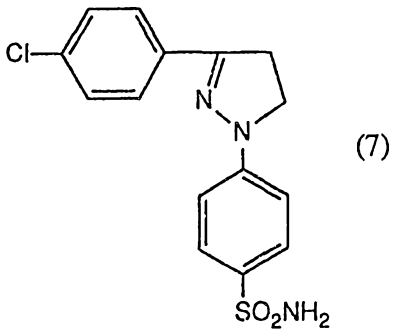

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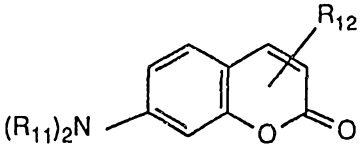
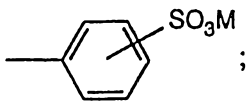


(8)

in which R_1 and R_2, independently, are OH, NH_2, O-C_1-C_4-alkyl, O-aryl, NH-C_1-C_4-alkyl, N(C_1-C_4-alkyl)$_2$, N(C_1-C_4-alkyl)(C_1-C_4-hydroxyalkyl), N(C_1-C_4-hydroxyalkyl)$_2$, NH-aryl, morpholino, S-C_1-C_4-alkyl(aryl), Cl or OH; R_3 and R_4, independently, are H, C_1-C_4-alkyl,

phenyl or a group of formula:



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R_5 is H, Cl or SO_3M; R_6 is CN, SO_3M, $S(C_1\text{-}C_4\text{-alkyl})_2$ or $S(aryl)_2$; R_7 is H, SO_3M, $O\text{-}C_1\text{-}C_4\text{-alkyl}$, CN, Cl, $COO\text{-}C_1\text{-}C_4\text{-alkyl}$, or $CON(C_1\text{-}C_4\text{-alkyl})_2$; R_8 is H, $C_1\text{-}C_4\text{-alkyl}$, Cl or SO_3M; R_9 and R_{10}, independently, are H, $C_1\text{-}C_4\text{-alkyl}$, SO_3M, Cl or $O\text{-}C_1\text{-}C_4\text{-alkyl}$; R_{11} is H or $C_1\text{-}C_4\text{-alkyl}$; R_{12} is H, $C_1\text{-}C_4\text{-alkyl}$, CN, Cl, $COO\text{-}C_1\text{-}C_4\text{-alkyl}$, $CON(C_1\text{-}C_4\text{-alkyl})_2$, aryl or O-aryl; M is is H, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra-$C_1\text{-}C_4$-alkylammonium, mono-, di- or tri-$C_1\text{-}C_4$-hydroxyalkylammonium or ammonium that is di- or tri-substituted with by a mixture of $C_1\text{-}C_4$-alkyl and $C_1\text{-}C_4$-hydroxyalkyl groups; and n is 0 or 1.

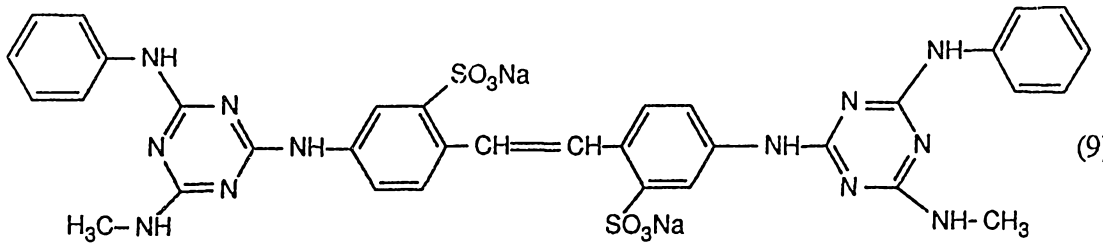
In the compounds of formulae (1) to (8), $C_1\text{-}C_4$-alkyl groups are, e.g., methyl, ethyl, n-propyl, isopropyl and n-butyl, especially methyl. Aryl groups are naphthyl or, especially, phenyl.

It will be appreciated that the protection afforded to the wearer of the textile material washed according to the invention will last longer when a fluorescent whitening agent is used which has a high lightfastness.

Furthermore, preferred fluorescent whitening agents for use in the present invention have a spectrum covering a relatively low wavelength range, that is exhibiting rather reddish shades. Examples of such fluorescent whitening agents include compounds of formula (1) in which R_1 and R_2 are each non-aromatic substituents, such as compounds of formula (1) in which R_1 and R_2, independently, are $NH\text{-}C_1\text{-}C_4$-alkyl, $O\text{-}C_1\text{-}C_4$-alkyl or morpholino; as well as compounds of formula (4) in which n is 1.

Preferred compounds of formula (1) are those in which R_1 and R_2, independently, are are O-methyl, O-phenyl, NH_2, NH-methyl, $N(methyl)_2$, N(methyl)(hydroxyethyl), NH-ethyl, $N(hydroxyethyl)_2$, NH-phenyl, S-methyl(phenyl), Cl or OH.

Specific examples of preferred compounds of formula (1) are those having the formulae:



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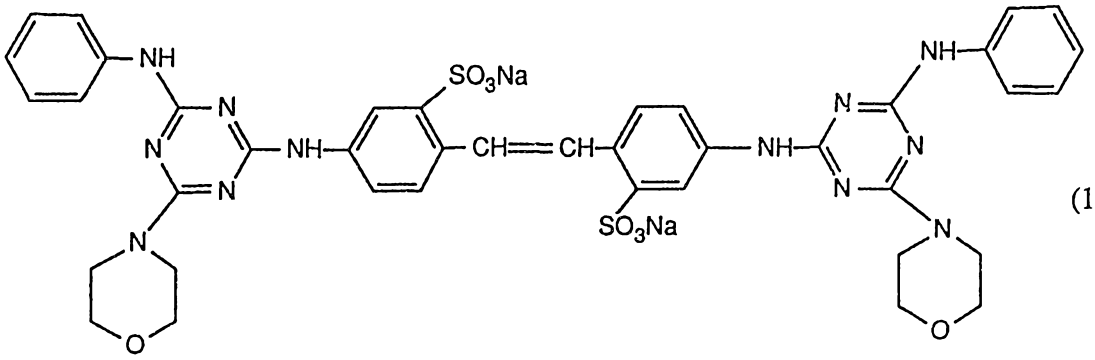

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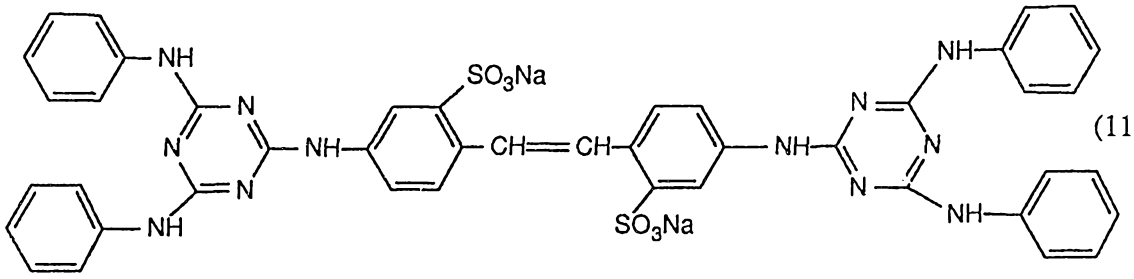

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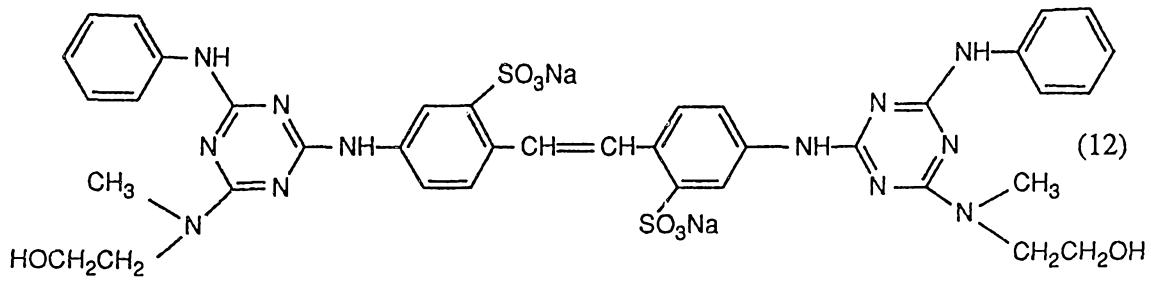

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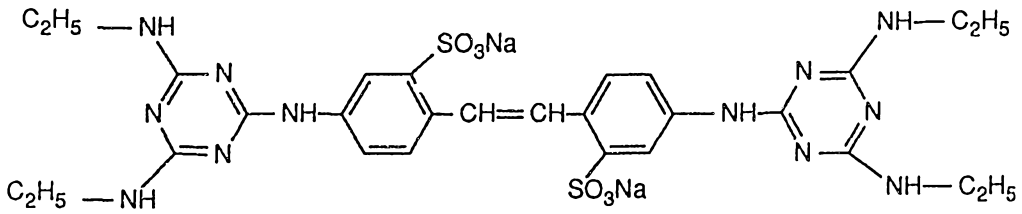

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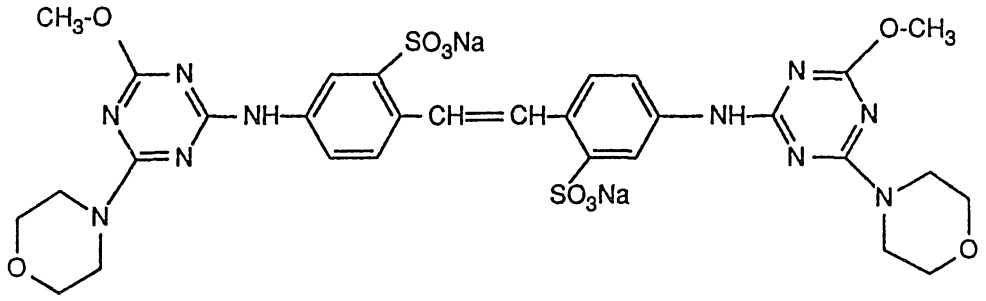

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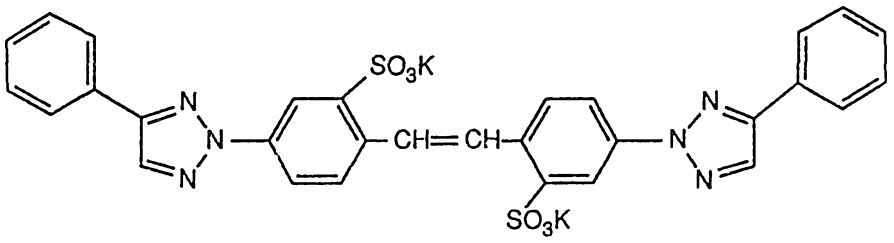
Specific preferred examples of compounds of formula (2) are those of formulae:



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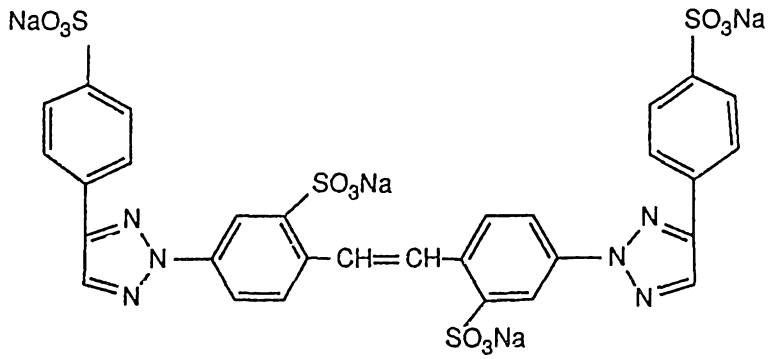

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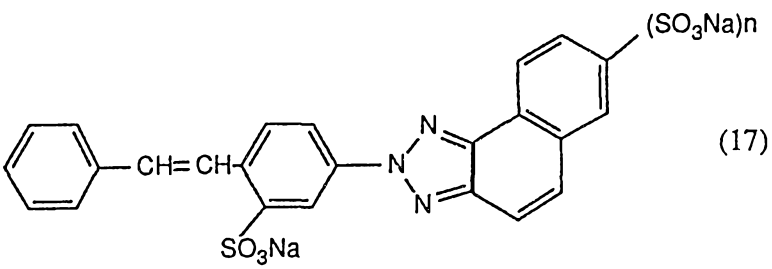

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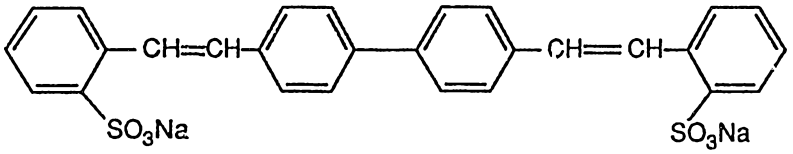
in which n has its previous significance.

Preferred examples of compounds of formula (4) are those having the formulae:



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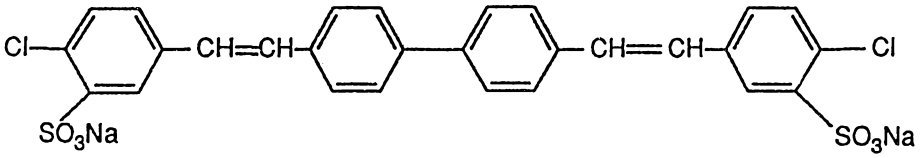

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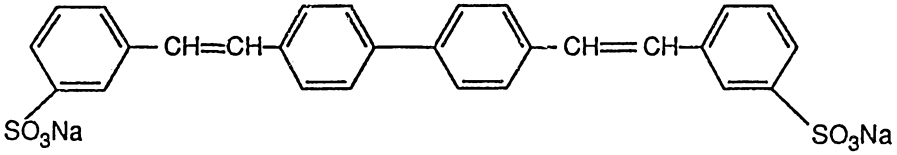

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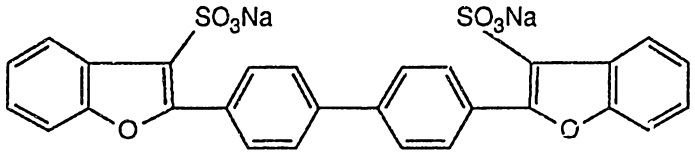
Preferred examples of compounds of formula (5) are those of formulae:



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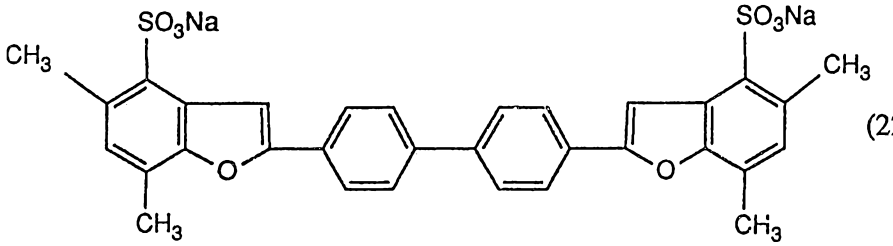

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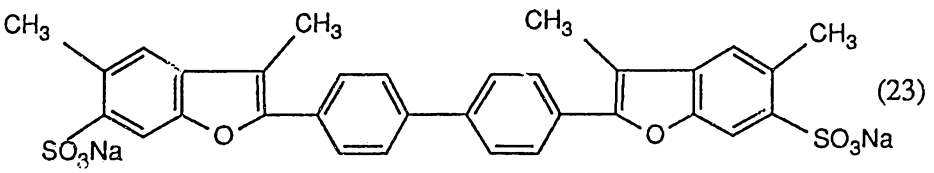

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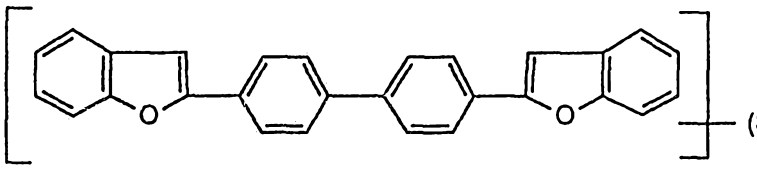

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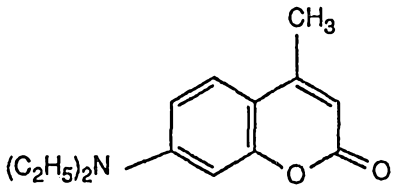
A preferred example of a compound of formula (8) is that having the formula:



(25)

The compounds of formulae (1) to (8) are known and may be obtained by known methods.

Although most are readily water-soluble, some of the fluorescent whitening agents for use in the detergent used according to the present invention may be only sparingly soluble in water and may need to be applied in dispersed form. For this purpose, they may be milled with an appropriate dispersant, conveniently using quartz balls and an impeller, down to a particle size of 1-2 microns.

As dispersing agents for such sparingly-soluble compounds there may be mentioned:

- acid esters or their salts of alkylene oxide adducts, e.g., acid esters or their salts of a polyadduct of 4 to 40 moles of ethylene oxide with 1 mole of a phenol, or phosphoric acid esters of the adduct of 6 to 30 moles of ethylene oxide with 1 mole of 4-nonylphenol, 1 mole of dinonylphenol or, especially, with 1 mole of compounds which have been produced by the addition of 1 to 3 moles of styrenes on to 1 mole of phenol;
- polystyrene sulphonates;
- fatty acid taurides;
- alkylated diphenyloxide-mono- or -di-sulphonates;
- sulphonates of polycarboxylic acid esters;
- addition products of 1 to 60, preferably 2 to 30 moles of ethylene oxide and/or propylene oxide on to fatty amines, fatty amides, fatty acids or fatty alcohols, each having 8 to 22 carbon atoms, or on to tri- to hexavalent C_3-C_6alkanols,

the addition products having been converted into an acid ester with an organic dicarboxylic acid or with an inorganic polybasic acid;

- lignin sulphonates; and, in particular
- formaldehyde condensation products, e.g., condensation products of lignin sulphonates and/or phenol and formaldehyde; condensation products of formaldehyde with aromatic sulphonic acids, e.g., condensation products of ditolylethersulphonates and formaldehyde; condensation products of naphthalenesulphonic acid and/or naphthol- or naphthylaminesulphonic acids and formaldehyde; condensation products of phenolsulphonic acids and/or sulphonated dihydroxydiphenylsulphone and phenols or cresols with formaldehyde and/or urea; or condensation products of diphenyloxide-disulphonic acid derivatives with formaldehyde.

The textile fibre material washed according to the present invention may be composed of any of a wide range of types of fibre such as wool, polyamide, cotton, polyester, polyacrylic, silk, polypropylene or any mixture thereof, preferably cotton, polyacrylic, silk or any mixture thereof, especially cotton.

The preferred fluorescent whitening agent for use in the detergent used according to the present invention will vary depending on the fibre from which the treated fabric is composed.

Thus, for the treatment of polyester fabrics, a fluorescent whitening agent of formula (6) is preferably used. For the treatment of polyamide, a fluorescent whitening agent of formula (7), (8) or (12) is preferably used. For wool, a fluorescent whitening agent of formula (7), (8) or (15) is preferably used

Relative to the use of a conventional UV absorber, the use in the present invention of a fluorescent whitening agent which absorbs radiation in the wavelength range 280-400 nm has the following advantages: easier application since it exhausts on to the fibre; coloured textile goods can be washed with a detergent composition according to the claimed use (previously it was generally believed that FWAs had no useful role to play in detergents for coloured goods - see, e.g., A.E.Lee "Technology developments in laundry products", Proc. of the 3rd World Conference on Detergents, Montreux, Sept. 1994, AOCS Press, p.73, § "Color variants"); the UV protection is regularly renewed on washing; yellowing of the textile material caused by o-hydroxy groups in the UV absorber is avoided; minor amounts of the fluorescent whitening agent provide very high extinction values; the textile

material is more wash resistant; and higher SPF values are attainable.

The use according the present invention, in addition to providing an improvement in the SPF of the washed textile material, may also increase the useful life of the textile material so washed, for example by preserving its tear strength and/or its lightfastness.

The present invention is further illustrated by the following Examples.

Examples 1 to 6

50g of bleached, mercerised cotton swatches are washed in 1 litre of tap water (12° German hardness) containing 4g of a detergent having the following composition (weight %):

8.0%	Sodium alkylbenzene sulfonate
2.9%	Tallow alcohol-tetradecane-ethylene glycol ether (14 mols EO)
3.5%	Sodium soap
43.8%	Sodium tripolyphosphate
7.5%	Sodium silicate
1.9%	Magnesium silicate
1.2%	Carboxymethyl cellulose
0.2%	EDTA
21.2%	Sodium sulfate
x%	fluorescent whitening agent (FWA) by weight on detergent
	Water to 100%.

The washing is conducted at 40°C. over 15 minutes. The swatches are then rinsed under cold running tap water for 30 seconds and dried. The wash treatment is repeated three times. After the third wash, the swatches are ironed at 160°C.

The whiteness (W) of the washed samples is measured with a DCI/SF 500 spectrophotometer according to the Ganz method. The Ganz method is described in detail in the Ciba-Geigy Review, 1973/1, and also in the article "Whiteness Measurement", ISCC Conference on Fluorescence and the Colorimetry of Fluorescent Materials, Williamsburg, February 1972, published in the Journal of Color and Appearance, 1, No.5 (1972).

The Sun Protection Factor (SPF) is determined by measurement of the UV light transmitted through the swatch, using a double grating spectrophotometer fitted with an Ulbricht bowl. Calculation of SPF is conducted as described by B.L.Diffey and J.Robson in J. Soc. Cosm. Chem. 40 (1989), pp. 130-131.

The results obtained are set out in the following Table.

Table

Example	FWA	Concentration FWA	W	SPF
-	-	-	79	1.6
1	Compound (9)	0.2%	211	6.1
2	Compound (10)	0.2%	202	3.9
3	Compound (14)	0.2%	200	5.2
4	Compound (15)	0.1%	207	4.2
5	Compound (18)	0.1%	201	3.4
6	Compound (23)	0.1%	208	3.1

SPF values are the average of 3 measurements at various points on the swatches. The relative variation of the results lies within a range of from about plus or minus 10%.

Compared with the control experiment (no FWA), the SPF values obtained to the invention are 2-4 times higher, after only 3 washes.

Example 7

A bleached, mercerised cotton swatch is dyed by the exhaustion method using 0.95% by weight on the fabric of a commercial blue reactive dye. The dyeing is conducted at a liquor ratio of 20:1, the temperature is raised from 25° to 100°C. over 40 minutes, and then held for 1 hour at 100°C. with the addition of 15g/l of sodium sulphate, before applying a final cold rinse.

The SPF of the dyed goods is then determined by the method described in Examples 1 to 6.

The dyed goods are then washed in the manner described in Examples 1 to 6 using the same detergent composition. The FWA compound used in the detergent is the compound of formula (18), at a level of 0.1 weight % of active substance, based on the weight of the detergent. The SPF value of the washed goods and also of goods washed with the same

detergent containing no FWA (for control purposes) is determined after 1, 3, 5 and 10 washes. The results are set out in the following Table.

Table

Example	number of washes	SPF	
		without fwa	with fwa
-	control pre-wash	23.7	23.7
7	one	22.5	23.8
	three	22.0	25.9
	five	20.9	26.9
	ten	19.8	28.7

The results in the Table demonstrate that the SPF of dyed fabrics can decrease significantly when the fabrics are washed with a detergent which does not contain an FWA. By contrast, washing with a detergent containing a compound of formula (18) not only eliminates this loss of protection against aggressive sunlight radiation, but also actually increases the SPF protection with successive washings.

The claims defining the invention are as follows:

1. A process for improving the sun protection factor of textile fibre material comprising applying to the fibre material one or more fluorescent whitening agents which absorb radiation in the wavelength range 280-400 nm.

2. A process according to claim 1 in which the fluorescent whitening agent is applied by washing the textile fibre material with a detergent comprising at least one fluorescent whitening agent.

3. Process according to claim 2 in which the washing of the textile fibre material is conducted at least once at a temperature in the range of from 10° to 100°C.

4. Process according to claim 3 in which the washing of the textile fibre material is conducted at least once at a temperature in the range of from 15° to 60°C.

5. Process according to any one of claims 2 to 4 in which the detergent composition used comprises:

i) 5-90% of an anionic surfactant and/or a nonionic surfactant;

ii) 5-70% of a builder;

iii) 0-30% of a peroxide;

iv) 0-10% of a peroxide activator and/or 0-3% of a bleaching catalyst;

v) 0.005-2% of at least one fluorescent whitening agent which absorbs radiation in the wavelength range 280-400 nm; and

vi) 0.005-10% of one or more auxiliaries, each by weight, based on the total weight of the detergent.

6. Process according to claim 5 in which the detergent composition used comprises:

i) 5-70% of an anionic surfactant and/or a nonionic surfactant;

ii) 5-40% of a builder;

iii) 1-12% of a peroxide;

iv) 1-6% of a peroxide activator and/or 0.1-3% of a bleaching catalyst;

v) 0.01-1% of at least one fluorescent whitening agent which absorbs radiation in the wavelength range 280-400 nm; and

vi) 0.1-5% of one or more auxiliaries, each by weight, based on the total weight of the detergent.

7. Process according to any of claims 1 to 6 in which the textile material contains 0.005 to 0.5% by weight of the fluorescent whitening agent, based on the weight of the textile material.

8. Process according to claim 7 in which the textile material contains 0.01 to 0.2% by weight of the fluorescent whitening agent, based on the weight of the textile material.

9. Process according to any of the preceding claims in which the fluorescent whitening agent used is one or more of those having one of the formulae:

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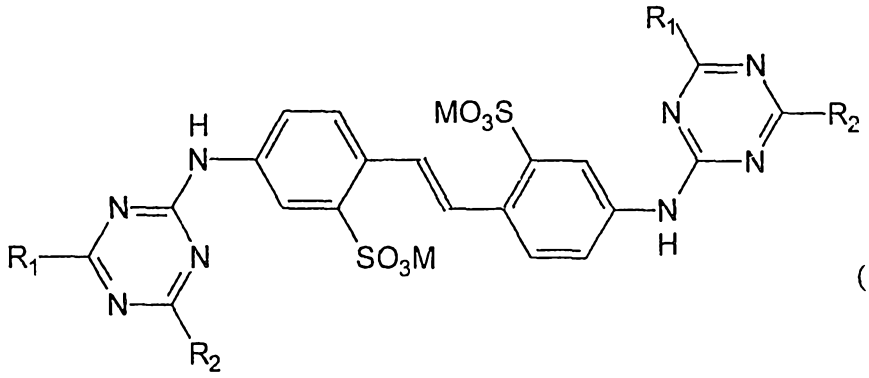

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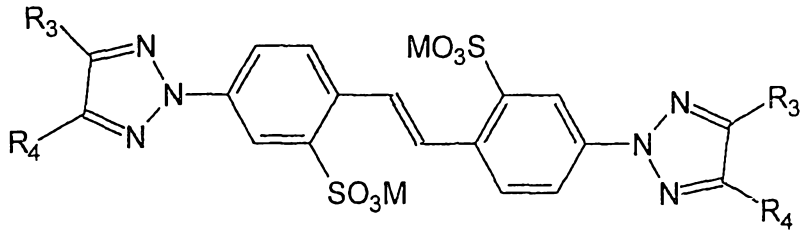

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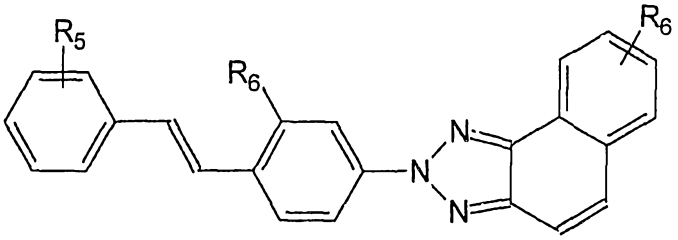

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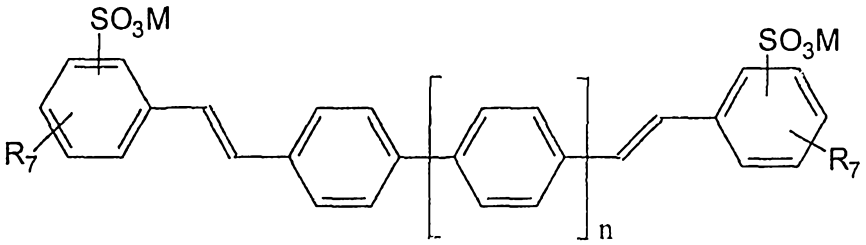

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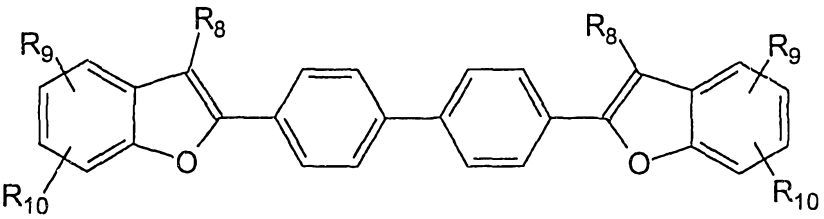

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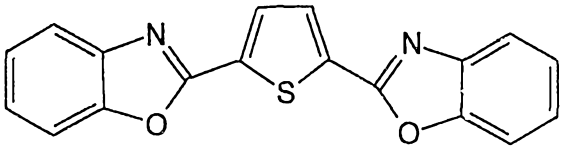

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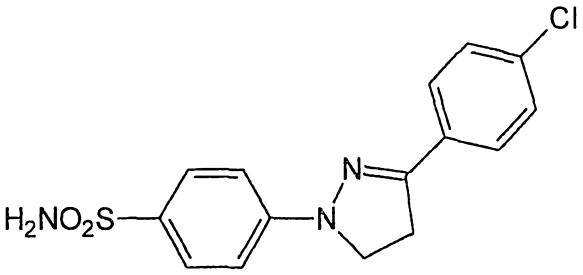

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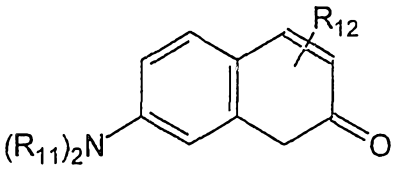
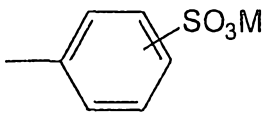


(8)

in which R_1 and R_2, independently, are OH, NH_2, O-C_1-C_4-alkyl, O-aryl, NH-C_1-C_4-alkyl, N(C_1-C_4-alkyl)$_2$, N(C_1-C_4-alkyl)(C_1-C_4-hydroxyalkyl), N(C_1-C_4-hydroxyalkyl)$_2$, NH-aryl, morpholino, S-C_1-C_4-alkyl, S-(aryl), Cl or OH; R_3 and R_4, independently, are H, C_1-C_4-alkyl, phenyl or a group of formula:



;

R_5 is H, Cl or SO_3M; R_6 is CN, SO_3M, S(C_1-C_4-alkyl)$_2$ or S(aryl)$_2$; R_7 is H, SO_3M, O-C_1-C_4-alkyl, CN, CI, COO-C_1-C_4-alkyl, or CON(C_1-C_4-alkyl)$_2$; R_8 is H, C_1-C_4-alkyl, Cl or SO_3M; R_9 and R_{10}, independently, are H, C_1-C_4-alkyl, SO_3M, Cl or O-C_1-C_4-alkyl; R_{11} is H or C_1-C_4-alkyl; R_{12} is H, C_1-C_4-alkyl, CN Cl, COO-C_1-C_4-alkyl, CON(C_1-C_4-alkyl)$_2$, aryl or O-aryl; M is H, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra-C_1-C_4-alkylammonium, mono-, di- or tri-C_1-C_4-hydroxyalkylammonium or ammonium that is di- or tri-substituted by a mixture of C_1-C_4-alkyl and C_1-C_4-hydroxyalkyl groups; and n is 0 or 1.

10. Process according to claim 9 in which the fluorescent whitening agent has the formula (1) and R_1 and R_2, independently, are non-aromatic substituents.

11. Process according to claim 9 in which the fluorescent whitening agent has the formula (1) and R_1 and R_2, independently, are NH-C_1-C_4-alkyl, O-C_1-C_4-alkyl or morpholino; or has the formula (4) in which n is 1.

12. Process according to claim 9 in which the fluorescent whitening agent has the formula (1) and R_1 and R_2, independently, are O-methyl, O-phenyl, NH_2, NH-methyl,

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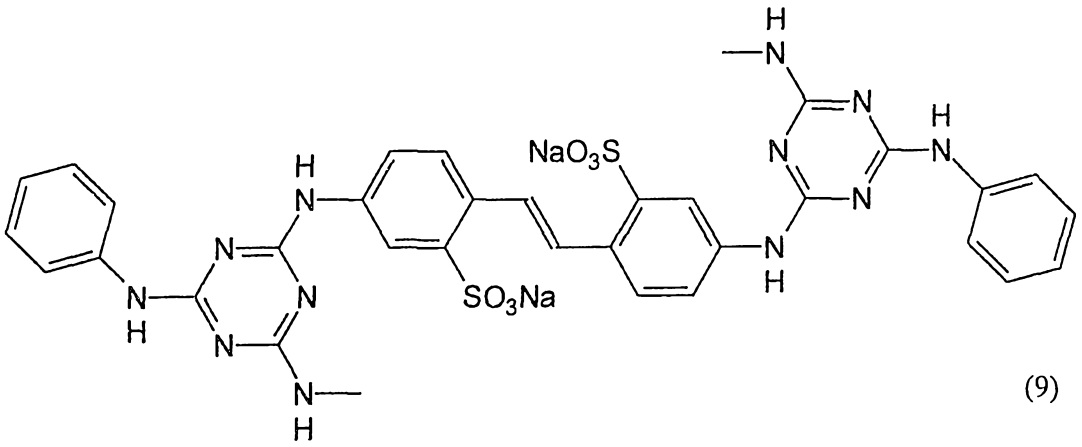
$N(methyl)_2$, N(methyl(hydroxyethyl), NH-ethyl, $N(hydroxyethyl)_2$, NH-phenyl, S-methyl, S-(phenyl), Cl or OH.

13. Process according to claim 9 in which the fluorescent whitening agent of formula (1) has the formula:



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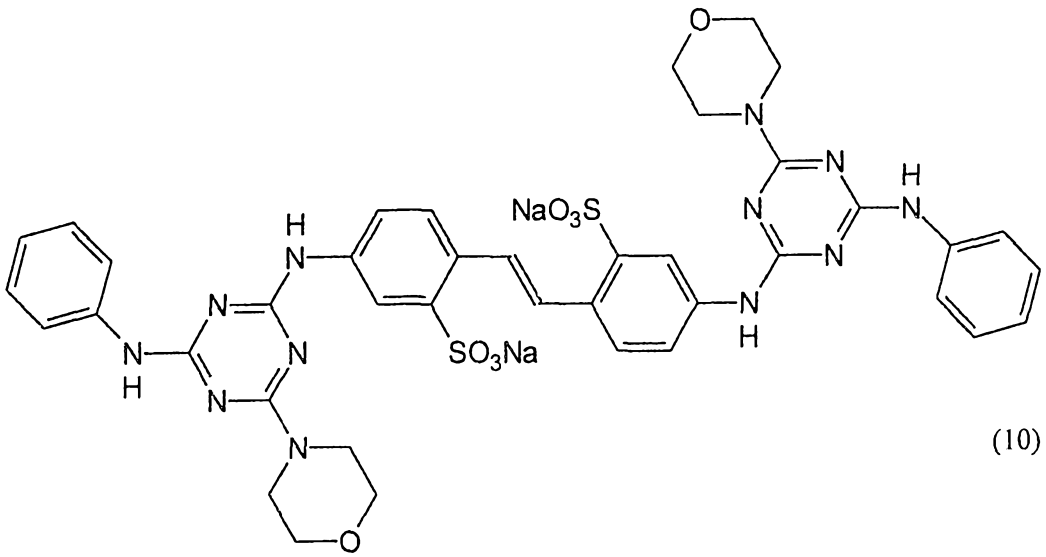

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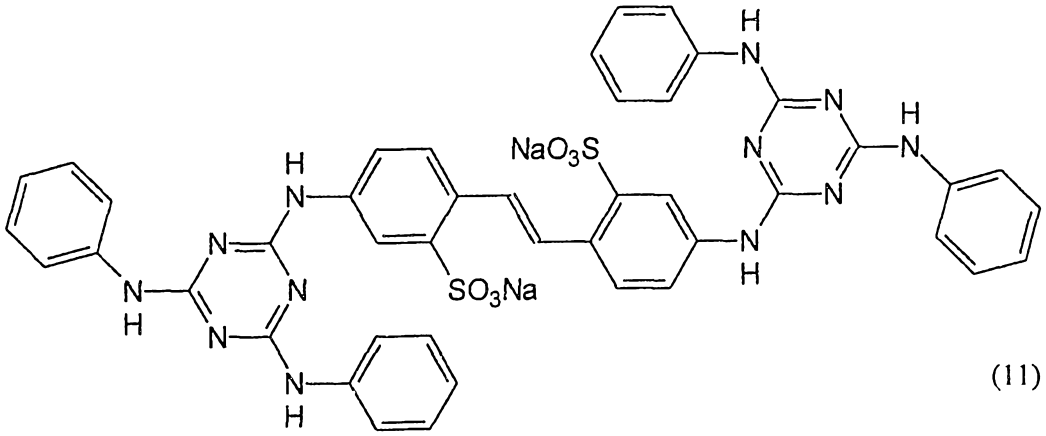

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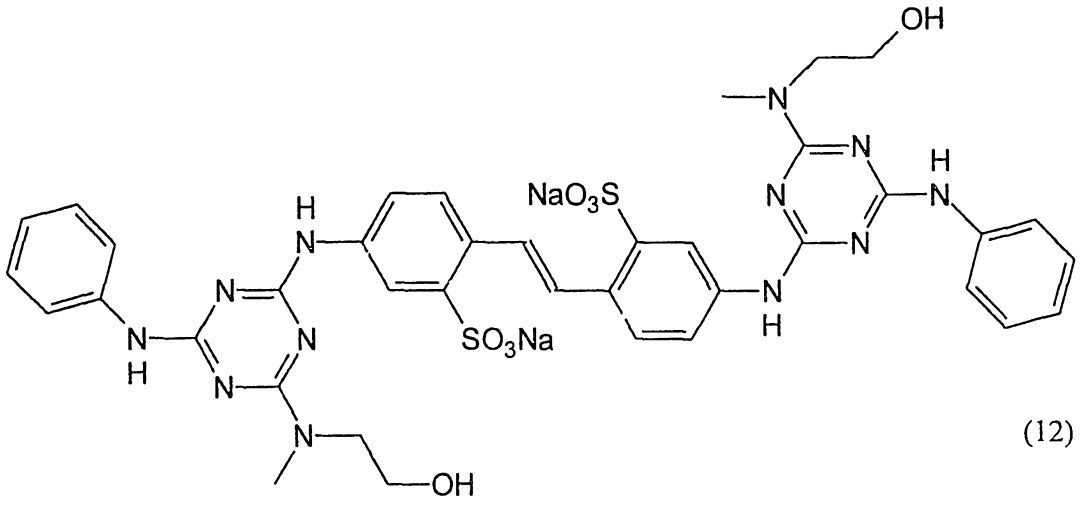

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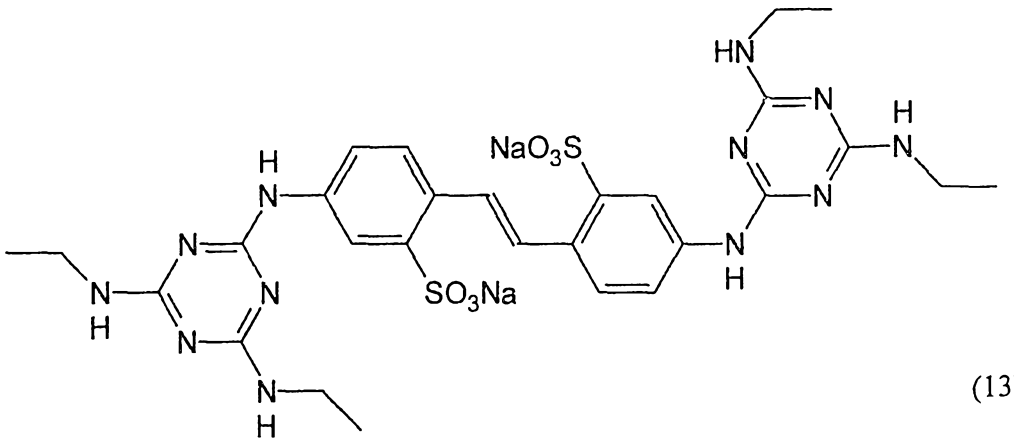

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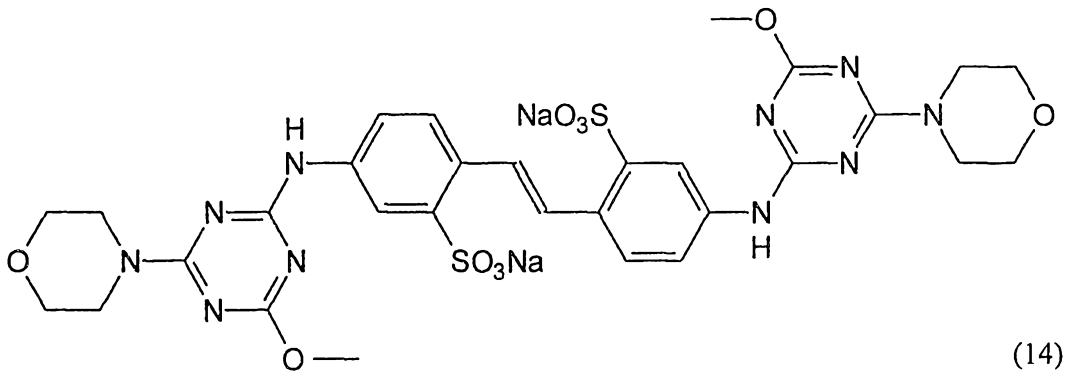

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14. Process according to claim 9 in which the fluorescent whitening agent of formula (2) has the formula:

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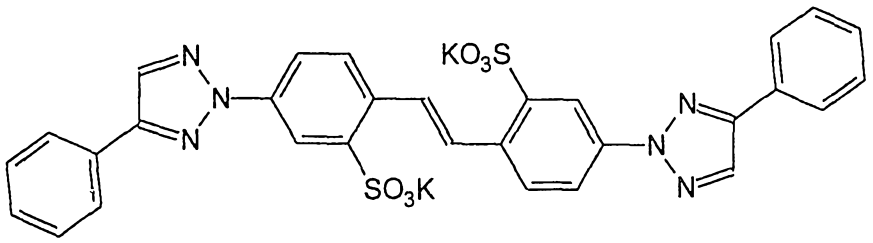

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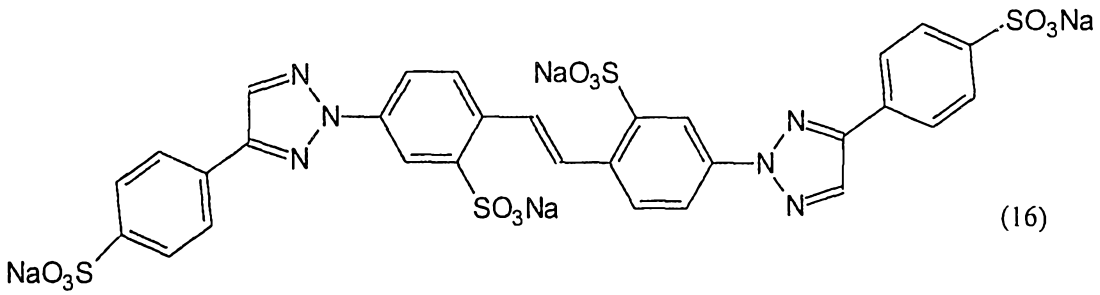

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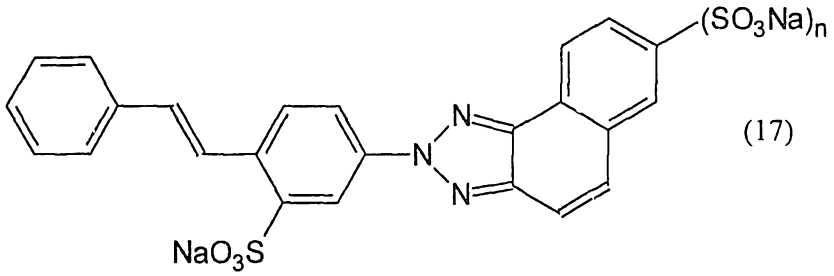

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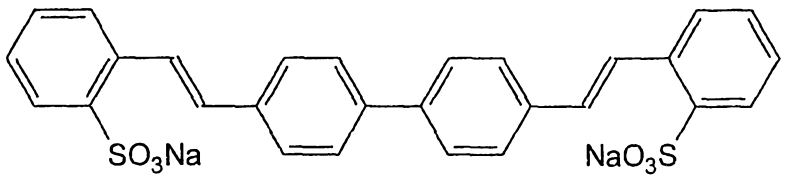
in which n is as defined in claim 9.

15. Process according to claim 9 in which the fluorescent whitening agent of formula (4) has the formula:



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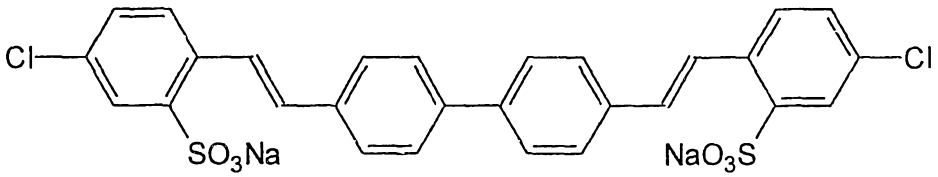

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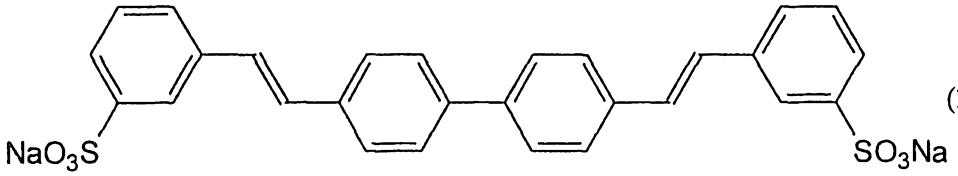
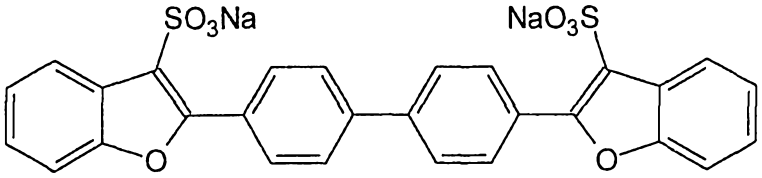
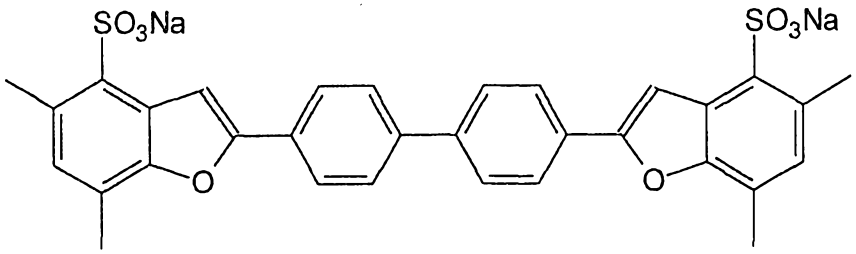


(20)

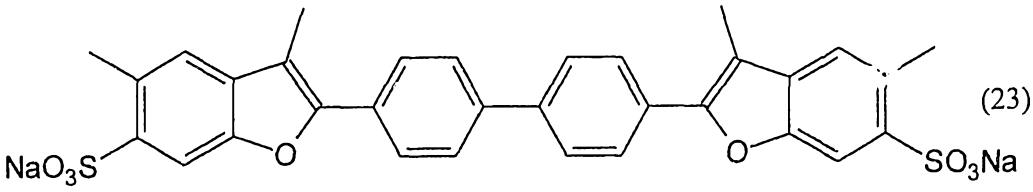
16. Process according to claim 9 in which the fluorescent whitening agent of formula (5) has the formula:



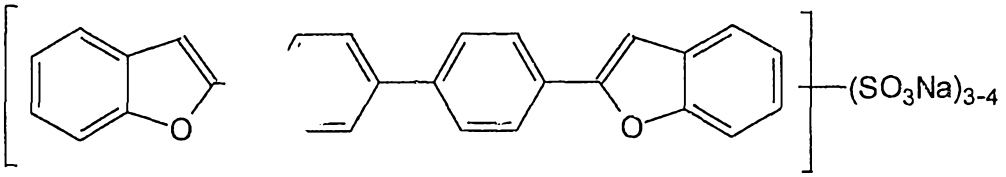
(21)



(22)

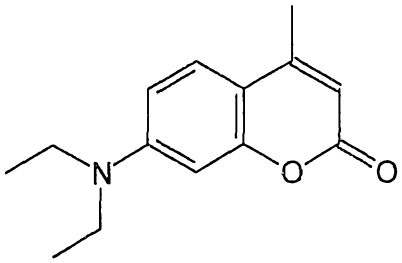


(23)



(24)

17. Process according to claim 9 in which the fluorescent whitening agent of formula (8) has the formula:



(25)

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18. Process according to any one of the preceding claims in which the textile fibre material is composed of wool, polyamide, cotton, polyester, polyacrylic, silk, polypropylene or any mixture thereof.

19. Process according to claim 18 in which the fibre material is composed of cotton, polyacrylic, silk or any mixture thereof.

20. Process according to claim 19 in which the fibre material is composed of cotton.

21. Process according to claim 18 in which the fibre material is composed of polyester and a fluorescent whitening agent of formula (6) is used.

22. Process according to claim 18 in which the fibre material is composed of polyamide and a fluorescent whitening agent of formula (7), (8) or (12) is used.

23. Process according to claim 18 in which the fibre material is composed of wool and a fluorescent whitening agent of formula (7), (8) or (16) is used.

24. Fluorescent whitening agent, which absorbs radiation in the wavelength range 280-400 nm, when used in a process according to any one of claims 1 to 23.

25. Detergent comprising at least one fluorescent whitening agent, which absorbs radiation in the wavelength range 280-400 nm, when used in a process according to any one of claims 1 to 23.

26. Textile fibre material having an improved sun protection factor when treated according to a process claimed in any one of claims 1 to 23.

27. A process for improving the sun protection factor of textile fibre material, substantially as hereinbefore described with reference to any one of the Examples.

29. Textile fibre material having an improved sun protection factor, substantially as hereinbefore described with reference to any one of the Examples.

Dated 16 January, 1998
Ciba Specialty Chemicals Holding Inc.

Patent Attorneys for the Applicant/Nominated Person
SPRUSON & FERGUSON

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Abstract of the Disclosure

Protective Use

The present invention relates to the use of a detergent comprising at least one fluorescent whitening agent, which absorbs radiation in the wavelength range 280-400 nm, for the improvement of the sun protection factor (SPF) of textile fibre material washed with the detergent.