

19



Europäisches Patentamt
European Patent Office
Office européen des brevets

11 Publication number:

**0 376 893
A2**

12

EUROPEAN PATENT APPLICATION

21 Application number: **89810985.5**

51 Int. Cl.⁵: **C11D 3/42**

22 Date of filing: **27.12.89**

30 Priority: **30.12.88 DE 3844341**

43 Date of publication of application:
04.07.90 Bulletin 90/27

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

71 Applicant: **SANDOZ AG**
Lichtstrasse 35
CH-4002 Basel(CH)
84 **BE CH FR GB IT LI NL**

Applicant: **SANDOZ-PATENT-GMBH**
Humboldtstrasse 3
D-7850 Lörrach(DE)
84 **DE**

72 Inventor: **Chavannes, Jean-Pierre**
2 rue de Montreux
F-68300 Saint-Louis(FR)
Inventor: **Forrer, Rolf-Heinz**
Leimgrubenweg 1
CH-4102 Binningen(CH)

54 **Liquid laundry detergent compositions containing optical brighteners.**

57 Liquid laundry detergent with the usual components and optical brighteners of the formulae indicated in claim 1 are storage stable compositions and the optical brighteners have nevertheless sufficient substantivity to the fibres of the substrate to be washed.

EP 0 376 893 A2

LIQUID LAUNDRY DETERGENT COMPOSITIONS CONTAINING OPTICAL BRIGHTENERS

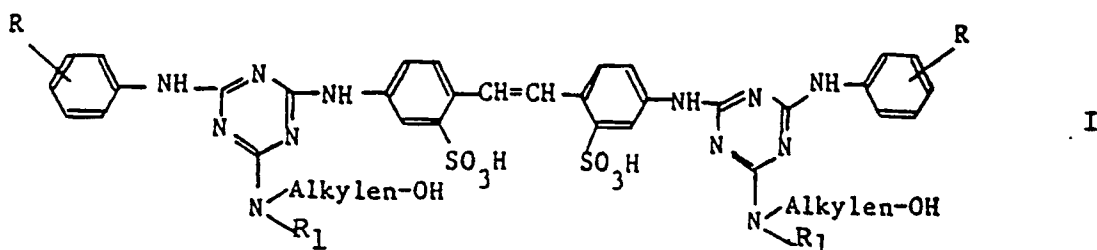
The invention relates to liquid laundry detergent compositions containing optical brighteners.

The use of optical brighteners in laundry detergent compositions has been known for a long time. In liquid compositions in general, optical brighteners with poor water solubility are used as dispersions because such products should have enough substantivity, which means that their affinity to the fibres of the substrate that is to be washed, should be high enough in order not to be washed out immediately. The use of such products, however, has the disadvantage that the detergent compositions have a poor storage stability, that is to say that the optical brightener will precipitate. If, on the other hand, optical brighteners were to be used which are more soluble in water, these products would have an insufficient substantivity to the fibres of the substrate to be washed.

It has been found that when using optical brighteners of a specific chemical structure which are water soluble, laundry detergent compositions with sufficient storage stability can be obtained.

Similar optical brighteners have been used in liquid detergent compositions as described in US Patent 4,233,167 and in European patent published application no. 106407. The problem to solve in these known detergent compositions was to find optical brighteners which would not counteract the effect of cationic softeners and would not provoke these softeners to be deposited on fabrics as a yellow film (USP 4,233,167) or optical brighteners which would not form insoluble complexes with the cationic surfactants contained in detergent compositions. The preferred compounds mentioned in these patent specifications do not have the desired substantivity.

The invention provides a liquid laundry detergent composition containing one or more optical brighteners of formula I



in alkali salt or alkyl-, hydroxyalkyl-, or ammonium salt form,

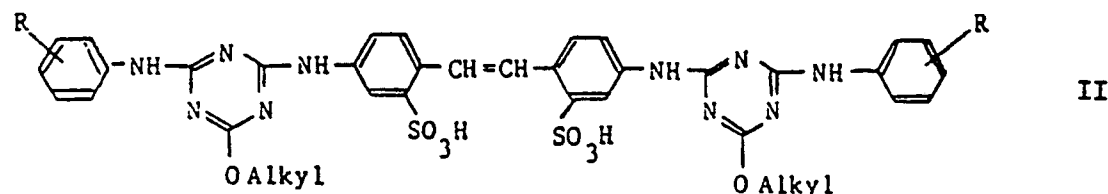
in which both groups R, independently, are hydrogen, halogen, C₁₋₂ alkyl, C₁₋₂ alkoxy, hydroxy or sulfonic acid groups,

each alkylene, independently, is an alkylene group with 2 or 3 carbon atoms,

each X, independently, is halogen, cyano, carboxamido, C₁₋₂ alkoxy or hydroxy,

and R₁ is hydrogen or Alkylene -X, with the proviso that if X = hydroxy, R should not be a sulfonic acid group in the para-position,

or containing optical brighteners of formula II

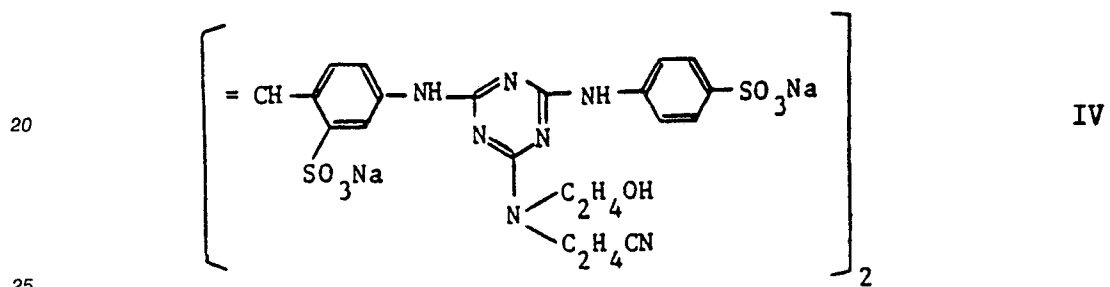
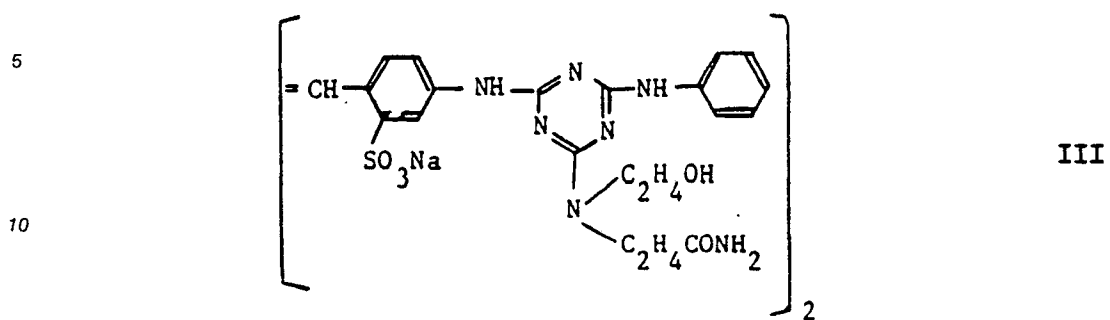


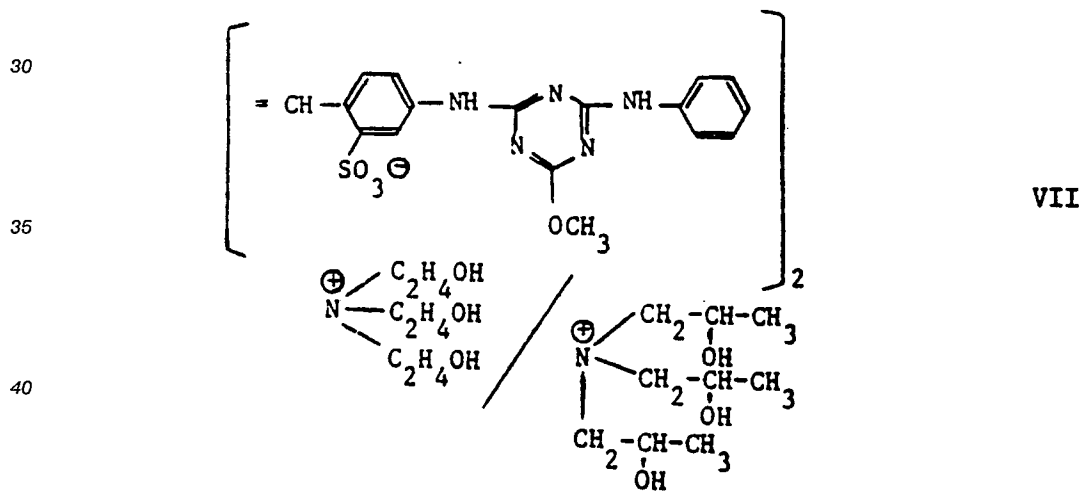
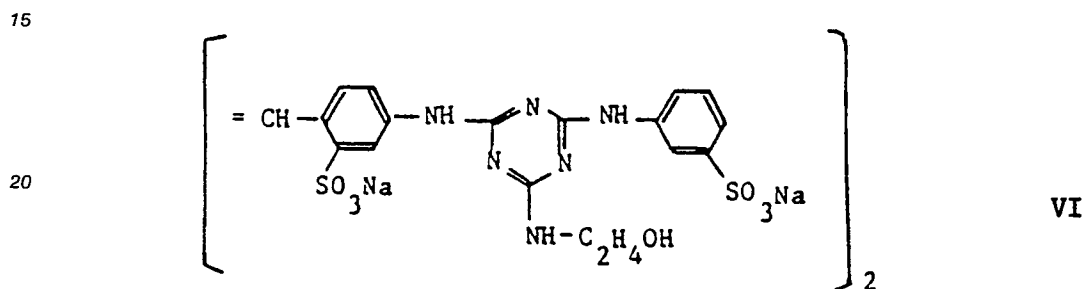
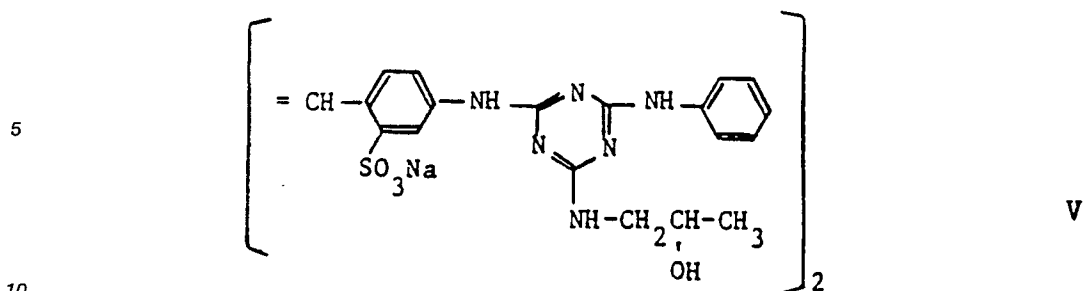
in which R is as defined above,

both alkyl groups, independently, have 1 or 2 carbon atoms, and both groups M are hydroxyalkylammonium cations.

Preferably, in formula I and II, both groups R are the same and both groups X are the same and the alkyl and alkylene groups have the same number of carbon atoms i.e. compounds of formulae I and II are preferably symmetrical. More preferably, in compounds of formula 1, X is other than hydroxy or R₁ is hydrogen. Especially preferred compounds have the structure of formulae III, IV, V, VI and/or VII. Most

preferred compound is the one of formula III.





The optical brighteners according to the invention are used in powder form or as solutions in water. Such solutions have a content of 18 to 75% by weight of active substance and preferably also contain hydrotropic substances. The active substances are well known and can be produced according to conventional processes.

Besides optical brighteners, the liquid laundry detergent compositions according to the invention contain the usual components of such compositions. In general, such components include anionic as well as non-ionic surfactants, builders, alkali, hydrotropic agents, buffers, enzymes and the like will be contained. It is also possible to include cationic softeners which will not precipitate.

The amounts of the components of such liquid laundry detergent composition are in the usual ranges. Typical detergent compositions contain from 0.05 to 0.15% by weight of optical brighteners (as 100% active substance), from 5 to 30%, preferably from 10 to 25% by weight of fatty acids, from 2 to 20%, preferably from 5 to 15% by weight of a further anionic surfactant, from 0.5 to 12%, preferably from 1.5 to 8% by weight of a non-ionic surfactant, to give in total from 20 to 50%, preferably from 30 to 50% by weight of

surfactants and from 5 to 15% by weight of builders. The amount of alkali should be sufficient to neutralize all acids present and to reach a pH value suitable for washing.

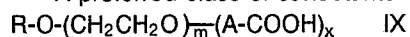
The fatty acids which are used as anionic surfactants are preferably saturated and unsaturated C₅₋₂₂ carboxylic acids, more preferably C₁₂₋₁₈. The fatty acids, for example coco fatty acid or oleic acid are added as such and converted to the salt form by addition of alkali e.g. NaOH, KOH or an organic base e.g. triethanolamine.

Further anionic surfactants which can be present may be any of the following conventional types:

- a) sulphates and sulphonates of fatty acids, fatty acid esters and fatty acid amides
- b) linear or branched C₅₋₁₈ alkyl sulphates and sulphonates
- c) sulphated ethoxylated compounds, particularly sulphated forms of any non-ionic surfactants which may be present
- d) polycarboxylic acid ester sulphates and
- e) C₅₋₁₈ alkylbenzenesulphonates and C₁₋₄ alkyl and dialkyl naphthalene sulphonates.

These compounds may be added in acid form and converted to their salt forms by addition of alkali.

A preferred class of surfactants which are only weakly anionic are of the formula IX



in which R is the residue of a C₈₋₂₂ fatty alcohol or of an alkylphenol having 10-24 C atoms;

A is a methylene or ethylene group;

m is a number from 1-20;

and x is an average value from 0.1 to 1.

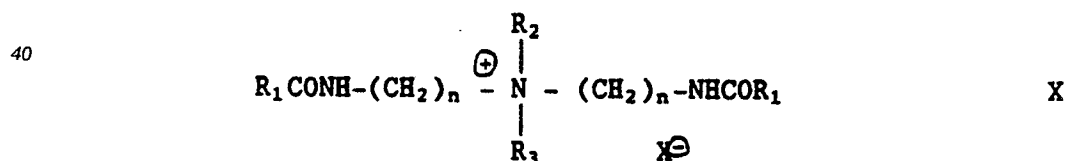
Compounds of formula IX are known or may be prepared by conventional methods from available starting materials. The most preferred component (B) is a compound of formula IX obtained by reacting a synthetic lauryl alcohol (C₁₂₋₁₅) with 4-5 moles ethylene oxide and subsequently with 0.8 mole chloracetic acid. The compounds are normally used in the form of their alkali metal salts, particularly sodium salts.

Nonionic surfactants which may be present include ethylene oxide (EO) / propylene oxide (PO) block copolymers (Pluronic), and the addition products of EO or PO, preferably EO, to fatty alcohols, fatty amines, fatty acids, fatty acid alkanolamides and alkylphenols. Such non-ionic surfactants are conventional and commercially available.

Hydrotropic compounds which may be present include for example urea, dicyandiamide and its derivatives, alcohols, water-soluble glycols, glycol ethers and glycol esters and C₁₋₄ alkylbenzenesulphonates, provided that the compounds display no cloud point in distilled water up to 100°. They act so as to prevent phase separation, that is to stabilize the liquid composition.

Sequestering agents include citric acid, nitrilotriacetic acid and other complex formers. Buffers may be used to stabilise the pH of the wash liquor in the neutral or alkali region. Buffer substances include sodium bicarbonate, sodium carbonate and sodium silicate.

Further optional components include cationic softeners, e.g., products of acylation and quaternization of a polyalkylene polyamine of the formula X



in which each R₁, independently, is C₁₂₋₁₈ alkyl or C₁₂₋₁₈ alkenyl;

each n, independently, is 2 or 3;

R₂ is C₁₋₄ alkyl, C₁₋₄ hydroxyalkyl, or C₁₋₄ hydroxyalkyl etherified with 1-10 ethylene oxide groups;

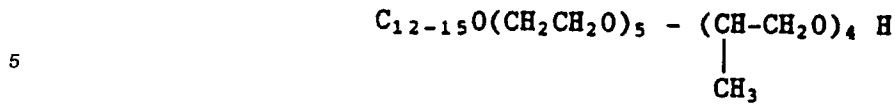
R₃ is C₁₋₄ alkyl or benzyl;

and X[⊖] is a halide, methylsulphate or ethylsulphate anion.

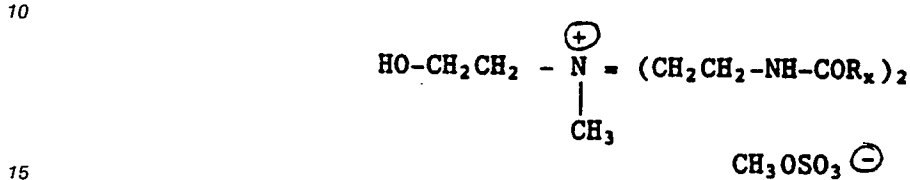
By selection of these additional components the washing effect of the liquid detergent can be adjusted for the desired field of use. The liquid detergent compositions of the invention are primarily useful as domestic laundry detergents. Not only do they display good washing power, they also produce a soft handle on laundered cotton goods. Being phosphate-free, they are ecologically acceptable. The liquid compositions of the invention are stable and do not separate into two phases, nor do the optical brighteners crystallize and precipitate on storage.

In the following examples 1 to 7 (table), the carboxymethylated ethylene oxide adduct of the formula C₁₂₋₁₅O(CH₂CH₂O)_{4,5} - (CH₂COONa)_{0,7}

as a 50% paste in water, the non-ionic surfactant of the formula



as a 99% paste in water, the softener of the formula



in which $R_x = 85\%$ oleic acid and 15% stearic acid residue, as a 90% solution in water, polyacrylic acid A with MW 100.00 as a solution of 29% of the semi-neutralized acid (sodium salt), polyacrylic acid B with MW 4500 as a solution of 49% are used as well as the optical brighteners with the given formulas in the following compositions:

Formula III as an aqueous solution that contains 28% active substance or as a powder with 89% active substance

Formula IV as an aqueous solution that contains 20% active substance

25 Formula V as an aqueous solution that contains 23% active substance or as a powder with 50% active substance

Formula VII as an aqueous solution that contains 34% active substance

Formula VI as an aqueous solution that contains 33% active substance.

30 Example 1 is a so-called fabric softener, Example 2 is a liquid laundry detergent for industrial use, Example 3 is a complete laundry detergent for domestic use, Example 4 is a liquid laundry detergent with fabric softener for domestic use, Examples 5 and 6 are liquid laundry detergents for domestic use, and Example 7 is a concentrated complete laundry detergent for domestic use.

35

40

45

50

55

Table

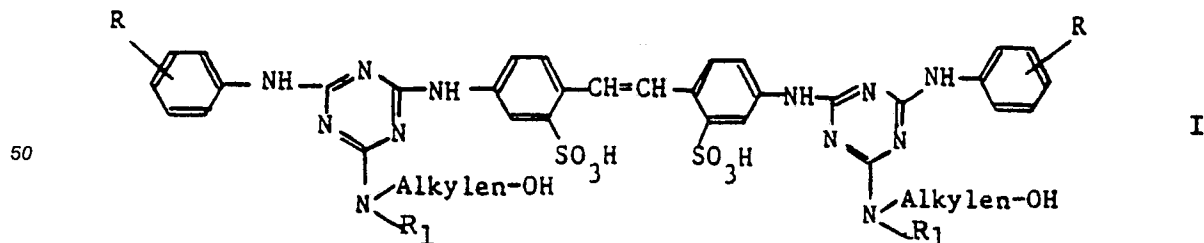
		Percentage by weight						
5	Example	1	2	3	4	5	6	7
Component								
	Demineralised water	86.4	65.0	57.8	27.5	31.7	30.5	53.9
	sodium xylenesulphonate	-	4.5	6.0	-	-	-	6.5
10	isopropanol	2.0	-	-	12.0	12.0	12.0	-
	ethylene glycol	-	3.0	-	-	-	-	-
	propylene glycol	5.0	-	-	-	-	-	-
	dodecylbenzene sulphonic acid	-	2.0	6.0	8.0	8.0	8.0	6.0
	coco fatty acid	-	-	6.0	15.0	8.0	12.0	6.0
15	oleic acid	-	2.0	-	5.0	5.0	5.0	-
	Carboxymethylated ethylene oxide adduct	-	-	-	15.0	20.0	20.0	-
	non-ionic surfactant	-	-	-	-	5.0	-	-
	softener	6.5	-	-	5.0	-	-	-
	sodium hydroxide	-	2.7	-	-	1.8	-	-
20	potassium hydroxide	-	-	6.2	-	-	-	5.1
	diethanolamine	-	-	-	11.7	-	8.0	-
	triethanolamine	-	-	-	-	8.0	4.0	-
	sodium hydrogen carbonate	-	-	2.5	-	-	-	-
	sodium silicate (Na ₂ O:SiO ₂)1:2	-	10.0	-	-	-	-	4.5
25	sodium nitrilotriacetate	-	3.0	-	-	-	-	2.0
	polyacrylic acid A	-	-	15.0	-	-	-	15.0
	polyacrylic acid B	-	7.5	-	-	-	-	-
	brightener III liquid	0.1	-	-	-	-	-	-
	III powder	-	0.3	-	-	-	-	-
30	IV liquid	-	-	0.5	-	-	-	-
	V liquid	-	-	-	0.8	-	-	-
	V powder	-	-	-	-	0.5	-	-
	VII liquid	-	-	-	-	-	0.5	-
	VI liquid	-	-	-	-	-	-	1.0
35	pH of the solution	100.0	100.0	100.0	100.0	100.0	100.0	100.0
		5.5	13.3	9.5	7.5	7.5	7.5	12.5

40

Claims

1. A liquid laundry detergent composition containing one or more optical brighteners of formula I

45



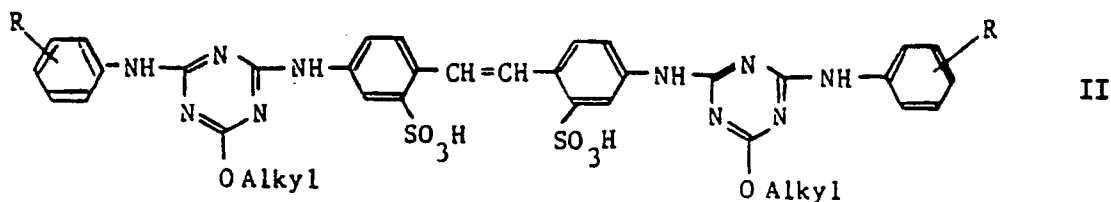
50

55 in alkali salt or alkyl-, hydroxyalkyl-, or ammonium salt form,
 in which both groups R, independently, are hydrogen, halogen, C₁₋₂ alkyl, C₁₋₂ alkoxy, hydroxy or sulfonic acid groups,
 each alkylene, independently, is an alkylene group with 2 or 3 carbon atoms,

each X, independently, is halogen, cyano, carboxamido, C₁₋₂ alkoxy or hydroxy,
and R₁ is hydrogen or Alkylene -X, with the proviso that if X = hydroxy, R should not be a sulfonic acid
group in the para-position,
or containing optical brighteners of formula II

5

10



in which R is as defined above,

15

both alkyl groups, independently, have 1 or 2 carbon atoms, and both groups M are hydroxyalkylammonium cations.

2. A liquid laundry detergent composition according to claim 1 in which the optical brighteners are added in powder form or as solutions in water, also containing hydrotropic substances.

20

3. A liquid laundry detergent composition according to any one of claims 1 and 2 containing anionic as well as non-ionic surfactants, sequestering agents, alkali, and optionally buffers, enzymes and/or cationic softeners.

4. A liquid laundry detergent composition according to any one of claims 1 to 3 that is phosphate free.

5. A liquid laundry detergent composition according to any one of claims 1 to 4 in which the optical brightener is of formula III.

25

6. A liquid laundry detergent composition according to any one of claims 1 to 4 in which the optical brightener is of formula IV.

7. A liquid laundry detergent composition according to any one of claims 1 to 4 in which the optical brightener is of formula V.

30

8. A liquid laundry detergent composition according to any one of claims 1 to 4 in which the optical brightener is of formula VI.

9. A liquid laundry detergent composition according to any one of claims 1 to 4 in which the optical brightener is of formula VII.

10. A liquid laundry detergent composition as described in any one of the Examples.

35

40

45

50

55