

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

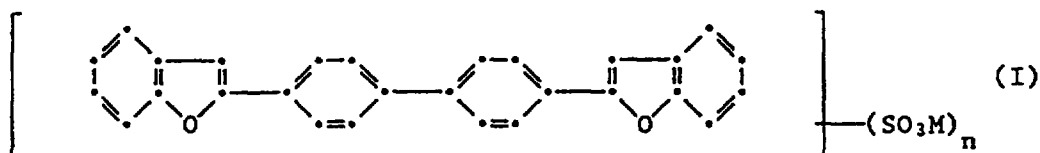
Because of the increased content of synthetic fibres and fibre blends in the textiles manufactured today and the desire no longer to have to wash coloured laundry separately and for energy saving measures, in many countries laundry is no longer washed at 90°C-95°C or at the boil but at lower temperatures. 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 (DE-A-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 exhibit outstanding bleaching effects at temperatures as low as 20°C, on the other hand they destroy the customary fluorescent whitening agents contained in detergents.

It has now been found that specific bis-benzofuranyl 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 bis-benzofuranyl 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 storage-stable dry detergents containing 0.5 to 30% of an inorganic or organic peracid or salts thereof or mixtures of peracids or salts thereof and 0.03% to 0.5% of a fluorescent whitening agent or a mixture of fluorescent whitening agents, wherein

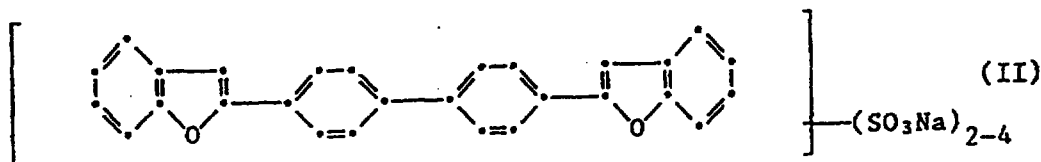
the fluorescent whitening agents are bis-benzofuranyl fluorescent whitening agents of the formula (I)



in which M is hydrogen or one equivalent of a non-chromophoric cation and n is 2 to 4, and where (I) may also be substituted by halogen, C₁-C₄alkyl or C₁-C₄alkoxy radicals R, and wherein the detergent contains mono- or polyperacid having alkyl chains of 3 to 20 carbon atoms and/or persulfate or mixtures thereof or salts thereof.

M in formula (I) is, for example, an alkaline earth metal, such as 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, non-, di- or tripropanol-ammonium or tri- or tetramethyl-ammonium.

In particular, the detergents contain as fluorescent whitening agents compounds of the formula



These fluorescent whitening agents of the formula I and II are known and can be prepared by known methods (DE-A-2,238,734).

The peracids or salts thereof are inorganic or organic compounds which are described in the literature or are commercially available and which bleach textiles at temperatures as low as 20°C. The organic peracids, for example mono- or polyperacids having alkyl chains of at least 3, preferably 6 to 20, carbon atoms, but in particular diperoxydicarboxylic acids having 6 to 12 carbon atoms, such as diperoxyazelaic acid, diperoxysebacic acid and/or diperoxyphthalic acid, are of particular

interest. However, it is also possible for highly active inorganic peracids, such as persulfate, to be used. The amount of organic peracids to be used is preferably 0.5% to 10%, in particular 1% to 5%, and the amount of inorganic peracids to be used is preferably 1% to 30%, in particular 10% to 20%, based on the total weight of detergent, and if appropriate in combination with small amounts of compounds which intensify the bleaching action of the peracids.

Mixtures of organic and/or inorganic peracids or peracid salts can of course also be used.

The peracids are added to the detergent in particular by mixing the components, for example with the aid of 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, anti-redeposition 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 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 the customary process:

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 EO)
 37 g of Na soap (chiefly of behenic acid and C_{14} - C_{20})
 458 g of Na tripolyphosphate
 79 g of Na silicate
 20 g of Mg silicate
 12 g of carboxymethylcellulose
 2 g of ethylenediaminetetraacetate
 222 g of Na sulfate
 1 g of fluorescent whitening agent (FWA) according to the formula (I) - (II).

The peracid B (70 g of K monopersulfate + 2 mg of anhydrous $CuSO_4$) 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:

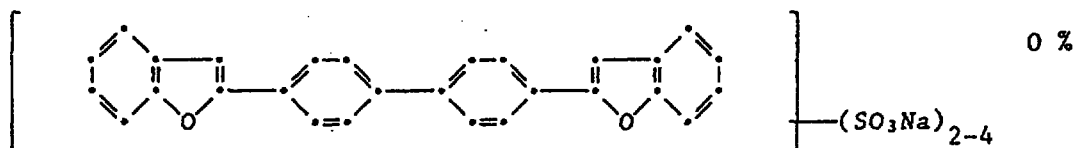
- on the one hand, for control of the starting value, immediately subjected to determination of the content of FWA by extraction and measurement of the spectrophotometric absorbance (theoretical: 0.1% of FWA, based on the weight of the granules A),
- on the other hand kept in cardboard packets suitable 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 to 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.

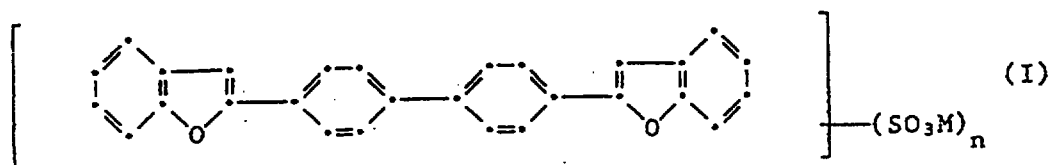
Example: The percentage FWA loss is determined under the conditions described above. Storage is in a closed packet at 20 to 25°C. After 6 months, the FWA loss is as follows:





Patent claims:

1. A storage-stable dry detergent containing 0.5 to 30% of an inorganic or organic peracid or salts thereof or mixtures of peracids or salts thereof and 0.03% to 0.5% of a fluorescent whitening agent or a mixture of fluorescent whitening agents, wherein the fluorescent whitening agents are bis-benzofuranyl fluorescent whitening agents of the formula (I)



in which M is hydrogen or one equivalent of a non-chromophoric cation and n is 2 to 4, and wherein the detergent contains mono- or polyperacid having alkyl chains of 3 to 20 carbon atoms and/or persulfate or mixtures thereof or salts thereof.

2. A detergent according to claim 1, which contains, as the peracid or peracid salt, a diperoxydicarboxylic acid having 6 to 20 carbon atoms and/or a persulfate or mixtures thereof or salts thereof.

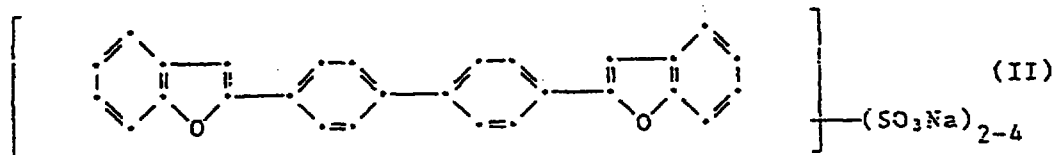
3. A detergent according to claim 2, which contains, as the peracid or peracid salt, a diperoxydicarboxylic acid having 6-12 carbon atoms and/or a persulfate or mixtures thereof or salts thereof.

4. A detergent according to any one of claims 1 to 3, which contains the peracid in combination with small amounts of compounds which intensify the bleaching action of the peracids.

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



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6. The use of a detergent according to any one of claims 1 to 5 for washing textiles at temperatures of 20 to 60°C.

7. The preparation of a detergent according to any one of claims 1 to 5 by mixing the components with the aid of screw metering systems and/or fluidized bed mixers.