

The present invention relates to storage-stable, concentrated, aqueous whitener formulations and to a process for their preparation and to the use thereof.

At the present time fluorescent whitening agents are preferably marketed in the form of aqueous solutions. Such formulations are prepared by suspending the moist filter cake or also the dry powder of the fluorescent whitening agent in water. Dispersants and thickeners are added to this suspension to increase homogeneity, wettability and stability. Besides these auxiliaries, an electrolyte is frequently also added. However, the auxiliaries which have been used up to now have not been able to prevent sedimentation of the whitening agent over a long period of time.

Surprisingly, it has now been found that storage-stable, concentrated, aqueous whitener formulations are obtained by adding to the aqueous suspension of the whitening agent minor amounts of an anionic polysaccharide. Such suspensions form hardly any deposits during storage. In addition to the good sedimentation properties, the suspensions remain homogeneous during storage.

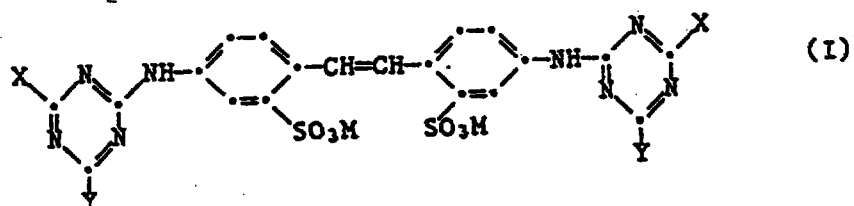
The formulations of this invention comprise

- a) 10 to 60 % by weight, based on the total weight of the whitener formulation, of an anionic fluorescent whitening agent,
- b) 0.01 to 1 % by weight, based on the total weight of the whitener formulation, of an anionic polysaccharide, and
- c) water, and optionally
- d) auxiliaries.

These formulations are in the form of suspensions.

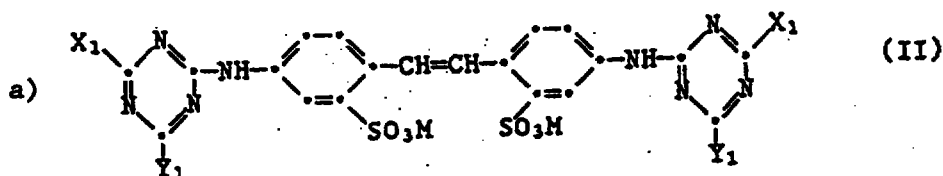
Preferably, such formulations contain anionic fluorescent whitening agents which contain at least one sulfonic acid radical.

The whitening agents are, for example, those of the triazine series of the formula:

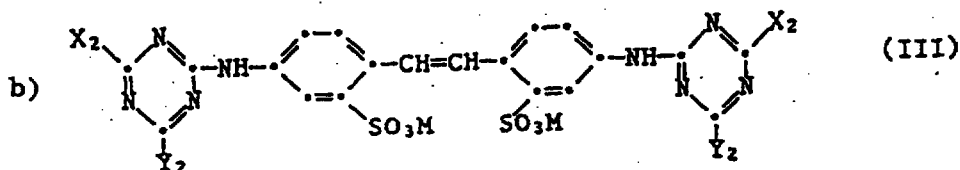


in which X and Y may be identical or different and are a secondary or tertiary amine radical or a mono- or disubstituted alkoxy group, and M is a hydrogen atom or a salt-forming cation.

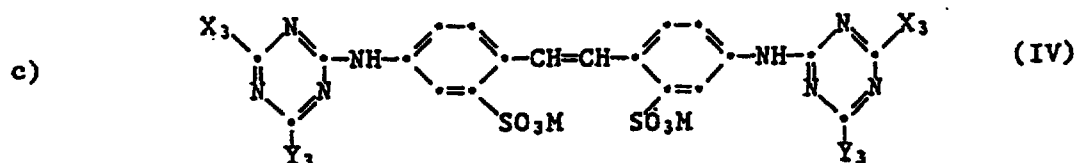
Particularly interesting whitening agents are those of the formula:



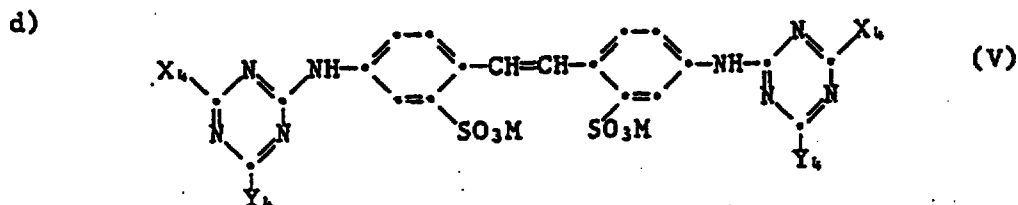
in which X₁ and Y₁ may be identical or different and are a phenylamino group which may be monosubstituted or disubstituted by alkyl radicals of 1 or 2 carbon atoms, the morpholino group, an alkylamino group of 1 to 4 carbon atoms which may be substituted by hydroxyl radicals, an alkoxy group of 1 to 4 carbon atoms, and M is hydrogen or a salt-forming cation.



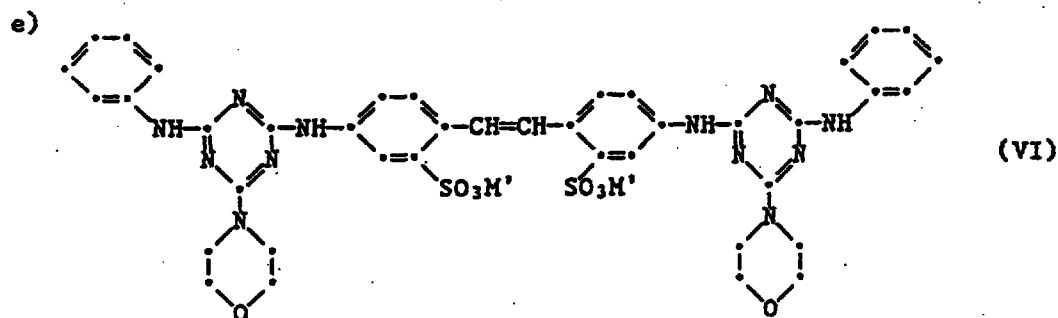
in which X₂ and Y₂ may be identical or different and are the phenylamino group, the morpholino group, an alkylamino group of 1 to 4 carbon atoms which may be substituted by hydroxyl radicals, and M is hydrogen or a salt-forming cation.



in which X_3 and Y_3 may be identical or different and are the phenylamino group, a morpholino group, the N-methyl-N-ethanolamino radicals, and M is hydrogen or a salt-forming cation.

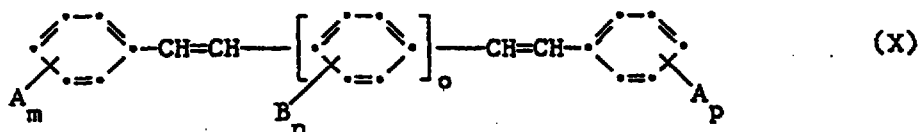


in which X_4 and Y_4 may be identical or different and are the morpholino group or the N-methyl-N-ethanolamino group, and M is hydrogen or a salt-forming cation.



in which M' is an alkali metal ion, where in the case of this fluorescent whitening agent the formulation contains 4 to 25 % by weight, based on the total weight of the suspension, of a strong electrolyte.

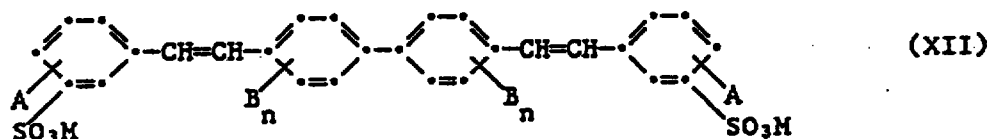
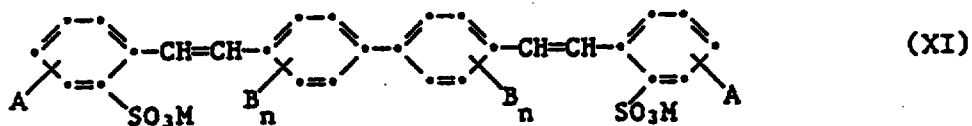
It is also possible to use fluorescent whitening agents of the distilbene series, for example compounds of the formula



in which A is a sulfonic acid radical, hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, or halogen, and B is hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkoxy or halogen, with the proviso that at least one substituent A is a sulfonic acid radical and m, n, o, and p are each independently of one another 1 or 2.

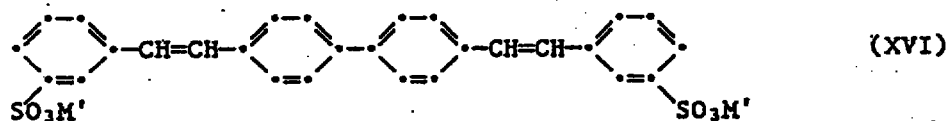
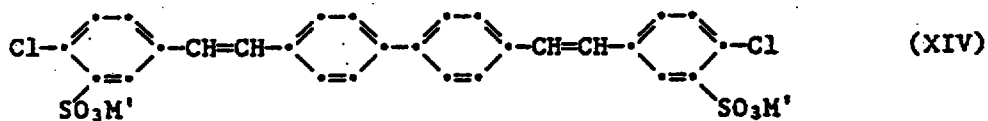
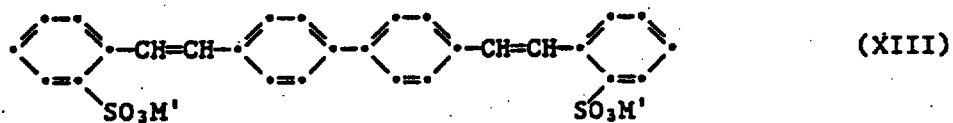
Preferred compounds are those in which o is 2.

Especially preferred compounds are those of the formula



where A, B and n are as defined above and M is a salt-forming cation.

Among these compounds, compounds of practical interest are those of the formulae



where M' is an alkali metal ion.

Suitable halogens are in particular fluorine, chlorine and bromine, chlorine being especially preferred, however.

Suitable C₁-C₄alkyl radicals are unbranched and branched alkyl radicals such as methyl, ethyl, n- and isopropyl, n-, sec- and tert-butyl. These C₁-C₄alkyl radicals may themselves be substituted by, for example, aryl (phenyl or naphthyl), C₁-C₄alkyl, C₁-C₄alkoxy, OH- or CN groups.

Examples of salt-forming cations M are alkali metal ions, ammonium ions or amine salt ions. Preferred amine salt ions are those of the formula $H^+NR_8R_9R_{10}$, in which R_8 , R_9 and R_{10} are each independently of one another hydrogen, alkyl, alkenyl, hydroxyalkyl, cyanoalkyl, haloalkyl or phenylalkyl, or in which R_8 and R_9 , when taken together, complete a 5- to 7-membered saturated nitrogen-containing heterocycle which may additionally contain a nitrogen or oxygen atom as ring member, for example a piperidine, piperazine, pyrrolidine, imidazoline or morpholine ring, and R^{10} is hydrogen.

Preferred distyrylbiphenyl compounds of the formula (X) are those in which the cation M is an alkali metal ion, an ammonium ion or an amine ion, potassium and sodium being especially important for practical reasons.

The anionic polysaccharides which may be used according to the invention belong to the group of the modified polysaccharides which can be derived from cellulose. They may be etherified cellulose, but also heteropolysaccharides which contain in the side chains further monosaccharides such as mannose and glucuronic acid.

The anionic polysaccharide is, for example, sodium carboxymethyl cellulose and, particularly preferably, xanthane.

The amount of polysaccharide is preferably from 0.01 to 1 % by weight, a range of from 0.05 to 0.5 % by weight being particularly preferred, based on the total weight of the formulation. However, these ranges may be exceeded in the case of very highly concentrated formulations or formulations of very low concentration.

The formulation may contain auxiliaries, for example electrolytes, preservatives such as chloroacetamide or aqueous formaldehyde solution, and fragrances.

The electrolyte may be sodium chloride, sodium sulfate, sodium carbonate or one of the corresponding potassium salts, or else mixtures of these substances. The amount of electrolyte may be from 0.1 to 25 % by weight, based on the total weight of the formulation, preferably from 0.1 to 20 % by weight.

The formulations of this invention are prepared by mixing the moist filter cake or also the dry powder of an anionic fluorescent whitening agent which preferably contains at least one sulfonic acid radical, in an amount of 10-60 % by weight, based on the total weight of the formulation, with 0.01-1 % by weight of anionic polysaccharide and water, and homogenizing the formulations.

The desired content of anionic fluorescent whitening agent in the suspension can be adjusted either by addition of water, aqueous electrolyte, suspension or further dry powder to the moist filter cake. This adjustment can be made before, during or after addition of the anionic polysaccharide. The amount of anionic fluorescent whitening agent is advantageously 10 to 60 % by weight, preferably 15 to 40 % by weight, based on the weight of the suspension.

The suspension is then mixed with the anionic polysaccharide until it is homogeneous.

The formulation can be incorporated into a detergent composition, for example by allowing the required amount of suspension to flow from a container into a mixing device which contains a suspension of the detergent composition or surfactant.

Accordingly, the present invention also relates to a process for the preparation of a detergent composition and to the detergent composition so obtained, which comprises mixing a suspension of surfactants customarily employed for detergents with a whitener suspension of this invention and drying the formulation so obtained. The resultant suspensions are advantageously dried by subjecting them to a spray drying process.

The whitener formulation of this invention can also be used for the preparation of liquid detergent compositions.

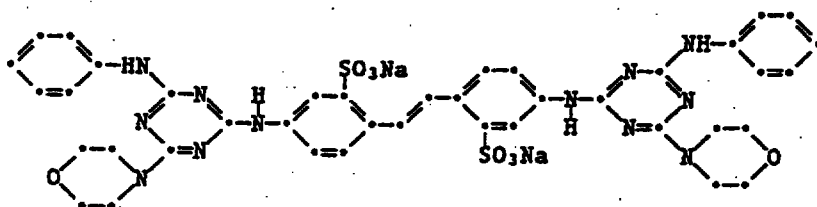
The invention is illustrated by the following non-limiting Examples in which parts are by weight.

Example 1

0.075 part of xanthane
0.2 part of chloroacetamide
1.3 parts of sodium sulfate, and
5 parts of sodium chloride
are dissolved in
61 parts of water.

To this solution are added, with stirring

32.5 parts of moist filter cake containing 12 parts of water,
0.5 part of sodium chloride and 20 parts of the fluorescent
whitening agent



(100)

and the formulation is homogenized.

The white whitener formulation has a viscosity of 108 cP (Haake VT 18, MVII, 22°C, D = 42 sec⁻¹) and forms no deposits after standing for two months at -5°C, at room temperature, and 40°C.

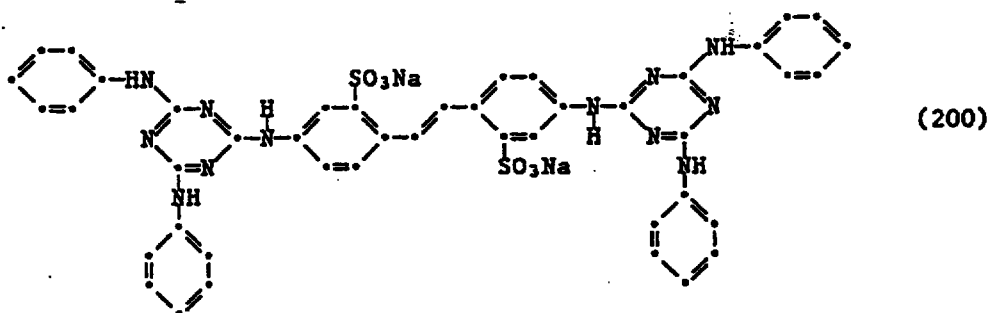
Example 2

As in Example 1,

0.075 part of xanthane
0.2 part of chloroacetamide
1.3 parts of sodium sulfate, and
5 parts of sodium chloride
are dissolved in
72 parts of water.

To this solution are added

21.5 parts of dry filter cake containing 1.5 parts of water and
20 parts of the fluorescent whitening agent



and the formulation is homogenized with stirring.

The properties of the whitener formulation correspond to those of the formulation of Example 1.

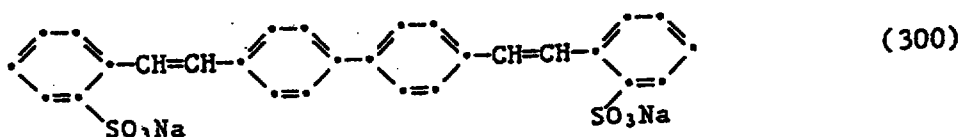
Example 3

As in Example 1,

- 0.1 part of chloroacetamide
- 3.0 parts of sodium chloride
- 1.0 part of tallow fatty alcohol (11 mol of ethylene oxide),
and
- 0.3 part of xanthane
are dissolved in
- 37.5 parts of water.

To this solution are added

- 58.1 parts of moist filter cake containing 56 parts of water and
44 parts of the fluorescent whitening agent



and the formulation is homogenized with stirring.

The whitener formulation forms no deposits after standing for several months at room temperature and at 40°C.

Example 4

As in Example 3,

0.1 part of chloroacetamide
0.1 part of xanthane, and
3.0 parts of sodium chloride
are dissolved in
5.9 parts of water.

To this solution are added

90.9 parts of moist filter cake containing 56 parts of water and
44 parts of the fluorescent whitening agent of the formula
(300), and the formulation is homogenized with stirring.

The whitener formulation is storage-stable at room temperature and
at 40°C.

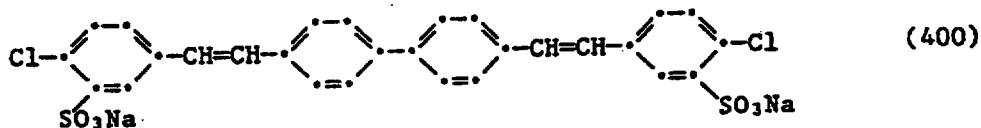
Example 5

As in Example 1,

0.5 part of 37% aqueous formaldehyde, and
2.0 parts of sodium carboxymethylcellulose
are dissolved in
33.5 parts of water.

To this solution are added

64.5 parts of the moist filter cake containing 53.5 parts of
water and 46.5 parts of the fluorescent whitening agent of
the formula



and the formulation is homogenized with stirring.

The suspension forms no deposits after standing for 3 months at room
temperature.

Example 6

As in Example 3,

0.1 part of chloroacetamide, and

0.1 part of xanthane

are dissolved in

8.9 parts of water.

To this solution are added

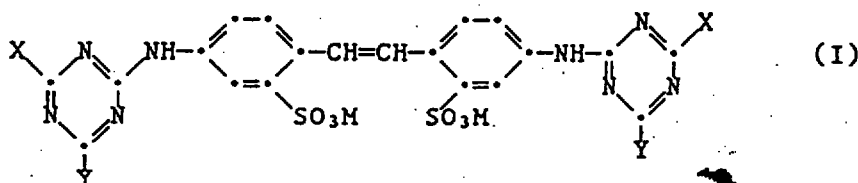
90.9 parts of the moist filter cake containing 56 parts of water and
44 parts of the fluorescent whitening agent of the formula
(300), and the formulation is homogenized with stirring.

The whitener formulation is storage-stable at room temperature and
at 40°C.



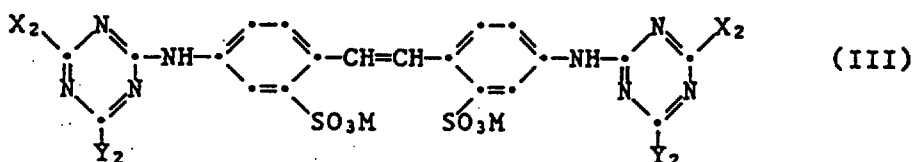
Patent claims

1. A storage-stable whitener formulation which comprises
 - a) 10 to 60 % by weight, based on the total weight of the whitener formulation, of an anionic fluorescent whitening agent,
 - b) 0.01 to 1 % by weight, based on the total weight of the whitener formulation, of an anionic polysaccharide, and
 - c) water.
2. A storage-stable whitener formulation according to claim 1, 15, 16 or 17, which contains 15-40 % by weight of whitening agent.
3. A storage-stable whitener formulation according to claim 1, which contains an electrolyte.
4. A storage-stable whitener formulation according to claim 1, which contains 2-25 % of electrolyte.
5. A storage-stable whitener formulation according to claim 1, 15, 16 or 17, which contains a fluorescent whitening agent of the formula



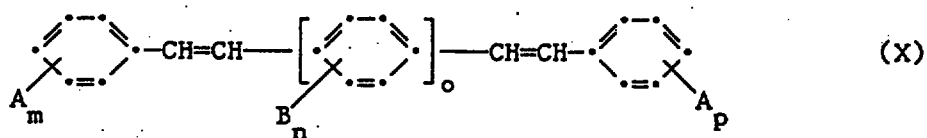
in which X and Y may be identical or different and are a secondary or tertiary amine radical or a mono- or disubstituted alkoxy group, and M is a hydrogen atom or a salt-forming cation.

6. A storage-stable whitener formulation according to claim 5, which contains a fluorescent whitening agent of the formula



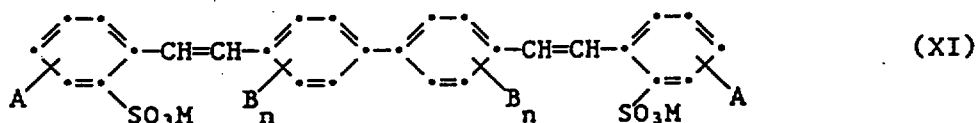
in which X_2 and Y_2 may be identical or different and are the phenylamino group, the morpholino group, an alkylamino group of 1 to 4 carbon atoms which may be substituted by hydroxyl radicals, and M is hydrogen or a salt-forming cation.

7. A storage-stable whitener formulation according to claim 1, 15, 16 or 17, which contains a fluorescent whitening agent of the formula



where A is a sulfonic acid radical, hydrogen, $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ alkoxy or halogen, and B is hydrogen, $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ alkoxy or halogen, with the proviso that at least one substituent A is a sulfonic acid radical and m, n, o and p are each independently of one another 1 or 2.

8. A storage-stable whitener formulation according to claim 7, which contains a fluorescent whitening agent of the formula

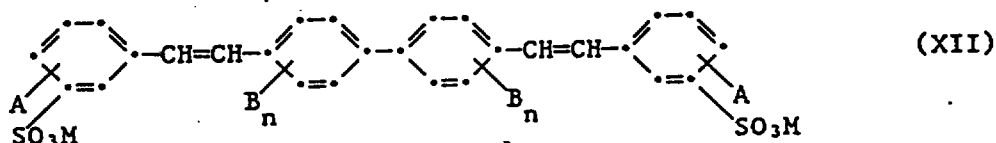


where A is a sulfonic acid radical, hydrogen, $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ alkoxy or halogen, and B is a sulfonic acid radical, hydrogen, $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ alkoxy or halogen, and each n independently of the other is 1 or 2, and M is a salt-forming cation.

9. A storage-stable whitener formulation according to claim 7, which

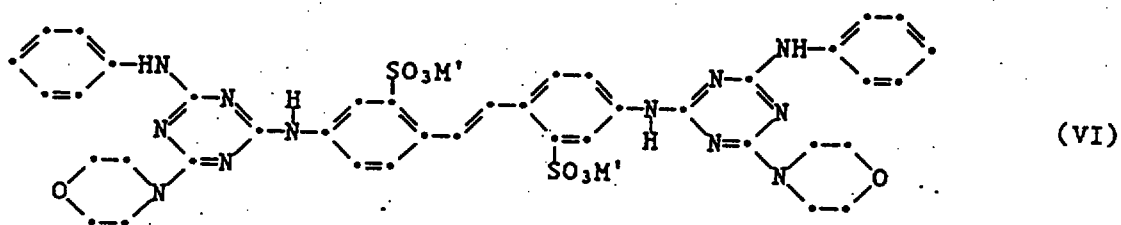


contains a fluorescent whitening agent of the formula

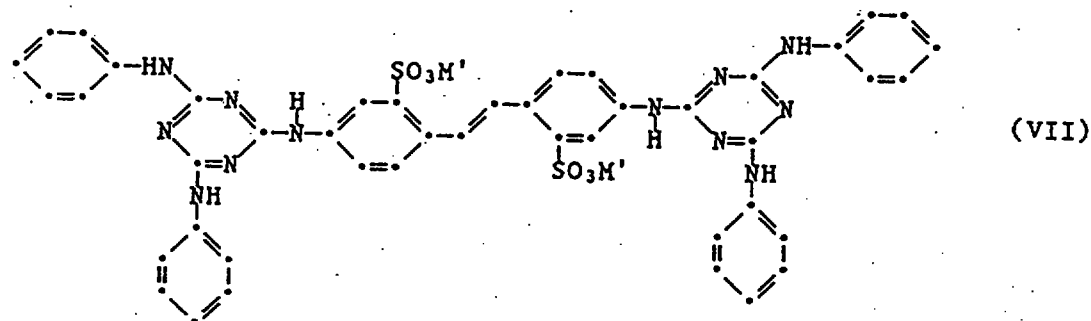


where A is a sulfonic acid radical, hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy or halogen, and B is hydrogen, C₁-C₄alkyl, C₁-C₄alkoxy or halogen, and each n independently of the other is 1 or 2, and M is a salt-forming cation.

10. A storage-stable whitener formulation according to claim 5, which contains a fluorescent whitening agent of the formula

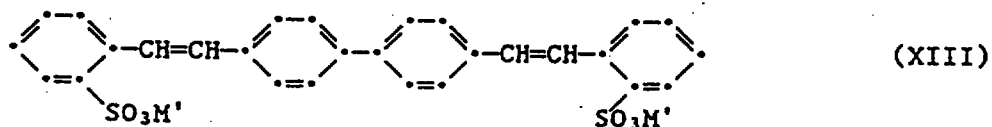


or

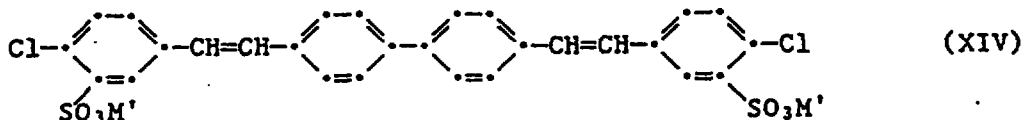


where M' is an alkali metal ion.

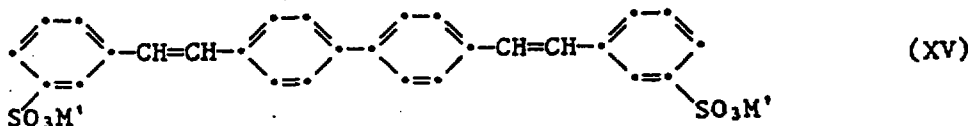
11. A storage-stable whitener formulation according to claim 7, which contains a fluorescent whitening agent of the formula



or



or



where M' is an alkali metal ion.

12. A storage-stable whitener formulation according to claim 1 or claim 15, wherein the anionic polysaccharide is xanthane.

13. A process for the preparation of a storage-stable whitener formulation according to claim 1 or claim 15, which comprises mixing the moist filter cake or the dry powder of the whitening agent according to claim 1 or claim 15 with an anionic polysaccharide and with water, and homogenizing the formulation.

14. The use of a storage-stable whitener formulation according to claim 1 or claim 15 for the preparation of a detergent composition.

15. A storage-stable whitener formulation which comprises

- a) 10 to 60 % by weight, based on the total weight of the whitener formulation, of an anionic fluorescent whitening agent,
- b) 0.01 to 1 % by weight, based on the total weight of the whitener formulation, of an anionic polysaccharide, and
- c) water, and optionally
- d) auxiliaries.

16. A storage-stable whitener formulation according to claim 15, wherein the auxiliary is an electrolyte or a mixture of electrolytes.

17. A storage-stable whitener formulation according to claim 16, which contains 0.1-25 % by weight of electrolyte.

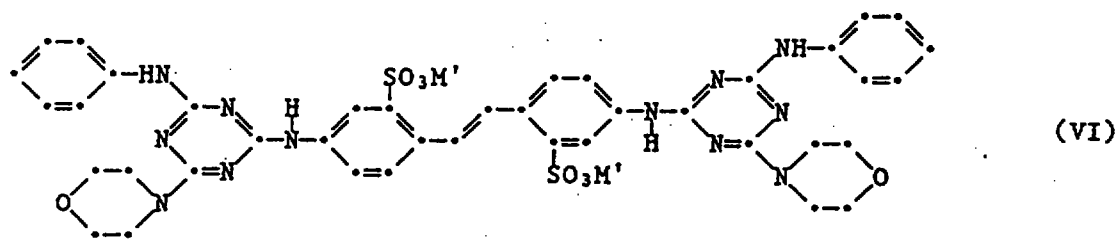


18. A storage-stable whitener formulation according to claim 1, 15, 16 or 17, wherein the anionic polysaccharide is a modified polysaccharide which can be derived from cellulose.

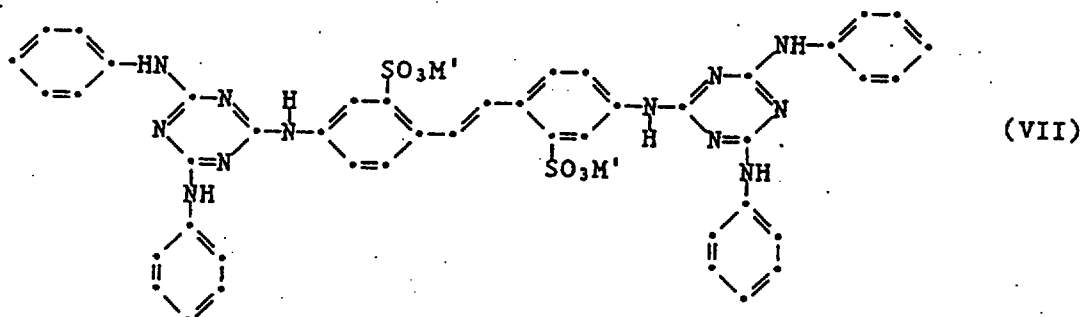
19. A storage-stable whitener formulation according to claim 18, wherein the modified polysaccharide is an etherified cellulose or a heteropolysaccharide having the basic structure of cellulose.

20. A storage-stable whitener formulation according to claim 15, which comprises

a) 10 to 60 % by weight, based on the total weight of the whitener formulation, of an anionic fluorescent whitening agent of the formula



or



where M' is an alkali metal ion,

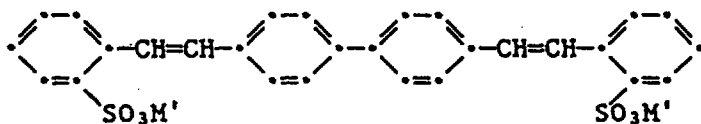
b) 0.01 to 1 % by weight of xanthane, based on the total weight of the whitener formulation,

c) water, and optionally

d) an electrolyte or a mixture of electrolytes.

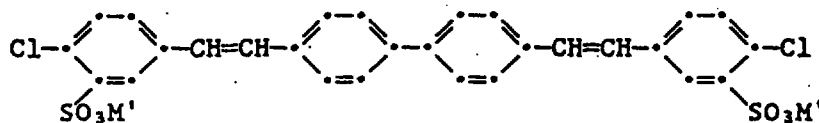
21. A storage-stable whitener formulation according to claim 15, which comprises

a) 10 to 60 % by weight, based on the total weight of the whitener formulation, of an anionic fluorescent whitening agent of the formula



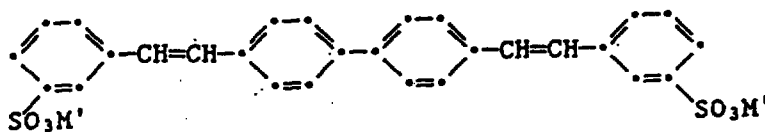
(XIII)

or



(XIV)

or



(XV)

where M' is an alkali metal ion,

b) 0.01 to 1 % by weight of xanthane, based on the total weight of the whitener formulation,

c) water, and optionally

d) an electrolyte or a mixture of electrolytes.