(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 170 290 B9

(12) **CORRECTED EUROPEAN PATENT SPECIFICATION**
Note: Bibliography reflects the latest situation

(15) Correction information:
Corrected version no 1 (W1 B1)
Corrections, see page(s) 4,7,18

(48) Corrigendum issued on:
13.09.2006 Bulletin 2006/37

(45) Date of publication and mention of the grant of the patent:
07.06.2006 Bulletin 2006/23

(21) Application number: **01123273.3**

(22) Date of filing: **12.06.1995**

(51) Int Cl.:
C07D 251/24 *(2006.01)* ***D06M 13/00*** *(2006.01)*
C07D 405/12 *(2006.01)* ***C07D 251/70*** *(2006.01)*
C07D 251/44 *(2006.01)* ***C07D 251/50*** *(2006.01)*
C07D 403/12 *(2006.01)* ***C07D 403/14*** *(2006.01)*
C07D 251/42 *(2006.01)*

(54) **Compounds having ultra-violet absorption properties**

Verbindungen mit UV absorbierenden Eigenschaften

Composés ayant des propriétés d'absorption d'UV

(84) Designated Contracting States:
BE CH DE FR GB IT LI

(30) Priority: **23.07.1994 GB 9414881**
01.09.1994 GB 9417562

(43) Date of publication of application:
09.01.2002 Bulletin 2002/02

(62) Document number(s) of the earlier application(s) in accordance with Art. 76 EPC:
95810388.9 / 0 693 483

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(56) References cited:
EP-A- 0 388 356
WO-A-94/04515
US-A- 4 895 945

Remarks:
The file contains technical information submitted after the application was filed and not included in this specification

EP 1 170 290 B9

Description

[0001] The present invention relates to new compounds which are useful as ultraviolet absorbing agents (UVAs) and to a method of improving the sun protection factor (SPF) of textile fibre material treated with the new compounds.

[0002] 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.

[0003] 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.

[0004] 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.

[0005] 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.

[0006] 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.

[0007] Most natural and synthetic textile materials are at least partially permeable to UV 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.

[0008] 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, even skin beneath clothing dyed in some dark shades may also require protection from UV radiation.

[0009] Such lightweight summer clothing normally has a density of 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.

[0010] 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.

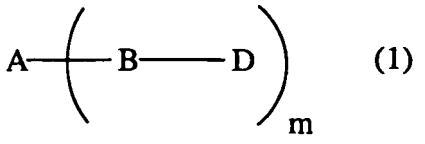
[0011] U.S. Patent No. 4,895,945 discloses chloroepoxytriazines useful for introducing epoxy functional groups into nucleophilic polymers.

[0012] EP-A 0 388 356 describes the application of triazine derivatives as UV absorbing agents in lenses, in particular in contact lenses.

[0013] It is already known, e.g. from WO 94/4515, that the application of specified types of UVA to a light-weight textile materials in general can effect an increase in the SPF value of the textile so treated. The increase in SPF value achieved thereby, however, is relatively modest.

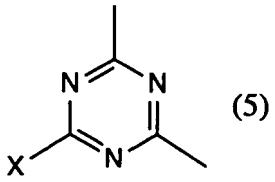
[0014] Certain new compounds have now been found which can be readily produced and which, unexpectedly, impart greatly increased SPF ratings to textile fibre materials treated with the new compounds.

[0015] Accordingly, the present invention provides a compound having the formula:

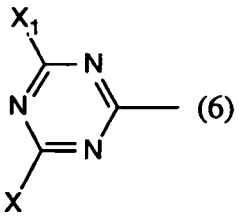


(1)

in which m is 1 or 2; A is a residue selected from those having the formulae:


(5)

or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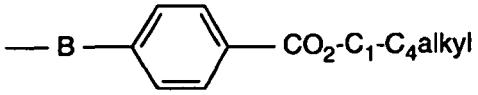
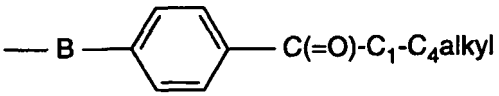
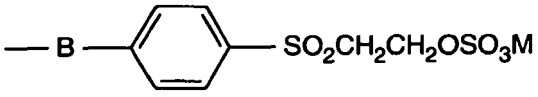
X is F, Cl or $NHCH_2OH$ and X_1 is F, Cl, $NHCH_2OH$ or a group having the formula:







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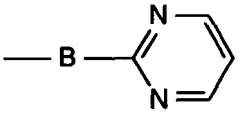
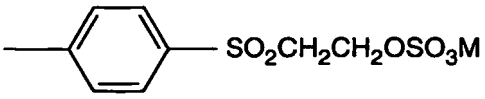

;

B is -O-, -NH- or $-SO_2-$; and

D is a group having one of the formulae:

CH_2-C(=O)-$NH(CH_2OH)$, CH_2-C(=O)-$N(CH_2OH)_2$ or $-CH_2CH_2-OSO_3M$ in which M is hydrogen, sodium, potassium,

calcium, magnesium, ammonium, mono-, di-, tri- or tetra-C_1-C_4alkylammonium or ammonium that is di- or tri-substituted by a mixture of C_1-C_4alkyl and C_1-C_4hydroxyalkyl groups, preferably sodium, or D may also be a group of formula:



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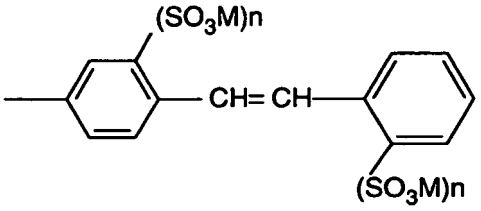
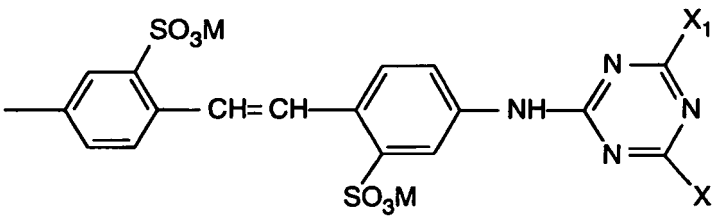


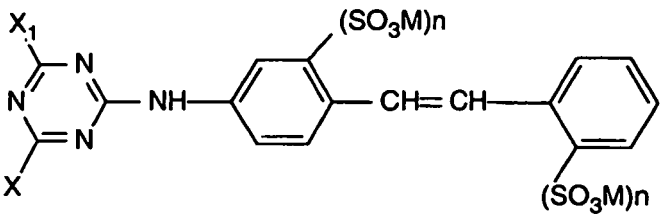
in which M has its previous significance and n is 0 or 1, provided that at least one SO_3M group is present, or the formula:



in which X, X_1 and M have their previous significance.

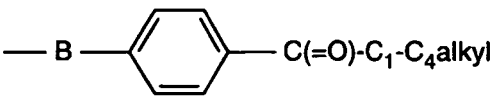
[0016] Preferred compounds of formula (1) include those having the formula:

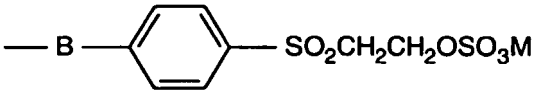
[deletion(s)]



(13)

in which n has its previous significance, provided that at least one group $-SO_3M$ is present, X is F or Cl and X_1 is F, Cl or a group having one of the formulae:





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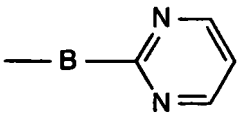
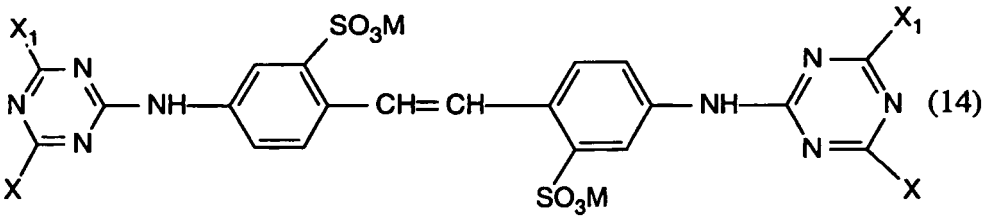
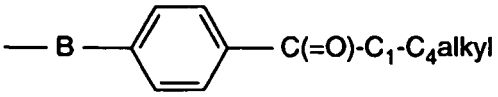


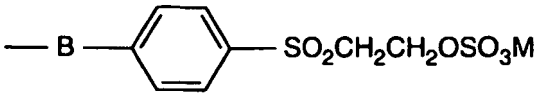
in which B and M have their previous significance;



(14)

in which each X is the same and is F or Cl and each X_1 is the same and is F, Cl or a group having one of the formulae:





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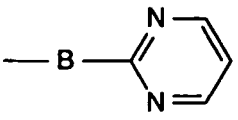
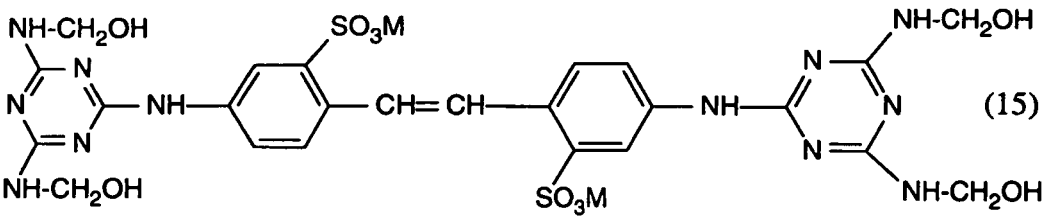


in which B and M have their previous significance, or



(15)

in which M has its previous significance but is preferably Na.

[0017] The compounds of formula (1) may be produced by reacting, under known reaction conditions, a compound of formula A-$(BH)_m$ in which A, B and m have their previous significance, with m moles of a compound L-D, in which D has its previous significance and L is a leaving group or atom, preferably a halogen atom, especially a chlorine atom.

[0018] The starting materials A-$(BH)_m$ and L-D are known compounds which are readily available.

[0019] The present invention also provides a method for the treatment of a textile fibre material, comprising treating the textile fibre material with 0.05 to 3.0% by weight, based on the weight of the textile fibre material, of one or more compounds having the formula (1).

[0020] The textile fibres treated according to the method of the present invention may be natural or synthetic fibres or mixtures thereof. Examples of natural fibres include vegetable fibres such as cotton, viscose, flax, rayon or linen, preferably cotton and animal fibres such as wool, mohair, cashmere, angora and silk, preferably wool. Synthetic fibres include polyester, polyamide and polyacrylonitrile fibres.

[0021] Preferably, textile fibres treated according to the method of the present invention have a density of less than 200 g/m^2 and have not been previously dyed in deep shades.

[0022] Some of the compounds of formula (1) used in the method of 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.

[0023] As dispersing agents for such sparingly-soluble compounds of formula (1) 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.

[0024] Depending on the type of compound of formula (1) used, it may be beneficial to carry out the treatment in a neutral, alkaline or acidic bath. The method is usually conducted in the temperature range of from 20 to 140°C.,for example at or near to the boiling point of the aqueous bath, e.g. at about 90°C.

[0025] Solutions of the compound of formula (1), or its emulsions in organic solvents may also be used in the method of the present invention. For example, the so-called solvent dyeing (pad thermofix application) or exhaust dyeing methods in dyeing machines may be used.

[0026] If the method of the present invention is combined with a textile treatment or finishing method, such combined treatment may be advantageously carried out using appropriate stable preparations which contain the compound of

formula (1) in a concentration such that the desired SPF improvement is achieved.

[0027] In certain cases, the compound of formula (1) is made fully effective by an after-treatment. This may comprise a chemical treatment such as treatment with an acid, a thermal treatment or a combined thermal/chemical treatment.

[0028] It is often advantageous to use the compound of formula (1) in admixture with an assistant or extender such as anhydrous sodium sulfate, sodium sulfate decahydrate, sodium chloride, sodium carbonate, an alkali metal phosphate such as sodium or potassium orthophosphate, sodium or potassium pyrophosphate or sodium or potassium tripolyphosphate, or an alkali metal silicate such as sodium silicate.

[0029] In addition to the compounds of formula (1), a minor proportion of one or more adjuvants may also be employed in the method of the present invention. Examples of adjuvants include emulsifiers, perfumes, colouring dyes, opacifiers, optical whitening agents, bactericides, nonionic surfactants, fabric care ingredients, especially fabric softeners, stain release or stain repellant ingredients or water-proofing agents, anti-gelling agents such as nitrites or nitrates of alkali metals, especially sodium nitrate, and corrosion inhibitors such as sodium silicate.

[0030] The amount of each of these optional adjuvants should not exceed 1% by weight on the treated fibre.

[0031] The method of the present invention, in addition to providing protection to the skin, also increases the useful life of a textile article treated according to the present invention. In particular, the tear resistance and/or lightfastness of the treated textile fibre material may be improved.

[0032] Accordingly, the present invention still further provides a method of increasing the SPF rating of textile fibre material, comprising treating the textile fibre material with 0.05 to 3.0% by weight, based on the weight of the textile fibre material, of one or more compounds having the formula (1).

[0033] The present invention also provides a textile fabric produced from a fibre treated according to the method of the present invention as well as an article of clothing produced from the said fabric.

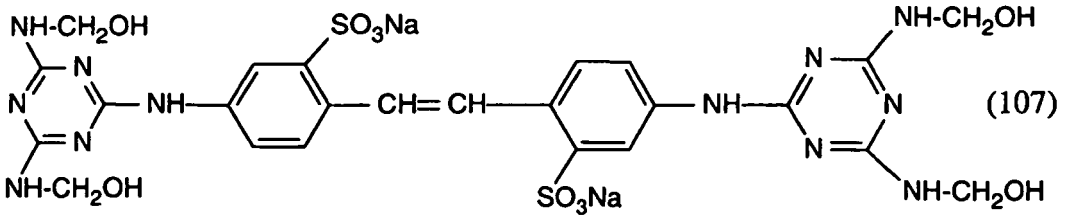
[0034] Such textile fabrics and articles of clothing produced from the said fabrics typically have an SPF rating of 20 and above whereas untreated cotton, for example, generally has an SPF rating of from 2 to 4.

[0035] The following Examples further illustrate the present invention.

[deletion(s)]

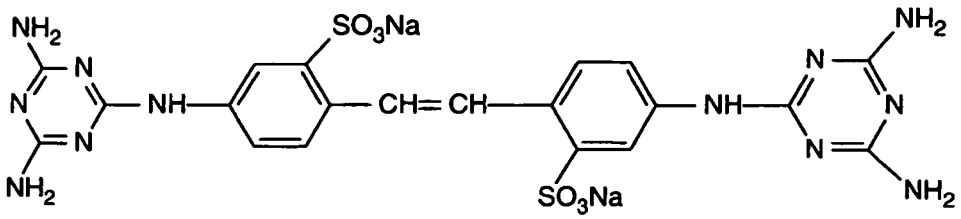
Example 1

[0036]



(107)

6.3 g. of the compound of formula:



are dissolved in 150 mls. of water at 60°C. and treated with 10 drops of 30 % caustic soda solution. After the dropwise addition of 32.4 g. of a 37 % formaldehyde solution, and subsequent stirring at 60-65°C. over 2.5 hours, 150 mls. of salt solution are added and the mixture is cooled to 10°C. The reaction mixture is filtered giving 7 g. of a solid product, corresponding to a yield of 93 % of the theoretical.

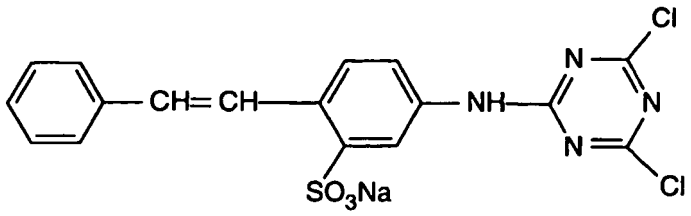
The product (107) has the following elemental analysis by weight:

Analysis for $C_{27}H_{26}N_{12}Na_2O_{10}S_2.1\ C_2H_5OH.\ 7.5H_2O$:

Req.%	C 33.47;	H 4.93;	N 18.00;	S 6.87;	Na 4.93
Found %	C 33.4;	H 4.7;	N 17.5;	S 6.7;	Na 5.0.

Example 2

[0037]



(108)

[0038] 3.4 g. of cyanuric chloride are stirred in a mixture of 100 mls of acetone and 50 mls of water. The mixture is chilled to -10°C. and a solution of 5.5 g. of 4-aminostilbene-2-sulfonic acid sodium salt in 50 mls of water is added over 30 minutes, followed by 10 mls of 1M sodium carbonate solution.

[0039] The resulting mixture is stirred for 2 hours at -5 to -10°C. and the solid is filtered off and dried, giving 6.8 g. of a white product corresponding to a yield of 74% of theory.

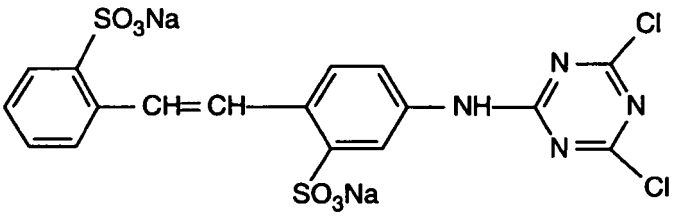
[0040] The compound (108) has the following elemental analysis by weight:

Analysis for $C_{17}H_{11}Cl_2N_4NaO_3S.\ 1.26\ H_2O$:

Req.%	C 43.63;	H 2.91;	N 11.97;	S 6.85;	Cl 15.15;	H_2O 4.85
Found %	C 43.7;	H 3.0;	N 12.0;	S 6.8;	Cl 15.0.;	H_2O 4.85.

Example 3

[0041]



(109)

[0042] Using the same procedure as in Example 2 but replacing 4-aminostilbene-2-sulfonic acid by 4-aminostilbene-2,2'-disulfonic acid disodium salt, 15.1 g. of the compound of formula (109) are obtained, corresponding to a yield of 55% of theory.

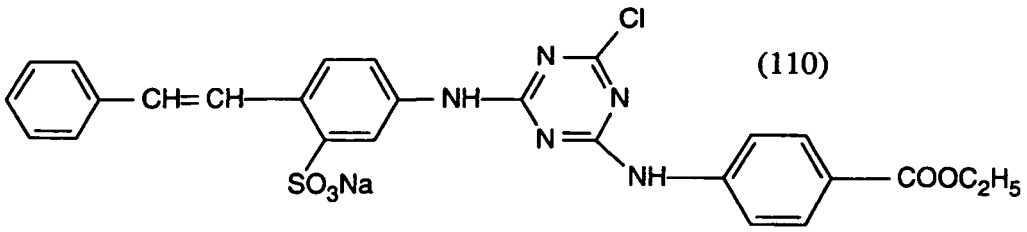
[0043] The compound (109) has the following elemental analysis by weight:

Analysis for $C_{17}H_{10}Cl_2N_4Na_2O_6S_2.\ 4.63\ H_2O$:

Req.%	C 32.37;	H 3.03;	N 8.88;	S 10.17;	Cl 11.24;	H_2O 13.22
Found %	C 32.4;	H 3.0;	N 8.9;	S 10.0;	Cl 11.5.;	H_2O 13.23.

Example 4

[0044]



A) Using the procedure described in Example 2, prior to the filtration step, Compound (108) is produced as a white dispersion.

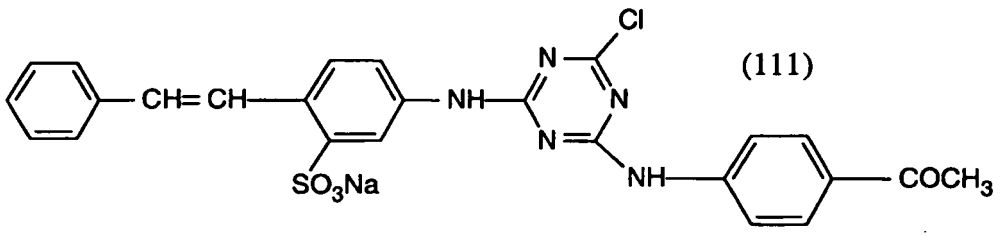
B) To this dispersion there are added 3 g. of 4-amino-ethylbenzoate, as a solid, followed by 10 mls of 1M sodium carbonate solution. The resulting pale yellow suspension is stirred for 18 hours at 25°C. and the solid product is filtered off and dried, giving 8.6 g. of the white compound of formula (110), corresponding to a yield of 83% of theory.

[0045] The compound (110) has the following elemental analysis by weight:

	Analysis for $C_{26}H_{21}ClN_5NaO_5S.\ 3.84\ H_2O.\ 0.14\ NaCl$:					
Req.%	C 47.9;	H 4.4;	N 10.75;	S 4.9;	Cl 6.21;	H_2O 10.61
Found %	C 47.9;	H 4.4;	N 10.8;	S 4.8;	Cl 6.5.;	H_2O 10.76.

Example 5

[0046]



A) Using the procedure described in Example 2, prior to the filtration step, Compound (108) is produced as a white dispersion.

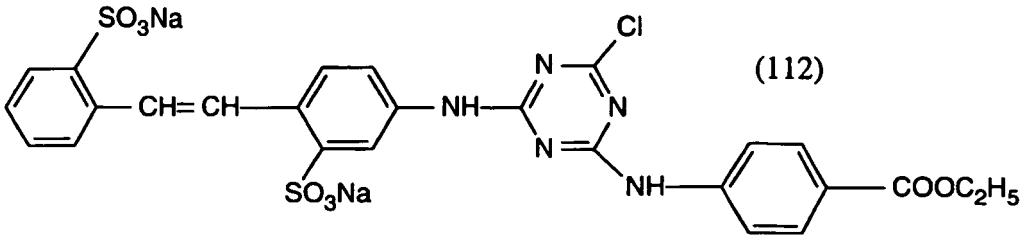
B) The procedure described in part B) of Example 4 is repeated except that 4-amino-ethylbenzoate is replaced by 4-amino-acetophenone. In this way, 4.8 g. of the white compound of formula (111) are produced, corresponding to a yield of 49% of theory.

[0047] The compound (111) has the following elemental analysis by weight:

	Analysis for $C_{25}H_{19}ClN_5NaO_4S.\ 3.96\ H_2O.\ 0.16\ NaCl$:					
Req.%	C 48.0;	H 4.31;	N 11.2;	S 5.12;	Cl 6.59;	H_2O 11.40
Found %	C 48.0;	H 4.4;	N 11.3;	S 5.1;	Cl 6.4.;	H_2O 11.42.

Example 6

[0048]



A) Using the procedure described in Example 3, prior to the filtration step, Compound (109) is produced as a dispersion.

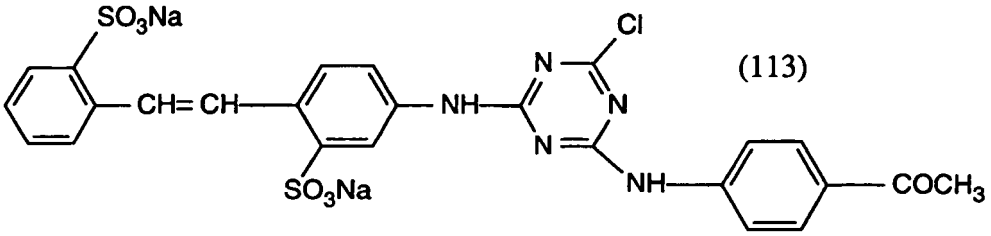
B) The procedure in part B) of Example 4 is used for the reaction of the compound of formula (109) with 4-amino-ethylbenzoate to obtain 31.9 g. of the yellow compound (112), corresponding to a yield of 78.6% of theory.

[0049] The compound (112) has the following elemental analysis by weight:

	Analysis for $C_{26}H_{20}ClN_5Na_2O_8S_2$. 6 H_2O. 0.5 NaCl:					
Req.%	C 38.4;	H 3.94;	N 8.6;	S 7.8;	Cl 6.5;	H_2O 13.28
Found %	C 38.9;	H 3.9;	N 9.2;	S 7.7;	Cl 6.6.;	H_2O 12.67.

Example 7

[0050]



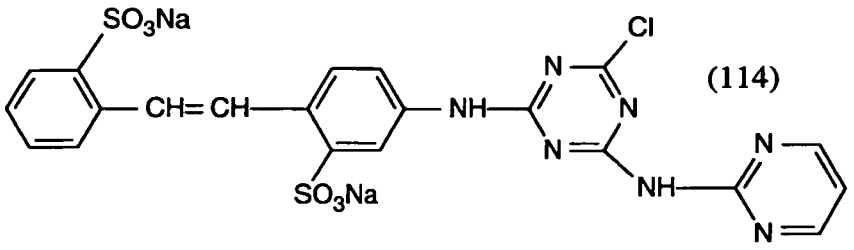
[0051] The procedure in Example 6 is repeated except that, in part B), 4-amino-acetophenone is used instead of 4-amino-ethylbenzoate. In this way, 6.3 g. of compound (113) are obtained, corresponding to a yield of 49% of theory.

[0052] The compound (113) has the following elemental analysis by weight:

	Analysis for $C_{25}H_{18}ClN_8Na_2O_7S_2$. 4.61 H_2O.:					
Req.%	C 41.19;	H 3.76;	N 9.61;	S 8.80;	Cl 4.86;	H_2O 11.39
Found %	C 41.4;	H 3.8;	N 9.7;	S 8.6;	Cl 5.3.;	H_2O 11.39.

Example 8

[0053]



(114)

[0054] The procedure in Example 6 is repeated except that, in part B), 2-amino-pyrimidine is used instead of 4-amino-ethylbenzoate. In this way, 9.2 g. of compound (114) are obtained, corresponding to a yield of 61% of theory.

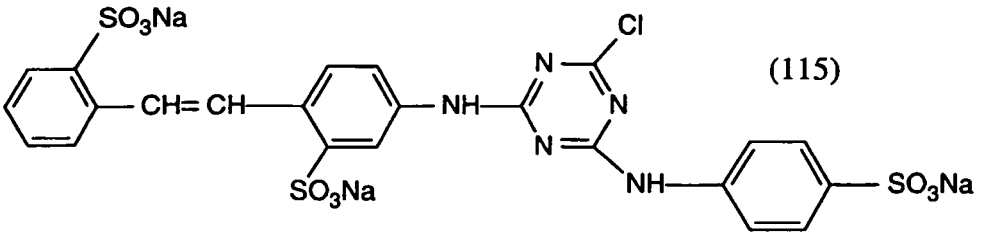
[0055] The compound (114) has the following elemental analysis by weight:

Analysis for $C_{21}H_{14}ClN_7Na_2O_6S_2$. 6 H_2O. 0.33 NaCl:

Req.%	C 34.37;	H 3.55;	N 13.37;	S 8.7;	Cl 6.4;	H_2O 14.7
Found %	C 34.4;	H 3.6;	N 13.9;	S 8.5;	Cl 6.3.;	H_2O 15.1.

Example 9

[0056]



(115)

[0057] The procedure in Example 6 is repeated except that, in part B), sulfanilic acid is used instead of 4-amino-ethylbenzoate. In this way, 16.9 g. of compound (115) are obtained, corresponding to a yield of 57.9% of theory.

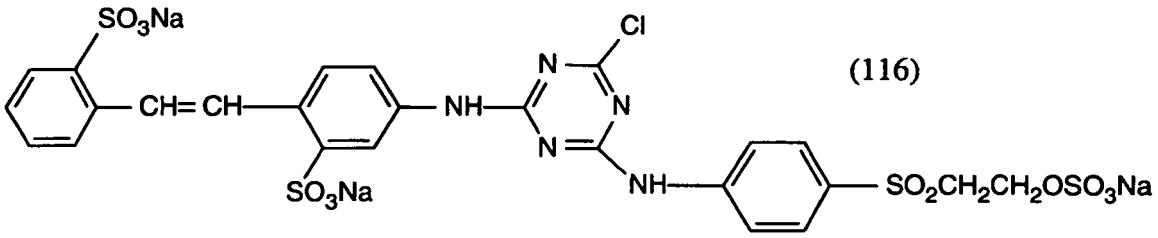
[0058] The compound (115) has the following elemental analysis by weight:

Analysis for $C_{25}H_{15}ClN_5Na_3O_9S_3$. 10.67 H_2O. 3.5 NaCl:

Req.%	C 25.7;	H 3.11;	N 6.0;	S 8.22;	Cl 13.7;	H_2O 16.45
Found %	C 25.7;	H 3.2;	N 6.5;	S 8.5;	Cl 13.7.;	H_2O 16.4.

Example 10

[0059]



(116)

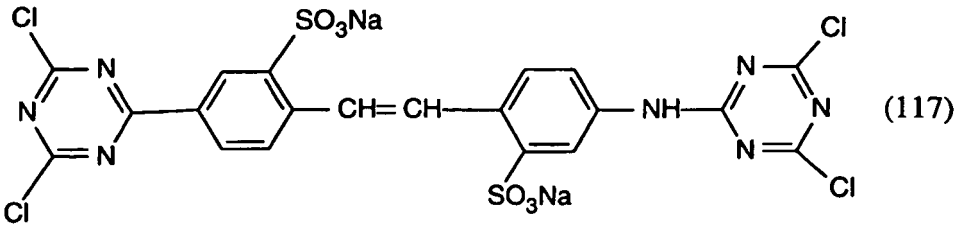
[0060] The procedure in Example 6 is repeated except that, in part B), 2-(4-aminophenylsulfonyl)-ethylhydrogen sulfate is used instead of 4-amino-ethylbenzoate. In this way, 19.5 g. of compound (116) are obtained, corresponding to a yield of 60% of theory.

[0061] The compound (116) has the following elemental analysis by weight:

	Analysis for $C_{25}H_{21}ClN_5Na_3O_{12}S_4$. 8 H_2O. 0.41 Na_2SO_4:					
Req.%	C 29.50;	H 3.63;	N 6.88;	S 13.86;	Cl 3.49;	H_2O 14.15
Found %	C 29.5;	H 3.50;	N 7.0;	S 13.7;	Cl 3.7.;	H_2O 14.38.

Example 11

[0062]



(117)

[0063] Using the procedure described in Example 2, 18.4 g. of cyanuric chloride are stirred in a mixture of 120 mls of acetone and 100 mls of water. The mixture is chilled to -10°C. and a solution of 25.4 g. of 4.4'-diaminostilbene-2,2'-disulfonic acid disodium salt in 50 mls of water is added over 30 minutes, followed by 50 mls of 1M sodium carbonate solution.

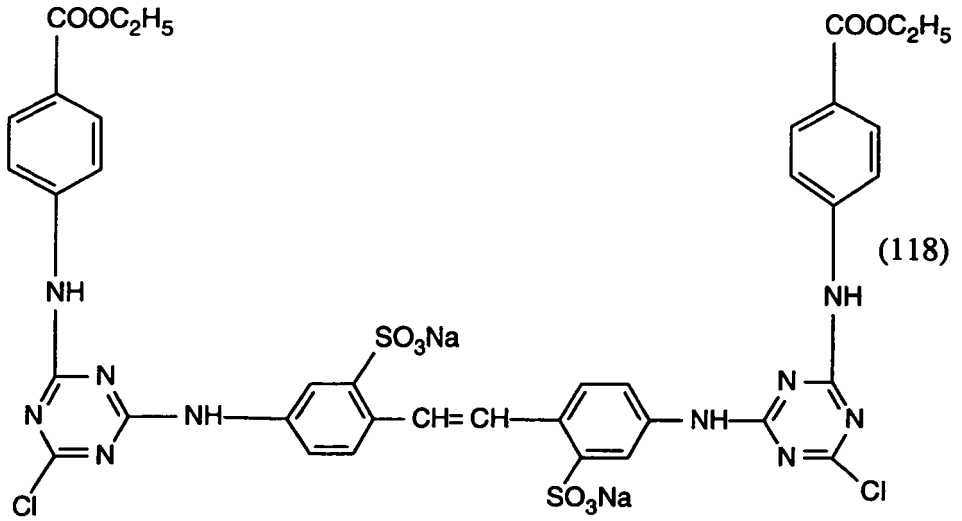
[0064] The resulting mixture is stirred for 2 hours at -5 to -10°C. and the solid is filtered off and dried, giving 24.1 g. of a white product corresponding to a yield of 67.9% of theory.

[0065] The compound (117) has the following elemental analysis by weight:

	Analysis for $C_{20}H_{10}Cl_4N_8Na_2O_6S_2$. 5 H_2O:				
Req.%	C 30.01;	H 2.51;	N 14.00;	S 8.01;	Cl 17.62;
Found %	C 30.0;	H 2.6;	N 14.0;	S 7.8;	Cl 17.6..

Example 12

[0066]



(118)

[0067] To the white suspension of the compound of formula (117) obtained in Example 11, prior to the filtration step, there is added 4-amino-ethylbenzoate in the manner described in Example 4.

[0068] In this way, 44.5 g. of compound (118) are obtained, corresponding to a yield of 92% of theory.

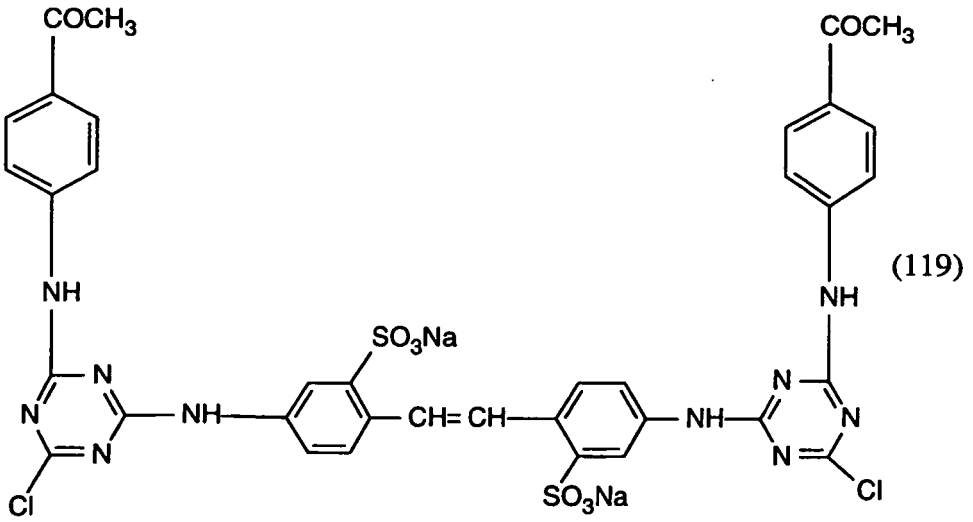
[0069] The compound (118) has the following elemental analysis by weight:

Analysis for $C_{38}H_{30}Cl_2N_{10}Na_2O_{10}S_2$. 6.5 H_2O. 1 NaCl:

Req.%	C 40.0;	H 3.77;	N 12.28;	Cl 9.34;	H_2O 10.26
Found %	C 40.0;	H 3.8;	N 12.3;	Cl 9.2.;	H_2O 10.0.

Example 13

[0070]



(119)

[0071] Using the procedure described in Example 12 but replacing 4-amino-ethylbenzoate by 4-amino-acetophenone, 29.1 g. of compound (119) are obtained, corresponding to a yield of 94.6% of theory.

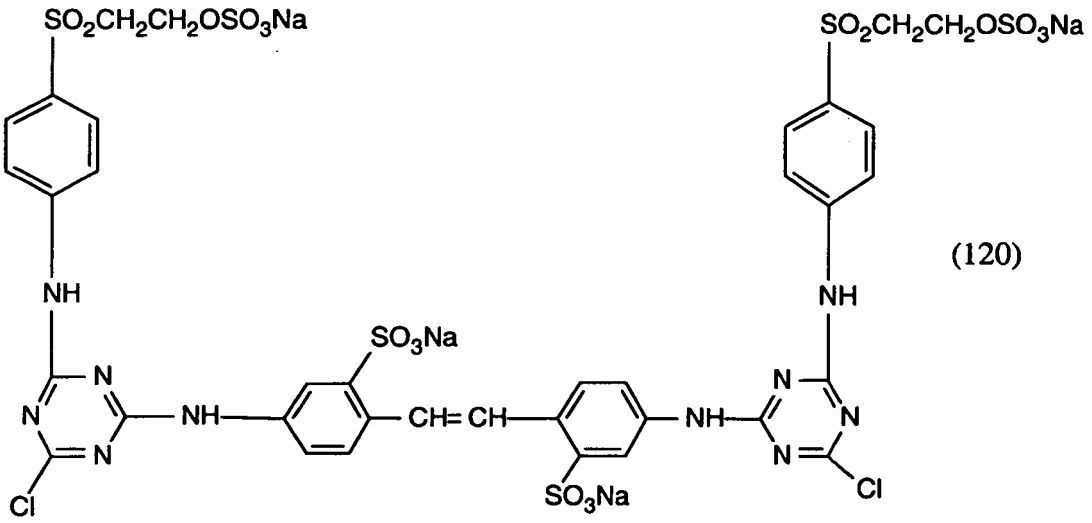
[0072] The compound (119) has the following elemental analysis by weight:

Analysis for $C_{36}H_{26}Cl_2N_{10}Na_2O_8S_2$. 16 H_2O. 0.6 NaCl:

Req.%	C 35.15;	H 4.71;	N 11.38;	Cl 7.50;	S 5.20;	H_2O 10.26
Found %	C 35.1;	H 4.8;	N 11.5;	Cl 7.7.;	S 5.2;	H_2O 23.5.

Example 14

[0073]



(120)

[0074] Using the procedure described in Example 12 but replacing 4-amino-ethylbenzoate by 2(4-aminophenylsulfonyl)-ethylhydrogensulfate, 46.2 g. of compound (120) are obtained, corresponding to a yield of 73.1% of theory.

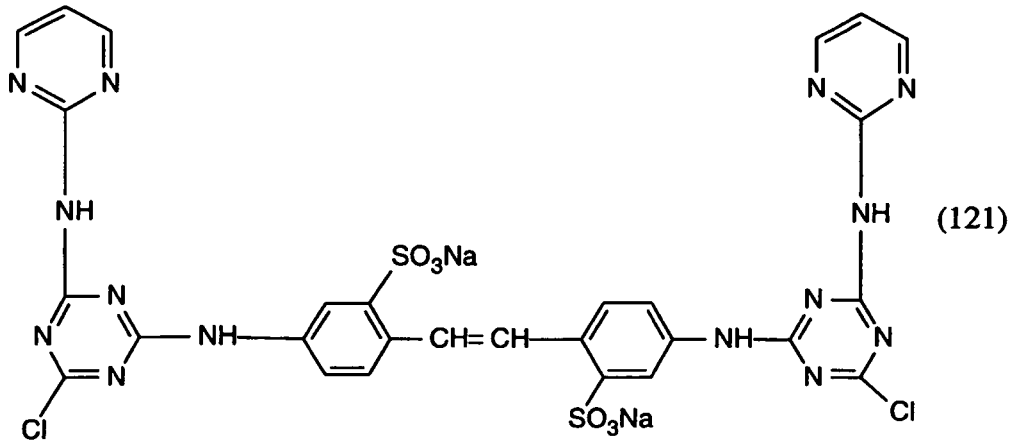
[0075] The compound (120) has the following elemental analysis by weight:

Analysis for $C_{36}H_{30}Cl_2N_{10}Na_4O_{18}S_6$. 12.05 H_2O. 18.2 NaCl:

Req.%	C 17.10;	H 2.14;	N 5.53;	S 7.59;	Cl 28.33;	H_2O 8.58
Found %	C 17.1;	H 2.1;	N 5.6;	S 7.5;	Cl 28.6;	H_2O 8.58.

Example 15

[0076]



(121)

[0077] Using the procedure described in Example 12 but replacing 4-amino-ethylbenzoate by 4-aminopyrimidine, 16.4 g. of compound (121) are obtained, corresponding to a yield of 79% of theory.

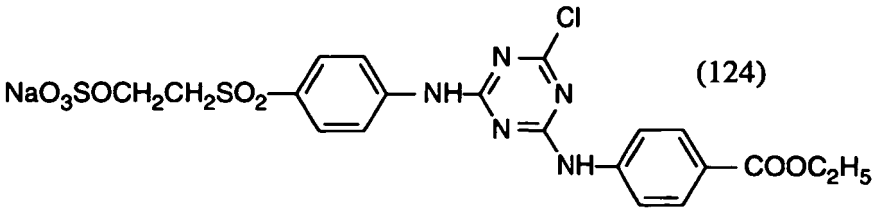
[0078] The compound (121) has the following elemental analysis by weight:

Analysis for $C_{26}H_{18}Cl_2N_{14}Na_2O_6S_2$. 7.3 H_2O. 0.7 NaCl. 1 CH_3COCH_3:

Req.%	C 33.42;	H 3.75;	N 18.85;	Cl 9.20;	S 6.15
Found %	C 33.3;	H 3.5;	N 19.0;	Cl 9.3;	S 6.1.

Example 16

[0079]



(124)

[0080] Using the procedure described in Example 2 but replacing 4-amino-stilbene-2-sulfonic acid sodium salt by a mixture of 2-(4-aminophenylsulfonyl)ethylhydrogen sulfate and 4-amino-ethylbenzoate, in the required stoichiometric proportions, 9.3 g. of the compound of formula (124) are obtained, corresponding to a yield of 73% of theory.

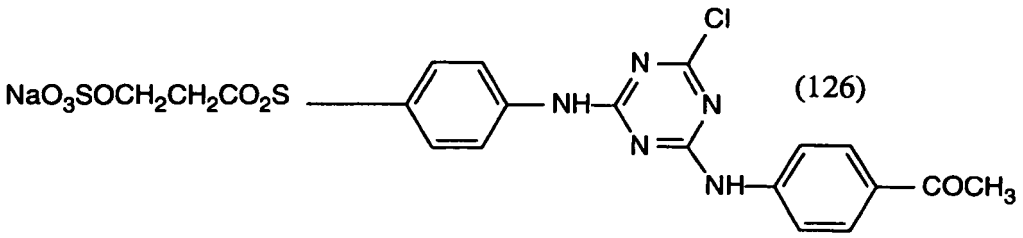
[0081] The compound (124) has the following elemental analysis by weight:

Analysis for $C_{20}H_{19}ClN_5NaO_8S_2$. 3.5 H_2O. 4.5 NaCl:

Req.%	C 25.40;	H 2.75;	N 7.41;	S 6.77;	H_2O 6.60
Found %	C 25.4;	H 2.6;	N 7.4;	S 6.2;	H_2O 6.5.

Example 17

[0082]



(126)

[0083] Using the procedure described in Example 2 but replacing 4-amino-stilbene-2-sulfonic acid sodium salt by a mixture of 2-(4-aminophenylsulfonyl)ethylhydrogen sulfate and 4-aminoacetophenone, in the required stoichiometric proportions, 8.9 g. of the compound of formula (126) are obtained, corresponding to a yield of 83% of theory.

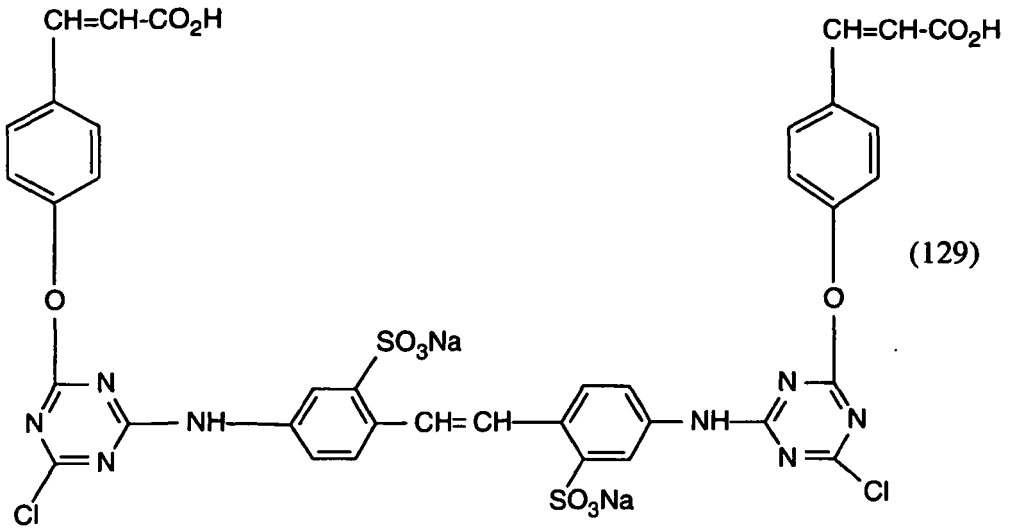
[0084] The compound (126) has the following elemental analysis by weight:

Analysis for $C_{18}H_{17}ClN_5NaO_7S_2$. 3.38 H_2O:

Req.%	C 36.10;	H 4.00;	N 11.70;	S 10.71;	Cl 5.92;	H_2O 10.17
Found %	C 37.0;	H 4.1;	N 11.8;	S 10.3;	Cl 5.8;	H_2O 10.18.

Example 18

[0085]



(129)

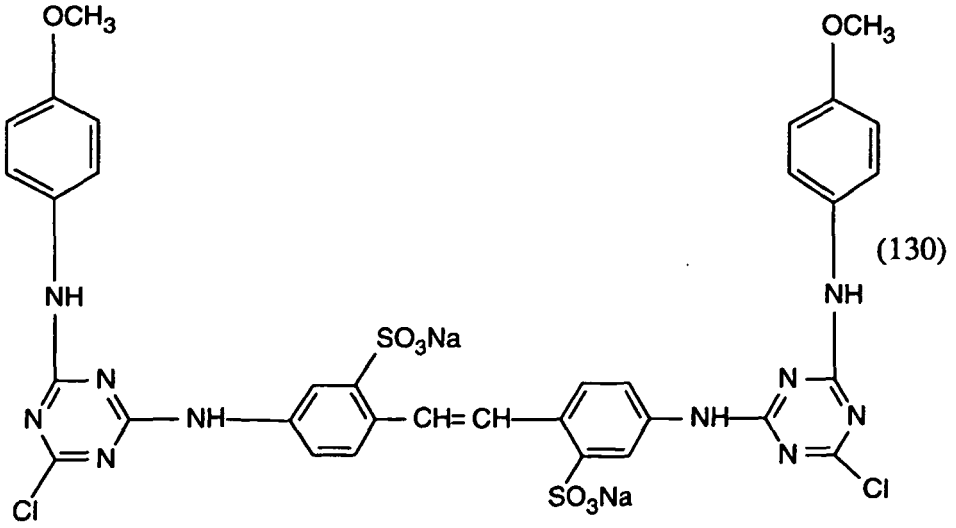
[0086] Using the procedure described in Example 12, compound (129) is prepared and has the following elemental analysis by weight:

Analysis for $C_{38}H_{24}Cl_2N_8Na_2O_{12}S_2$. 11.69 H_2O:

Req.%	C 38.80;	H 4.06;	N 9.53;	S 5.45;	Cl 6.03;	H_2O 17.90
Found %	C 38.2;	H 4.0;	N 9.4;	S 5.3;	Cl 6.2;	H_2O 17.91.

Example 19

[0087]



(130)

[0088] Using the procedure described in Example 12, compound (130) is prepared and has the following elemental analysis by weight:

Analysis for $C_{34}H_{26}Cl_2N_{10}Na_2O_8S_2$. 7.60 H_2O:

Req.%	C 40.01;	H 4.07;	N 13.72;	S 6.28;	Cl 6.95;	H_2O 13.42
Found %	C 41.1;	H 3.8;	N 14.3;	S 5.8;	Cl 7.5;	H_2O 13.41.

Example 20

[0089] Separate samples of bleached cotton cretonne are foularded (80% liquor uptake) with an aqueous bath containing:

5 g/l $MgCl_2$
250 g/l product of Example 1

to provide a concentration of 0.1% or 0.5% by weight of active ingredient on the cotton substrate.

[0090] As the product of Example 1 is insoluble in water, it is added as a 5% (w/w) aqueous dispersion which is obtained by milling 5% of the product of Example 1 and 1% of Pluronic F 108 (polypropylene glycol containing 80% ethylene oxide) in the presence of glass beads in deionised water.

[0091] The foularding is conducted at either alkaline pH (pH adjusted to 10-11 with soda) or at acidic pH (pH adjusted to 4-4.5 with acetic acid). Drying of the treated cotton samples is effected at 80°C. for two minutes, followed by thermofixing for one minute at 170°C.

[0092] 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.

[0093] In order to evaluate the wash fastness of the treated cotton samples, respective samples are washed once, five times or ten times in an aqueous bath containing 7g/l of a standard ECE detergent having the 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

(continued)

21.2% Sodium sulfate
Water to 100%.

[0094] Each wash is conducted at 60°C. for 15 minutes at a liquor ratio of 1:10.
[0095] The results obtained are set out in the following Table 1.
[deletion(s)]

Table 1

Example	Test UVA	Concn. FWA	Treatment	SPF			
			alkaline/ acidic	number of washes			
				none	one	five	ten
-	none (control)	-	acidic	4.1	4.1	4.1	4.2
20	cpd. of Ex.1	0.1% 0.5%	slightly acidic	10 23	15 26	12 27	12 27

Examples 21 to 31

[0096] Separate samples of bleached cotton cretonne are foularded (80% liquor uptake) with an aqueous bath containing:

10 g/l Na_2SO_4
50 g/l product of relevant Example

to provide a concentration of 0.1% or 0.2% by weight of active ingredient on the cotton substrate.
[0097] As the products of the relevant Examples are insoluble in water, they are added as a 5% (w/w) aqueous dispersion which is obtained by milling 5% of the product of the relevant Example and 1% of Pluronic F 108 in the presence of glass beads in deionised water.
[0098] The remaining procedure is as described in Example 20.
[0099] The results obtained are set out in the following Table 2.

Table 2

Example	Test UVA	Concn. FWA	Treatment	SPF			
			alkaline/ acidic	number of washes			
				none	one	five	ten
-	none (control)	-	neutral	7	5		6
21	cpd. of Ex.2	0.2%	neutral	34	22	29	29
22	cpd. of Ex.4	0.1%	neutral	29	31	22	19
23	cpd.ofEx.5	0.1%	neutral	39	36	22	23
24	cpd. of Ex.13	0.2%	neutral	26	40	36	29
25	cpd. of Ex.15	0.1%	neutral	21	19	13	11
26	cpd. of Ex.17	0.2%	neutral	18	14	9	12
27	cpd. of Ex.18	0.2%	neutral	30	34	31	28
28	cpd. of Ex.19	0.2%	neutral	38	23	22	20
29	cpd. of Ex.11	0.2%	neutral	18	13	7	15
30	cpd. of Ex.12	0.2%	neutral	29	36	21	19
31	cpd. of Ex. 14	0.2%	neutral	28	32	31	28

(continued)

Example	Test UVA	Concn. FWA	Treatment	SPF			
			alkaline/ acidic	number of washes			
				none	one	five	ten

Examples 32 to 34

[0100] Separate samples of bleached cotton cretonne are foularded (80% liquor uptake) with an aqueous bath containing:

4 g/l $NaHCO_3H$
50 g/l urea
50 g/l product of relevant Example

to provide a concentration of 0.2% by weight of active ingredient on the cotton substrate.

[0101] As the products of the relevant Examples are insoluble in water, they are added as a 5% (w/w) aqueous dispersion which is obtained by milling 5% of the product of the relevant Example and 1 % of Pluronic F 108 in the presence of glass beads in deionised water.

[0102] The remaining procedure is as described in Example 20 except that the thermofixing is conducted for 2 minutes at 130°C.

[0103] The results obtained are set out in the following Table 7.

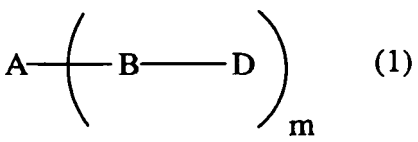
Table 3

Example	Test UVA	Concn. UVA	SPF			
			number of washes			
			none	one	five	ten
-	none (control)	-	7	5	5	4
32	cpd. of Ex.11	0.2%	28	15	15	24
33	cpd. of Ex.12	0.2%	45	49	45	34
34	cpd. of Ex.14	0.2%	33	35	36	48

[0104] The results in the Tables 1 to 3 demonstrate the substantial increase in the SPF values of cotton samples treated according to the present invention and that cotton samples treated according to the present invention are fast to washing.

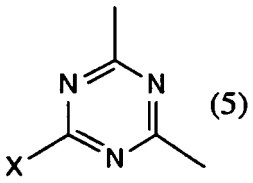
Claims

1. A compound having the formula:



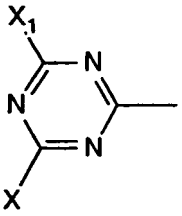
(1)

in which m is 1 or 2; A is a residue selected from those having the formulae:



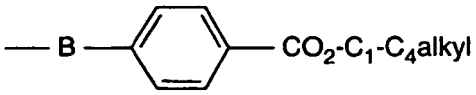
(5)

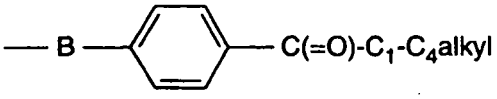
or

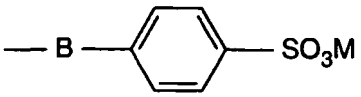


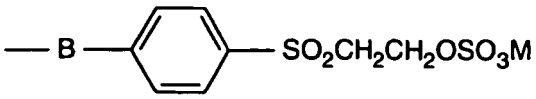
(6)

X is F, Cl or $NHCH_2OH$ and X_1 is F, Cl, $NHCH_2OH$ or a group having the formula:

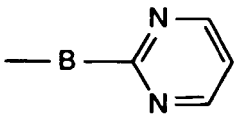






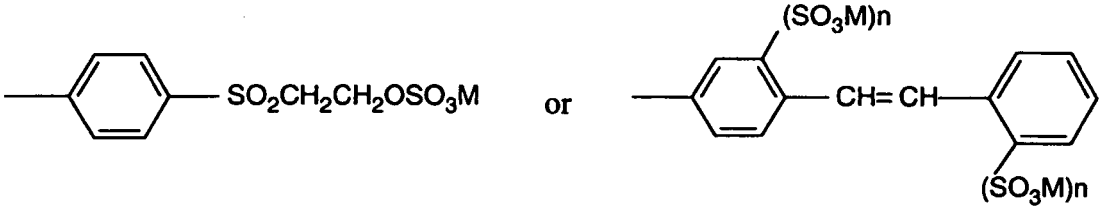


or

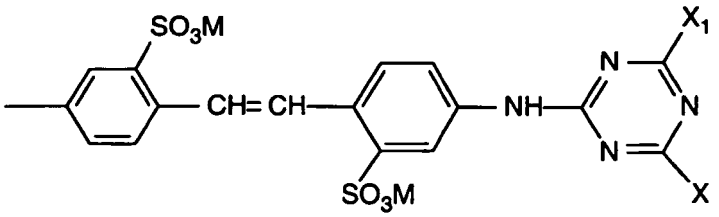


;

B is -O-, -NH- or $-SO_2-$; and
D is a group having one of the formulae:
CH_2-C(=O)-$NH(CH_2OH)$, CH_2-C(=O)-$N(CH_2OH)_2$ or CH_2CH_2-OSO_3M in which M is hydrogen, sodium, potassium, calcium, magnesium, ammonium, mono-, di-, tri- or tetra-C_1-C_4alkylammonium or ammonium that is di- or tri-substituted by a mixture of C_1-C_4alkyl and C_1-C_4hydroxyalkyl groups, or D may also be a group of formula:



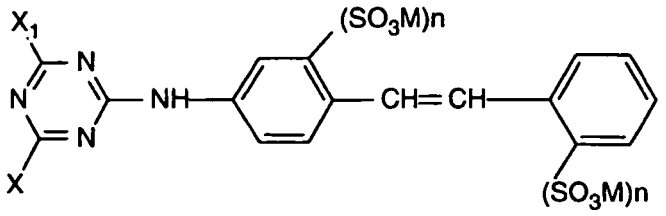
in which M has its previous significance and n is 0 or 1, provided that at least one SO_3M group is present, or the formula:



in which X, X_1 and M have their previous significance.

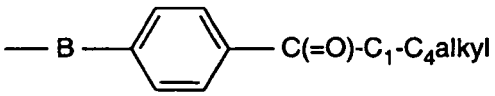
2. A compound according to claim 1 in which M is sodium.

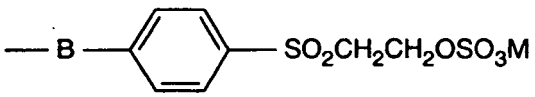
3. A compound according to claim 1 in which the compound of formula (1) has the formula:



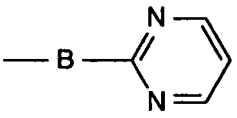
(13)

in which M and n are as defined in claim 1, provided that at least one SO_3M group is present, X is F or Cl and X_1 is F, Cl or a group having one of the formulae:





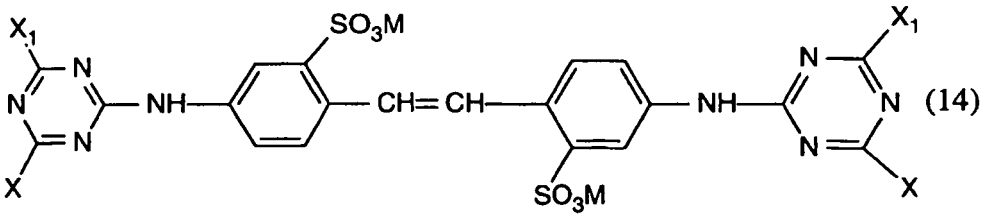
or



in which B and M are each as defined in claim 1.

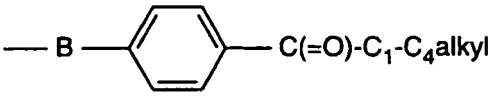
4. A compound according to claim 3 in which X is Cl, B is NH and M is Na.

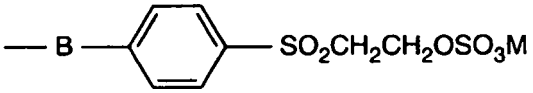
5. A compound according to claim 1 in which the compound of formula (1) has the formula:



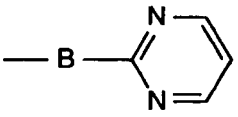
(14)

in which each X is the same and is F or Cl and each X_1 is the same and is F, Cl or a group having the formula:





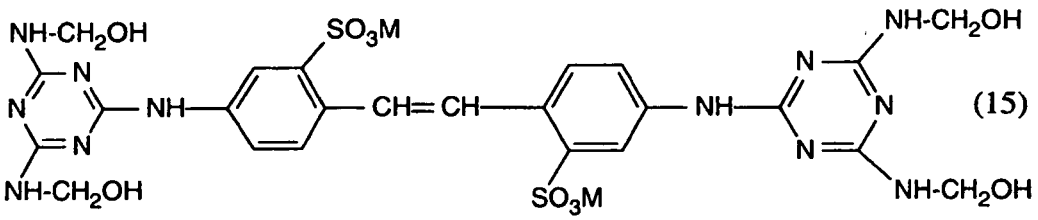
or



in which B and M are each as defined in claim 1.

6. A compound according to claim 5 in which each X is Cl, B is NH and M is Na.

7. A compound according to claim 1 in which the compound of formula (1) has the formula:



(15)

in which M is as defined in claim 1.

8. A compound according to claim 7 in which M is Na.

9. A process for the production of a compound of formula (1) comprising reacting a compound of formula A-$(BH)_m$ in which A, B and m are as defined in claim 1, with m moles of a compound L-D, in which D is as defined in claim 1 and L is a leaving group or atom.

10. A process according to claim 9 in which L is a halogen atom.

11. A process according to claim 10 in which L is a chlorine atom.

12. A method for the treatment of a textile fibre material, comprising treating the textile fibre material with 0.05 to 3.0% by weight, based on the weight of the textile fibre material, of one or more compounds having the formula (1) as defined in claim 1.

13. A method according to claim 12 in which the textile fibres treated are cotton, viscose, flax, rayon, linen, wool, mohair, cashmere, angora, silk, polyester, polyamide or polyacrylonitrile fibres.

14. A method according to claim 13 in which the textile fibres treated are cotton fibres.

15. A method according to any of claims 12 to 14 in which the textile fibres treated have a density of less than 200 g/m^2 and have not been previously dyed in deep shades.

16. A method according to any of claims 12 to 15 in which the compound of formula (1) is only sparingly soluble in water and is applied in dispersed form.

17. A method according to any of claims 12 to 16 in which, in addition to the compound of formula (1), a minor proportion of one or more adjuvants is also employed.

18. A method according to claim 17 in which the adjuvants are emulsifiers, perfumes, colouring dyes, opacifiers, optical whitening agents, bactericides, nonionic surfactants, fabric care ingredients, anti-gelling agents or corrosion inhibitors.

19. A method according to claim 18 in which the amount of each of the adjuvants does not exceed 1 % by weight on the treated fibre.

20. A method of increasing the SPF rating of textile fibre material, comprising treating the textile fibre material with 0.05 to 3.0% by weight, based on the weight of the textile fibre material, of one or more compounds having the formula (1) as defined in claim 1.

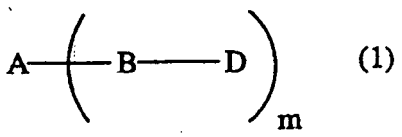
21. A method according to claim 20 whereby the tear resistance and/or lightfastness of the treated textile fibre material are also improved.

22. A textile fabric produced from a fibre treated according to a method as claimed in any of claims 12 to 21.

23. An article of clothing produced from a textile fabric according to claim 22.

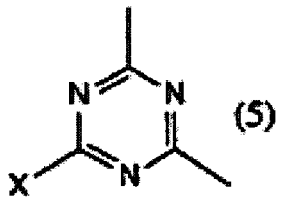
Patentansprüche

1. Verbindung der Formel:



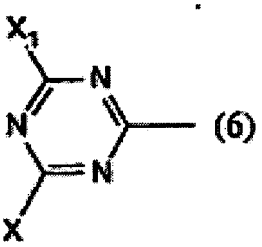
(1)

worin m 1 oder 2 ist; A ein Rest ist, gewählt aus solchen der Formeln:



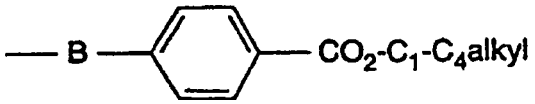
(5)

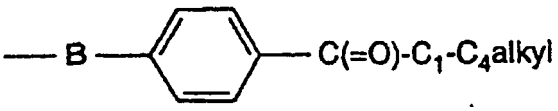
oder

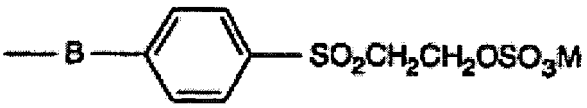


(6)

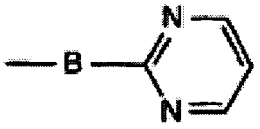
X bedeutet F, Cl oder $NHCH_2OH$ und X_1 bedeutet F, Cl, $NHCH_2OH$ oder eine Gruppe der Formel:







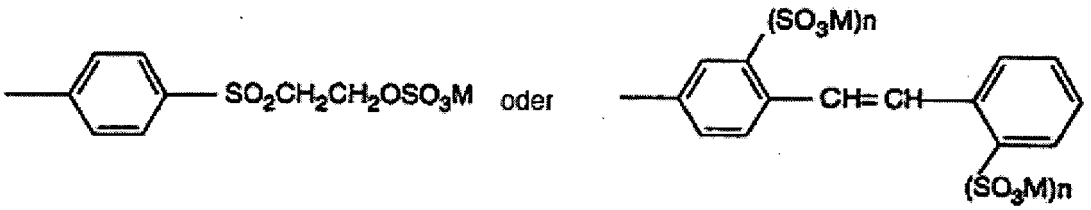
oder



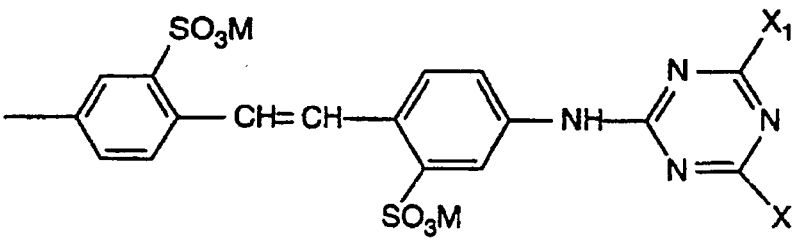
;

B bedeutet -O-, -NH- oder $-SO_2-$; und

D eine Gruppe mit einer der Formeln ist:
CH_2-C(=O)-NH(CH_2OH), CH_2-C(=O)-N(CH_2OH_2) oder CH_2CH_2-OSO_3M, worin M Wasserstoff, Natrium, Kalium, Calcium, Magnesium, Ammonium, Mono-, Di-, Tri-, oder Tetra-C_1-C_4alkylammonium oder Ammonium ist, welches di- oder tri-substituiert ist durch eine Mischung aus C_1-C_4alkyl- und C_1-C_4hydroxyalkylgruppen, oder D ebenso eine Gruppe der Formel sein kann:



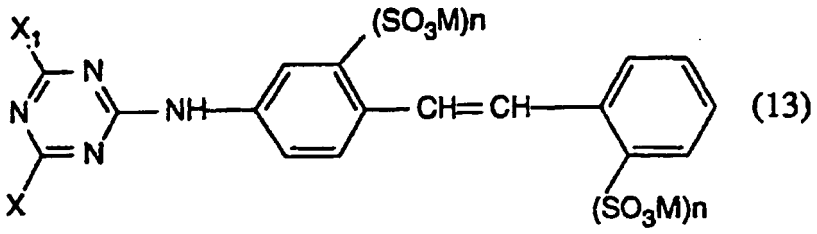
worin M die vorangehende Bedeutung hat und n 0 oder 1 ist, mit der Maßgabe, dass mindestens eine SO_3M-Gruppe vorliegt, oder der Formel:



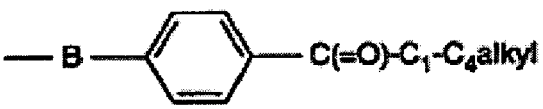
worin X, X_1 und M die vorangehende Bedeutung haben.

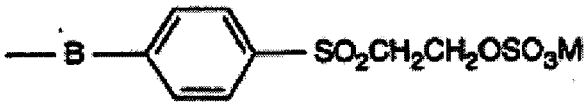
2. Verbindung nach Anspruch 1, worin M Natrium ist.

3. Verbindung nach Anspruch 1, wobei die Verbindung der Formel (1) die Formel aufweist:

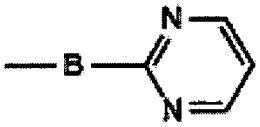


worin M und n wie in Anspruch 1 definiert sind, mit der Maßgabe, dass mindestens eine SO_3M-Gruppe vorliegt, X F oder Cl ist und X_1 F, Cl oder eine Gruppe mit einer der Formeln ist:





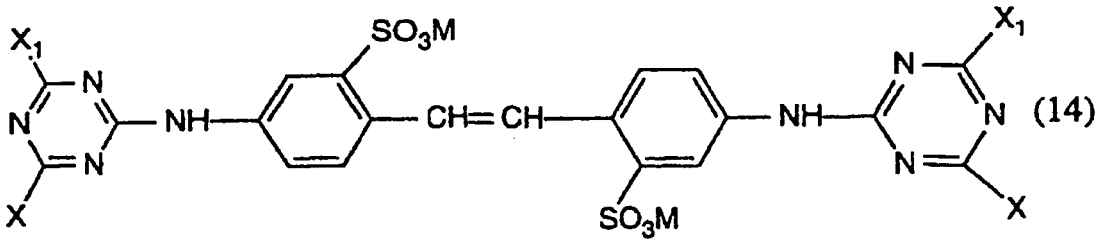
oder



worin B und M wie in Anspruch 1 definiert sind.

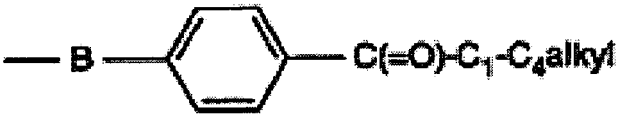
4. Verbindung nach Anspruch 3, worin X Cl ist, B NH ist und M Na ist.

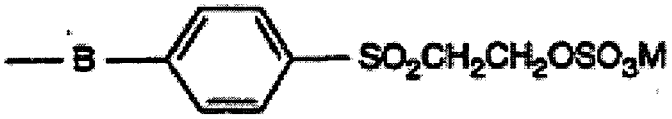
5. Verbindung nach Anspruch 1, wobei die Verbindung der Formel (1) die Formel aufweist:



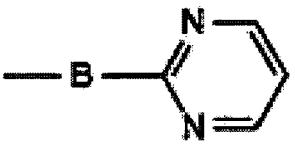
(14)

worin jedes X gleich ist und F oder Cl ist, und jedes X_1 gleich ist und F, Cl oder eine Gruppe der Formel ist:





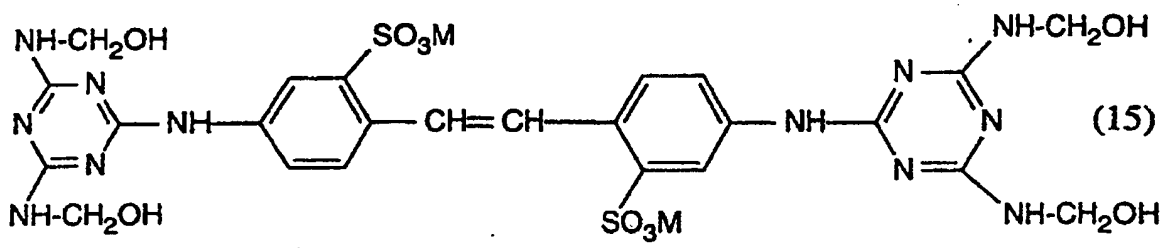
oder



worin B und M wie in Anspruch 1 definiert sind.

6. Verbindung nach Anspruch 5, wobei jedes X Cl ist, B NH ist und M Na ist.

7. Verbindung nach Anspruch 1, wobei die Verbindung der Formel (1) die Formel aufweist:



(15)

worin M wie in Anspruch 1 definiert ist.

8. Verbindung nach Anspruch 7, wobei M Na ist.

9. Verfahren zur Herstellung einer Verbindung der Formel (1), umfassend das Umsetzen einer Verbindung der Formel $A-(BH)_m$, worin A, B und m wie in Anspruch 1 definiert sind, mit m Molen einer Verbindung L-D, worin D wie in Anspruch 1 definiert ist und L eine Abgangsgruppe oder ein Abgangsatom ist.

10. Verfahren nach Anspruch 9, wobei L ein Halogenatom ist.

11. Verfahren nach Anspruch 10, wobei L ein Chloratom ist.

12. Verfahren zur Behandlung eines Textilfasermaterials, umfassend das Behandeln des Textilfasermaterials mit 0,05 bis 3,0 Gew.-%, bezogen auf das Gewicht des Textilfasermaterials, an einer oder mehreren Verbindungen der Formel (1) wie in Anspruch 1 definiert.

13. Verfahren nach Anspruch 12, wobei die zu behandelnden Textilfasern Baumwoll-, Viskose-, Flachs-, Rayon-, Leinen-, Woll-, Mohair-, Cashmere-, Angora-, Seide-, Polyester-, Polyamid- oder Polyacrylnitrilfasern sind.

14. Verfahren nach Anspruch 13, wobei die zu behandelnden Textilfasern Baumwollfasern sind.

15. Verfahren nach irgendeinem der Ansprüche 12 bis 14, wobei die zu behandelnden Textilfasern eine Dichte von weniger als 200g/m^2 aufweisen und nicht vorher mit tiefen Farbtönungen gefärbt worden sind.

16. Verfahren nach irgendeinem der Ansprüche 12 bis 15, wobei die Verbindung der Formel (1) nur beschränkt wasserlöslich ist und in dispergierter Form aufgebracht wird.

17. Verfahren nach irgendeinem der Ansprüche 12 bis 16, wobei zusätzlich zu der Verbindung der Formel (1) ebenso ein kleiner Anteil einer oder mehrerer Hilfsmittel eingesetzt wird.

18. Verfahren nach Anspruch 17, wobei die Hilfsmittel Emulgiermittel, Duftstoffe, färbende Farbstoffe, Trübungsmittel, optische Weißmacher, Bakterizide, nichtionische Tenside, Textilpflegebestandteile, Antigeliermittel oder Korrosionsinhibitoren sind.

19. Verfahren nach Anspruch 18, wobei die Menge jedes der Hilfsmittel 1 Gew.-% auf der behandelten Faser nicht überschreitet.

20. Verfahren zur Erhöhung der SPF-Bewertung von Textilfasermaterial, umfassend das Behandeln des Textilfasermaterials mit 0,05 bis 3,0 Gew.-% , bezogen auf das Gewicht des Textilfasermaterials, an einer oder mehreren Verbindungen der Formel (1) wie in Anspruch 1 definiert.

21. Verfahren nach Anspruch 20, wobei die Reißfestigkeit und/oder Lichtbeständigkeit des behandelten Textilfaserma-

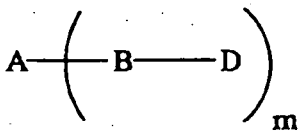
terials ebenso verbessert werden.

22. Textilstoff, hergestellt aus einer Faser, welche nach einem Verfahren gemäß mindestens einem der Ansprüche 12 bis 21 behandelt worden ist.

23. Bekleidungsartikel, hergestellt aus einem Textilstoff gemäß Anspruch 22.

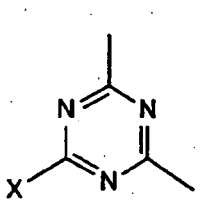
Revendications

1. Composé de formule :

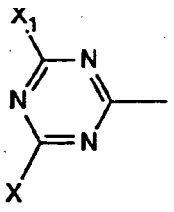


(1)

dans laquelle m vaut 1 ou 2 ; A représente un groupe choisi parmi ceux de formule :

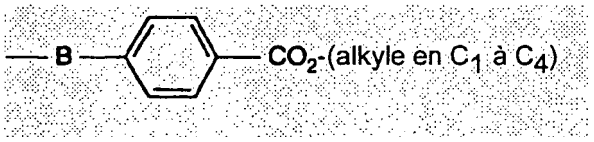


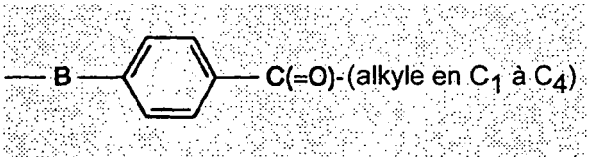
(5) ou

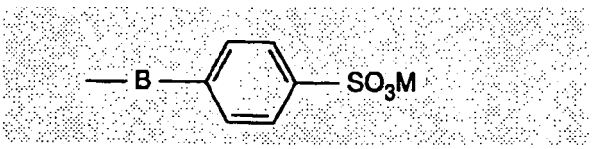


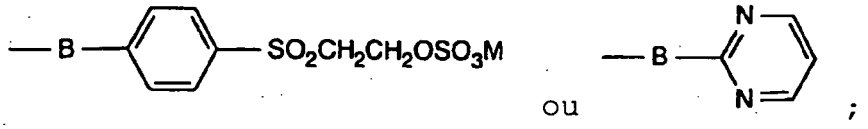
(6)

X représente un atome de fluor, de chlore ou un groupe $NHCH_2OH$ et X_1 représente un atome de fluor, de chlore, un groupe $NHCH_2OH$ ou un groupe de formule :

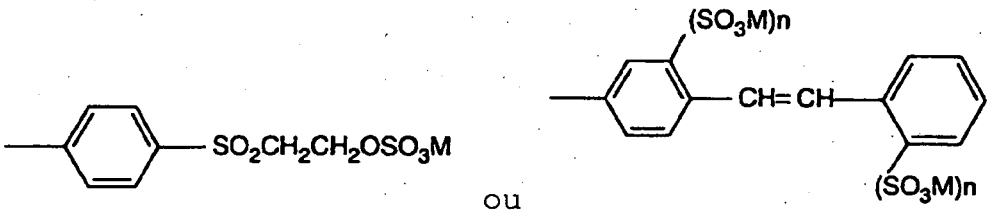




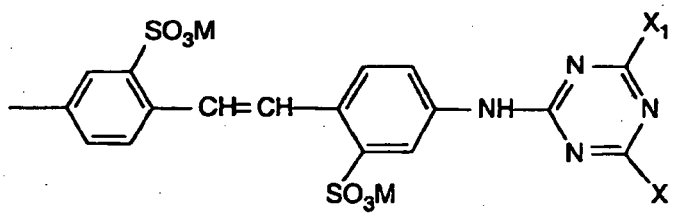




B représente -O-, -NH- ou -SO_2- ; et
D représente un groupe ayant l'une des formules : CH_2-C(=O)-NH(CH_2OH), CH_2-C(=O)-N(CH_2OH)$_2$ ou CH_2CH_2-OSO_3M dans laquelle M représente un atome d'hydrogène, de sodium, de potassium, de calcium, de magnésium, un groupe ammonium, mono-, di-, tri- ou tétra-(alkyle en C_1 à C_4)ammonium ou ammonium qui est di- ou tri-substitué par un mélange de groupes alkyle en C_1 à C_4 et hydroxyalkyle en C_1 à C_4, ou D peut également représenter un groupe de formule :



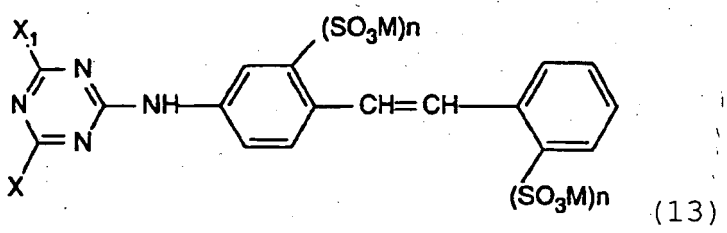
dans laquelle M a la signification précédente et n vaut 0 ou 1, à condition qu'au moins un groupe SO_3M soit présent, ou de formule :



dans laquelle X, X_1 et M ont la signification précédente.

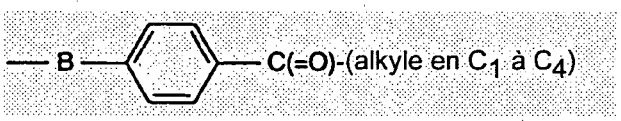
2. Composé selon la revendication 1, dans lequel M représente un atome de sodium.

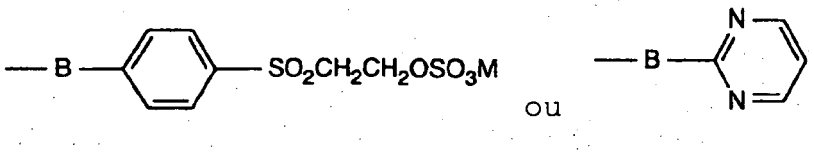
3. Composé selon la revendication 1, dans lequel le composé de formule (1) possède la formule :



(13)

dans laquelle M et n sont tels que défini dans la revendication 1, à condition qu'au moins un groupe SO_3M soit présent, X représente un atome de fluor ou de chlore et X_1 représente un atome de fluor, de chlore ou un groupe ayant l'une des formules :

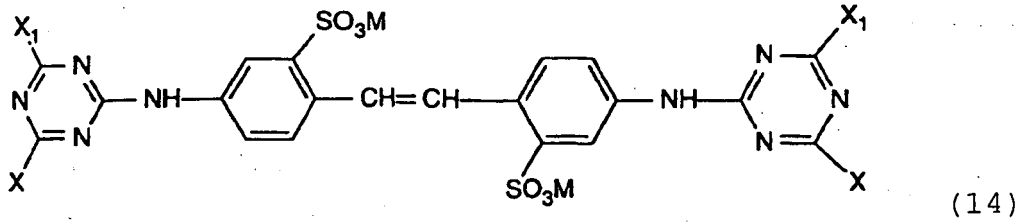




dans laquelle B et M sont chacun tels que défini dans la revendication 1.

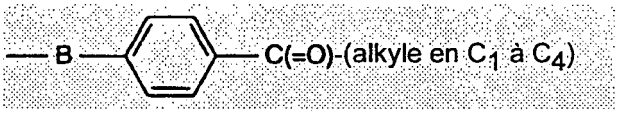
4. Composé selon la revendication 3, dans lequel X représente un atome de chlore, B représente un groupe NH et M représente un atome de sodium.

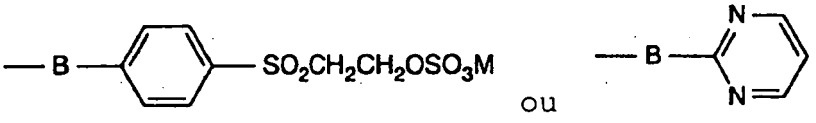
5. Composé selon la revendication 1, dans lequel le composé de formule (1) possède la formule :



(14)

dans laquelle tous les X sont identiques et représentent un atome de fluor ou de chlore et tous les X_1 sont identiques et représentent un atome de fluor, de chlore ou un groupe de formule :

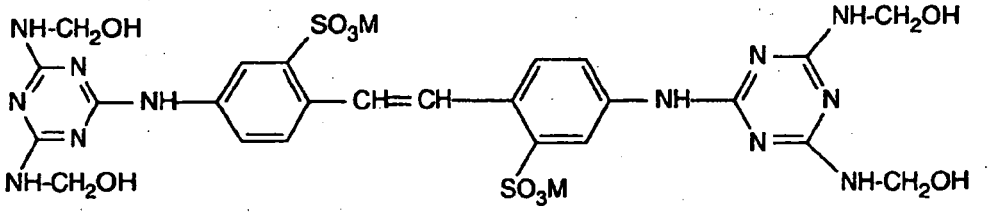




dans laquelle B et M sont chacun tels que défini dans la revendication 1.

6. Composé selon la revendication 5, dans lequel chaque X représente un atome de chlore, B représente un groupe NH et M représente un atome de sodium.

7. Composé selon la revendication 1, dans lequel le composé de formule (1) possède la formule :



(15)

dans laquelle M est tel que défini dans la revendication 1.

8. Composé selon la revendication 7, dans lequel M représente un atome de sodium.

9. Procédé de production d'un composé de formule (1) comprenant les étapes consistant à faire réagir un composé de formule $A-(BH)_m$, dans laquelle A, B et m sont tels que défini dans la revendication 1, avec m moles d'un composé L-D dans lequel D est tel que défini dans la revendication 1 et L représente un atome ou un groupe quittant.

10. Procédé selon la revendication 9, dans lequel L représente un atome d'halogène.

11. Procédé selon la revendication 10, dans lequel L représente un atome de chlore.

12. Procédé de traitement d'une matière de fibre textile, comprenant le traitement de la matière de fibre textile avec 0,05% à 3,0% en poids, par rapport au poids de la matière de fibre textile, d'un ou plusieurs composés de formule (1) tels que défini dans la revendication 1.

13. Procédé selon la revendication 12, dans lequel les fibres textiles traitées sont des fibres de coton, de viscose, de lin, de rayonne, de lin, de laine, de mohair, de cachemire, de poil angora, de soie, de polyester, de polyamide ou de polyacrylonitrile.

14. Procédé selon la revendication 13, dans lequel les fibres textiles traitées sont des fibres de coton.

15. Procédé selon l'une quelconque des revendications 12 à 14, dans lequel les fibres textiles traitées ont une densité inférieure à 200 g/m^2 et n'ont pas été préalablement teintes en coloris intenses.

16. Procédé selon l'une quelconque des revendications 12 à 15, dans lequel le composé de formule (1) n'est que modérément hydrosoluble et est mis en oeuvre sous forme dispersée.

17. Procédé selon l'une quelconque des revendications 12 à 16 dans lequel, en plus du composé de formule (1), une proportion mineure d'un ou plusieurs adjuvants est également utilisée.

18. Procédé selon la revendication 17, dans lequel les adjuvants sont des émulsifiants, des parfums, des colorants, des opacifiants, des azurants optiques, des bactéricides, des tensio-actifs non ioniques, des ingrédients pour l'entretien du tissu, des agents antigélifiants ou des inhibiteurs de corrosion.

19. Procédé selon la revendication 18, dans lequel la quantité de chacun des adjuvants ne dépasse pas 1% en poids de la fibre traitée.

20. Procédé permettant d'augmenter l'indice de protection solaire d'une matière de fibre textile comprenant le traitement de la matière de fibre textile avec 0,05% à 3,0% en poids, par rapport au poids de la matière de fibre textile, d'un ou plusieurs composés de formule (1) tels que défini dans la revendication 1.

21. Procédé selon la revendication 20, dans lequel la résistance au déchirement et/ou la solidité à la lumière de la matière de fibre textile traitée sont également améliorées.

22. Tissu textile produit à partir d'une fibre traitée selon un procédé tel que défini dans l'une quelconque des revendications 12 à 21.

23. Article d'habillement produit à partir d'un tissu textile selon la revendication 22.