

COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952
APPLICATION FOR A STANDARD PATENT

Ciba-Geigy AG, incorporated in Switzerland, of Klybeckstrasse 141, 4002 Basle, SWITZERLAND, hereby apply for the grant of a standard patent for an invention entitled:

Stable Detergents Containing Fluorescent Whitening Agents
which is described in the accompanying complete specification.

Details of basic application(s):-

<u>Basic Applic. No:</u>	<u>Country:</u>	<u>Application Date:</u>
5009/87-9	CH	23 December 1987

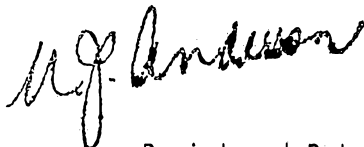
The address for service is:-

Spruson & Ferguson
Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia

DATED this TWENTY FOURTH day of NOVEMBER 1988

Ciba-Geigy AG

By:



Registered Patent Attorney

TO: THE COMMISSIONER OF PATENTS
OUR REF: 77207
S&F CODE: 52760

COMMONWEALTH OF AUSTRALIA

Patents Act 1952 - 1969

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made by CIBA-GEIGY AG for a patent for an invention entitled:

Stable detergents containing fluorescent whitening agents

I, Werner Waldegg of CIBA-GEIGY AG, Klybeckstrasse 141, 4002 Basle, Switzerland do solemnly and sincerely declare as follows:

1. I am authorised by the applicant for the patent to make this declaration on its behalf.
2. The basic application~~(s)~~ as defined by Section 141 of the Act was ~~(were)~~ made in Switzerland on December 23, 1987

by CIBA-GEIGY AG, 4002 Basle, Switzerland

3. Claude Eckhardt, 16, Rue des Jonquilles, 68400 Riedisheim, France,
Heinz Hefti, Fasanenstrasse 2, 4153 Reinach, Switzerland,
Hans Rudolf Meyer, Bollwerkstrasse 102, 4102 Binningen, Switzerland and
Kurt Weber, Rennweg 98, 4052 Basle, Switzerland

~~is~~ (are) the actual inventor(s) of the invention and the facts upon which the applicant is entitled to make the application are as follows: The said applicant is the assignee of the actual inventor(s).

4. The basic application~~(s)~~ referred to in paragraph 2 of this Declaration was ~~(were)~~ the first application~~(s)~~ made in a Convention country in respect of the invention the subject of the application.

DECLARED at Basle, Switzerland on
October 25, 1988

CIBA-GEIGY AG



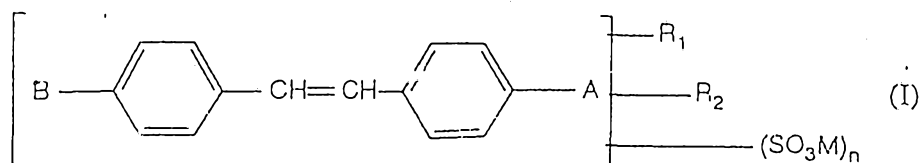
Werner Waldegg
Single Signature, by special power

To: The Commissioner of Patents

(12) PATENT ABRIDGMENT (11) Document No. AU-B-25935/88
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 624587

- (54) Title
STABLE DETERGENTS CONTAINING FLUORESCENT WHITENING AGENTS
- (51)⁴ International Patent Classification(s)
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C11D 003/395
- (21) Application No. : **25935/88** (22) Application Date : **25.11.88**
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- (31) Number (32) Date (33) Country
5009/87 23.12.87 CH SWITZERLAND
- (43) Publication Date : **06.07.89**
- (44) Publication Date of Accepted Application : **18.06.92**
- (71) Applicant(s)
CIBA-GEIGY AG
- (72) Inventor(s)
CLAUDE ECKHARDT; HEINZ HEFTI; HANS RUDOLF MEYER; KURT WEBER
- (74) Attorney or Agent
SPRUSON & FERGUSON, GPO Box 3898, SYDNEY NSW 2001
- (56) Prior Art Documents
AU 25934/88 C11D 3/39 3/395 3/42
US 4865759
US 4177347
- (57) Claim

1. A storage-stable detergent which contains 0.5 to 30% based on total weight of the detergent of a bleaching system of diperoxy-dodecanedioic acid or salts thereof or a mixture of diperoxidodecanedioic acid or salts thereof with an inorganic salt, said bleaching system being capable of bleaching textiles at a temperature from 20° to 60°C, and 0.03% to 0.5% based on total weight of the detergent of a fluorescent whitening agent or a mixture of fluorescent whitening agents wherein the fluorescent whitening agents are stilbene fluorescent whitening agents of the formula (I):



in which A is hydrogen, -SO₃M, halogen, phenyl or phenylpyrazol-1-yl;
B is benzofuran-2-yl if A is hydrogen, 2-(stilben-4-yl)-oxadiazol-5-yl if
A is halogen, phenylpyrazol-1-yl if A is phenylpyrazol-1-yl,
benzoxazol-2-yl if A is -SO₃M or phenyl, or naphthoxazol-2-yl if A is
hydrogen; R₁ and R₂ independently of one another are hydrogen,
halogen, C₁-C₄ alkyl or C₁-C₄ alkoxy; M is hydrogen or one

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equivalent of a non-chromophoric cation and n is zero to 2, but the compound of the formula (I) contains at least one $-\text{SO}_3\text{M}$ group.

624587 S & F Ref: 77207

FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

Class Int Class

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

Name and Address
of Applicant: Ciba-Geigy AG
Klybeckstrasse 141
4002 Basle
SWITZERLAND

Address for Service: Spruson & Ferguson, Patent Attorneys
Level 33 St Martins Tower, 31 Market Street
Sydney, New South Wales, 2000, Australia

Complete Specification for the invention entitled:

Stable Detergents Containing Fluorescent Whitening Agents

The following statement is a full description of this invention, including the best method of performing it known to me/us

Stable detergents containing fluorescent whitening agents

Abstract

Detergents which, in addition to inorganic and/or organic peracids, contain specific stilbene compounds as fluorescent whitening agents. These detergents are stable for several months and already show the customary cleaning properties at washing temperatures of 20-60°C.



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Stable detergents containing fluorescent whitening agents

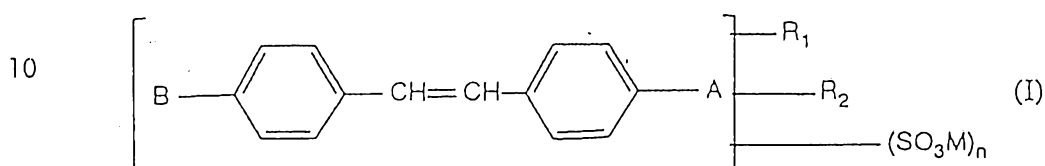
The Application relates to storage-stable detergents which, in addition to at least one peracid or salts thereof, contain at least one specific fluorescent whitening agent of the stilbene type, and to their use for washing textiles.

Because of the increased content of synthetic fibres and fibre blends in the textiles manufactured today and the desire no longer to have to wash coloured laundry separately and for energy saving measures, in many countries laundry is no longer washed at 90°C-95°C or at the boil but at lower temperatures. This means that it has been necessary for the perborates which have usually so far been contained in detergents and act as bleaching agents to be activated by auxiliaries, such as tetraacetylenediamine (TAED) in order to achieve acceptable bleaching effects even at washing temperatures of 60-80°C. At still lower washing temperatures, even the perborate/activator systems no longer give satisfactory results.

Detergents which contain stronger bleaching agents, for example peracids, have therefore been described for some time (German Offenlegungsschrift 2,756,583, EP-A-145,438, GB 2,141,754, GB 2,141,755, US 4,028,263 and GB 59,272). Although these novel bleaching agents on the one hand already exhibit outstanding bleaching effects at temperatures from 20°C, on the other hand they destroy the customary fluorescent whitening agents contained in detergents.

It has now been found that specific stilbene compounds surprisingly have an excellent stability in detergents which contain such strong bleaching agents. Under average storage conditions and even under intensified conditions (temperatures above 30°C and atmospheric humidity above 60%), these specific stilbene fluorescent whitening agents are completely stable, or are at most degraded to a degree which causes no trouble in practice, in the detergent for several months.

The application thus relates to a storage-stable detergent which contains 0.5 to 30% based on total weight of the detergent of a bleaching system of diperoxidodecanedioic acid or salts thereof or a mixture of diperoxidodecanedioic acid or salts thereof with an inorganic salt, said
5 bleaching system being capable of bleaching textiles at a temperature from 20° to 60°C, and 0.03% to 0.5% based on total weight of the detergent of a fluorescent whitening agent or a mixture of fluorescent whitening agents wherein the fluorescent whitening agents are stilbene fluorescent whitening agents of the formula (I):



in which A is hydrogen, $-\text{SO}_3\text{M}$, halogen, phenyl or phenylpyrazol-1-yl; B is benzofuran-2-yl if A is hydrogen, 2-(stilben-4-yl)-oxadiazol-5-yl if A is halogen, phenylpyrazol-1-yl if A is phenylpyrazol-1-yl, benzoxazol-2-yl if A is $-\text{SO}_3\text{M}$ or phenyl, or naphthoxazol-2-yl if A is
15 hydrogen; R_1 and R_2 independently of one another are hydrogen, halogen, $\text{C}_1\text{-C}_4$ alkyl or $\text{C}_1\text{-C}_4$ alkoxy; M is hydrogen or one equivalent of a non-chromophoric cation and n is zero to 2, but the compound of the formula (I) contains at least one $-\text{SO}_3\text{M}$ group.

M in formula (I) is, for example, an alkaline earth metal, such as
20 magnesium or calcium, but preferably an alkali metal, such as lithium, sodium or potassium, or substituted or unsubstituted ammonium, such as ammonium, mono-, di- or triethanol-ammonium, mono-, di- or tripropanol-ammonium or tri- or tetramethyl-ammonium.

The invention also relates to a method of cleaning textiles, which
25 method comprises washing said textiles at temperatures of 20-60°C with a detergent of the invention in an amount which effectively cleans said textiles.

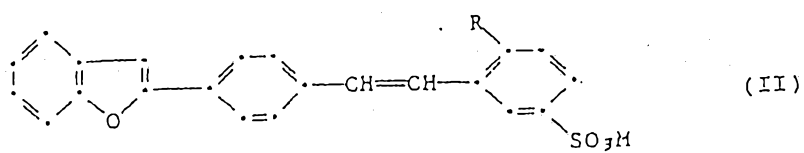
The invention further relates to the preparation of a detergent according to the invention by dry mixing with the aid of automatic screw
30 metering systems and/or fluidized bed mixers.

In particular, the detergents contain as fluorescent whitening



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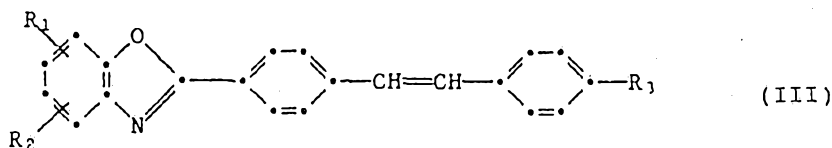
agents compounds of the formulae:



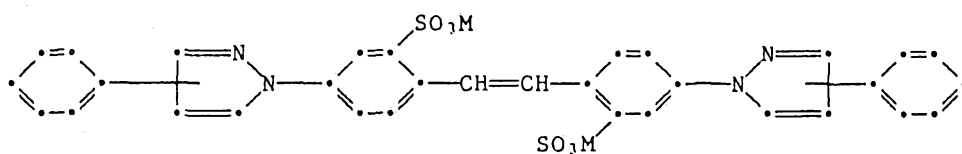
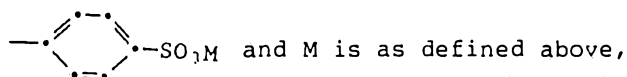
in which R is H or halogen and M is as defined above,



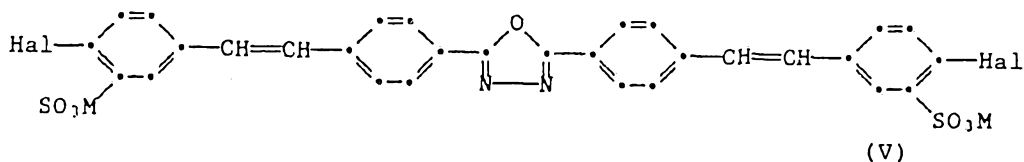
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in which R₁ and R₂ are H or C₁-C₄alkyl, R₃ is -SO₃M or



in which M is as defined above, and/or



in which M is as defined above.

All these fluorescent whitening agents of the formula I to V are known and can be prepared by known methods.

The peracids and salts thereof are inorganic or organic compounds which are described in the literature or are commercially available and which already bleach textiles at temperatures from 20°C. A suitable organic peracid is diperoxydodecanedioic acid (DPDDA). The amount of organic peracid to be used is preferably 0.5% to 10%, in particular 1% to 5%. However, it is also possible for highly active inorganic peracids, such as persulfate and/or percarbonate, to be used. The amount of these inorganic peracids is preferably 1% to 30%, in particular 10% to 20%, based on the total weight of detergent. Optionally and advantageously they are used in combination with small amounts of catalytically acting divalent metal salts, such as are described in US 4,655,782 and US

4,655,953. Metal salts of copper and/or manganese are preferably used.

Mixtures of the organic and inorganic peracids or peracid salts or only mixtures of the inorganic peracids can of course also be used.

The peracids are added to the detergent by dry mixing, for example with the aid of automatic screw metering systems and/or fluidized bed mixers.

The detergents are dry detergents of customary compositions. As a rule, in addition to the combination according to the invention of peracid and fluorescent whitening agent, they contain, for example, anionic, nonionic, amphoteric and/or cationic surfactants, builders, for example pentasodium tripolyphosphate or substitute products, such as phosphonates, polycarboxylates, acrylic/maleic copolymers, zeolites, nitrilotriacetate and ethylenediaminetetraacetic acid, soil-suspending agents, for example sodium carboxymethylcellulose, salts for adjusting the pH, for example alkali metal or alkaline earth metal silicates, foam regulators, for example soaps, salts for adjusting the spray-drying and granulation properties, for example sodium sulfate, perfumes and if appropriate antistatic and softening agents, enzymes, photobleaching agents, pigments and/or toning agents. These constituents should of course be stable towards the bleaching system used.

As a result of the combination according to the invention, it is possible to provide detergents which meet the customary standard, for example as regards to washing power, spot removal and refreshing the appearance of the washed articles, even if washing is carried out at temperatures of 20°C-60°C. Coloured laundry and white laundry can thus advantageously be washed together regardless of the fibre.

The following examples illustrate the invention without limiting it thereto. Percentage data are percentages by weight.

Detergent formulation

The detergents of the following examples are prepared in two stages by customary processes:

Granules A are first prepared by drying and granulating a slurry consisting of about 1 part of water and 1 part of detergent of the following composition:

84 g of linear dodecylbenzenesulfonate
31 g of tallow alcohol tetradecane-ethylene glycol ether (14 mol of ethylene oxide)
37 g of Na soap (chiefly of behenic acid and C₁₄-C₂₀)
458 g of Na tripolyphosphate
79 g of Na silicate
20 g of Mg silicate
12 g of carboxymethylcellulose
2 g of ethylenediamine tetraacetate
222 g of Na sulfate
1 g of fluorescent whitening agent (FWA) according to the formula (II)-(V).

The peracid B (15 g of DPDDA) is homogeneously admixed in the dry state to 500 g of these granules A, which have a residual moisture content of 5% after drying.

Storage test

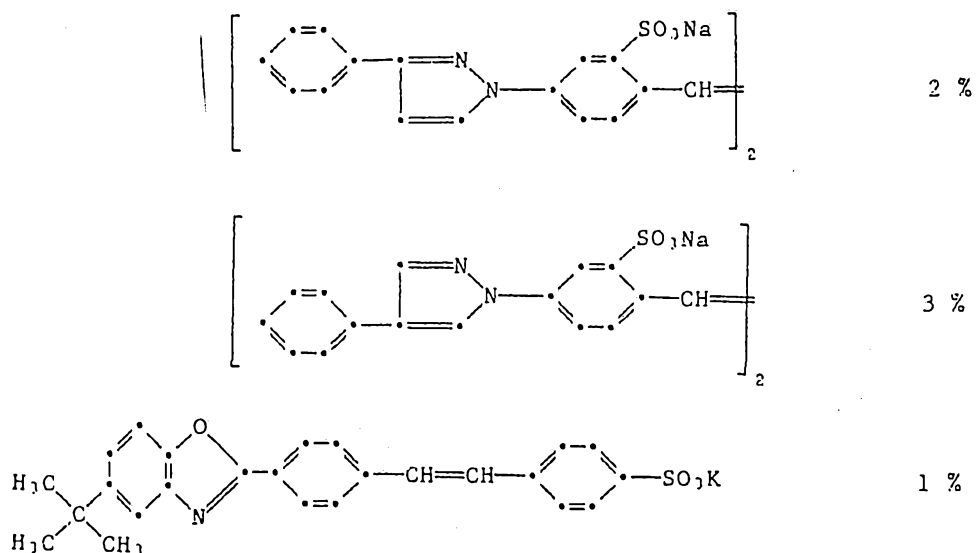
Samples of the detergent D (granules A + peracid B) thus obtained are:

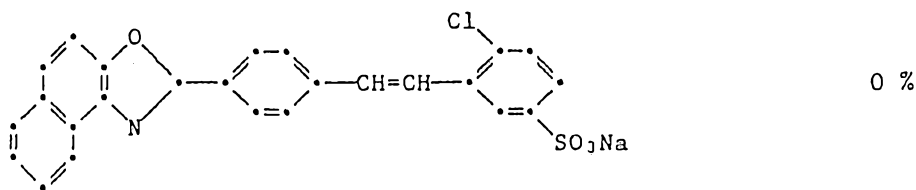
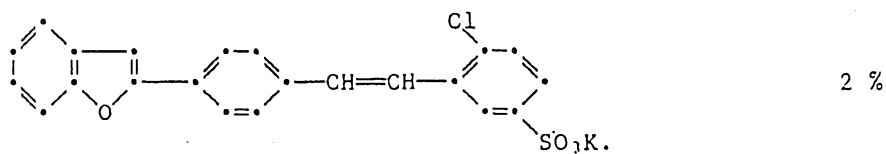
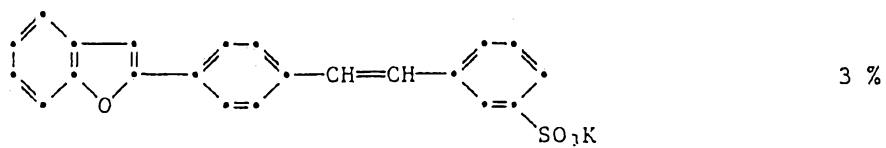
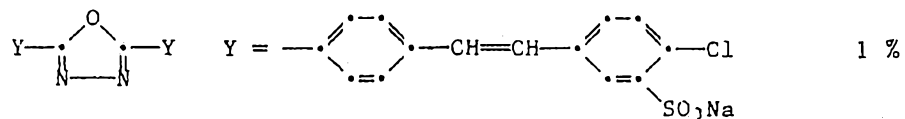
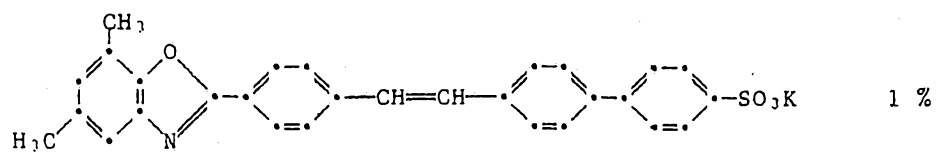
- on the one hand, for control of the starting value, immediately analyzed for the content of FWA by extraction and measurement of the spectrophotometric absorbance (theoretical: 0.1% of FWA, based on the weight of the granules A),
- on the other hand kept in cardboard packets suitable for commercial washing powder, that is to say with a coating, under selected and controlled conditions of temperature and atmospheric humidity for certain periods of time. After storage, the FWA content of each detergent is immediately determined. The difference from the starting value is expressed as a percentage and is a measure of the stability of the FWA towards the corresponding bleaching agent in the washing powder.

The abovementioned FWA determination is carried out as follows:

The washing powder is homogenized thoroughly by grinding and 1 g thereof is admixed with 200 ml of solvent consisting of 9 parts of dimethyl sulfoxide and 1 part of water, and the mixture is stirred at room temperature for 30 minutes. It is then centrifuged for 30 minutes. A sample of the clear solution thus obtained is transferred with a pipette into a 1 cm quartz cell and its absorbance is measured in the UV range at the absorption maximum against a standard solution of the particular FWA. The absorbance is proportional to the FWA concentration. The reproducibility of the results is about $\pm 1\%$ if the test conditions are kept exactly the same.

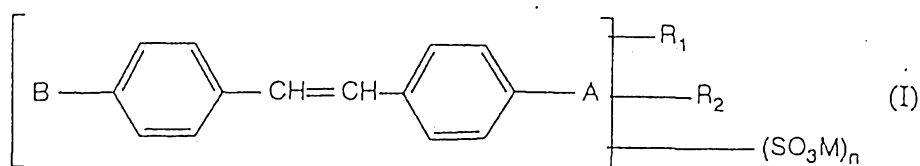
Example : The percentage FWA loss is determined under the conditions described above. Storage is in a closed packet at 20 to 25°C. After 6 months, the FWA loss is as follows:





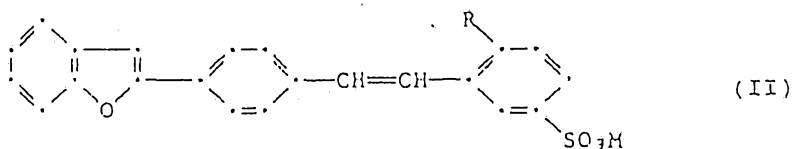
The claims defining the invention are as follows:

1. A storage-stable detergent which contains 0.5 to 30% based on total weight of the detergent of a bleaching system of diperoxy-dodecanedioic acid or salts thereof or a mixture of diperoxidodecanedioic acid or salts thereof with an inorganic salt, said bleaching system being capable of bleaching textiles at a temperature from 20° to 60°C, and 0.03% to 0.5% based on total weight of the detergent of a fluorescent whitening agent or a mixture of fluorescent whitening agents wherein the fluorescent whitening agents are stilbene fluorescent whitening agents of the formula (I):

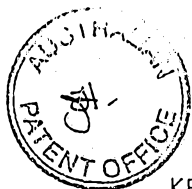


- in which A is hydrogen, $-\text{SO}_3\text{M}$, halogen, phenyl or phenylpyrazol-1-yl; B is benzofuran-2-yl if A is hydrogen, 2-(stilben-4-yl)-oxadiazol-5-yl if A is halogen, phenylpyrazol-1-yl if A is phenylpyrazol-1-yl, benzoxazol-2-yl if A is $-\text{SO}_3\text{M}$ or phenyl, or naphthoxazol-2-yl if A is hydrogen; R_1 and R_2 independently of one another are hydrogen, halogen, $\text{C}_1\text{-C}_4$ alkyl or $\text{C}_1\text{-C}_4$ alkoxy; M is hydrogen or one equivalent of a non-chromophoric cation and n is zero to 2, but the compound of the formula (I) contains at least one $-\text{SO}_3\text{M}$ group.
2. A detergent according to claim 1, which contains, as the inorganic salt, a persulfate and/or a percarbonate, with the addition of a catalyst.

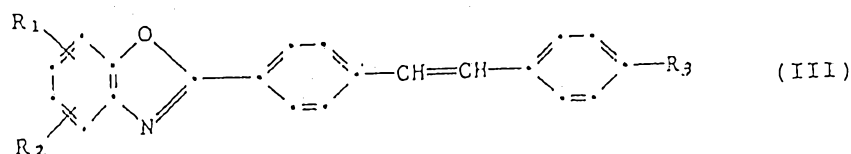
3. A detergent according to claim 1 or claim 2, which contains, as the fluorescent whitening agent, a compound of the formula (II):



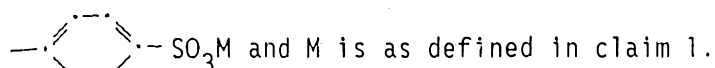
- in which R is H or halogen and M is as defined in claim 1.



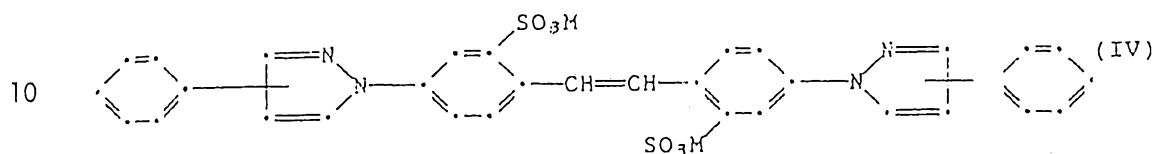
4. A detergent according to any one of claims 1 to 3, which contains, as the fluorescent whitening agent, a compound of the formula (III)



5 in which R_1 and R_2 are H or C_1-C_4 alkyl, R_3 is $-SO_3M$ or

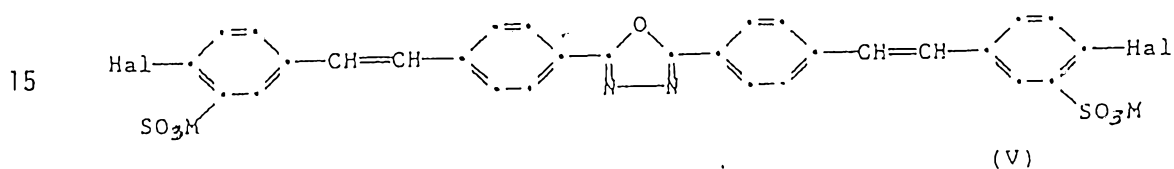


5. A detergent according to any one of claims 1 to 3, which contains, as the fluorescent whitening agent, a compound of the formula (IV)



in which M is as defined in claim 1.

6. A detergent according to any one of claims 1 to 3, which contains, as the fluorescent whitening agent, a compound of the formula (V)



in which M is as defined in claim 1.

7. A method of cleaning textiles, which method comprises washing said textiles with a detergent according to any one of claims 1 to 6 at temperatures of 20-60°C in an amount which effectively cleans said textiles.

8. The preparation of a detergent according to any one of claims 1 to 6 by dry mixing with the aid of automatic screw metering systems and/or fluidized bed mixers.



9. A storage-stable detergent which contains 0.5 to 30% based on total weight of the detergent of a bleaching system of diperoxy-dodecanedioic acid or salts thereof or a mixture of diperoxidodecanedioic acid or salts thereof with an inorganic salt, said bleaching system being
5 capable of bleaching textiles at a temperature from 20° to 60°C, and 0.03% to 0.5% based on the total weight of the detergent of a fluorescent whitening agent or a mixture of fluorescent whitening agents, wherein the fluorescent whitening agents are stilbene fluorescent whitening agents, which detergent is substantially as herein described with reference to
10 the Detergent Formulation.

10. A method of cleaning textiles, which method comprises washing said textiles at temperatures of 20-60°C with a detergent as claimed in claim 9 in an amount which effectively cleans said textiles.

DATED this TWENTY-FOURTH day of MARCH 1992

Ciba-Geigy AG

Patent Attorneys for the Applicant
SPRUSON & FERGUSON



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