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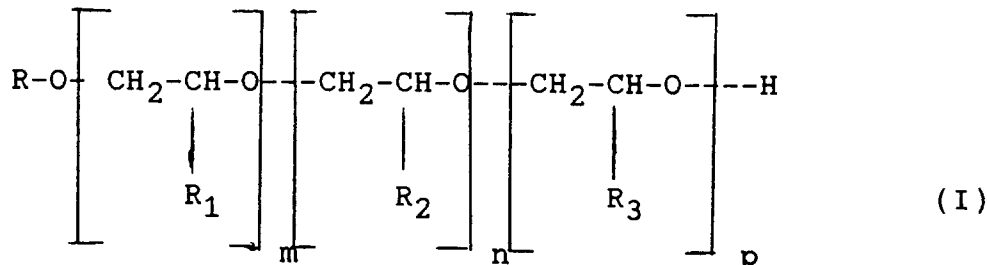
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(54) **Optical bleacher formulations**

(57) Fluid formulations consisting of 10-40% of anionic optical bleachers containing at least one sulfonic group and 90-60% of a compound or a mixture of compounds of formula I



wherein the groups are defined in the disclosure. The formulations are useful in the manufacture of detergents.

Description

The present invention relates to fluid formulations, containing from 10 to 50% of optical bleachers and their use for the preparation of detergents.

At present, most optical bleachers are preferably marketed and employed in the form of solutions or aqueous suspensions. With respect to the products in powder form, these have the advantage for the consumer of being easy to handle and dose also when used with automatic devices; moreover, they do not give rise to the formation of irritating dust in the work environment.

However, the drawback of these liquid preparations is their instability, that is to say, during storage there is a general tendency for separation to take place resulting in the sedimentation of the solid phase and therefore a lack of homogeneity of the preparation.

Even if improvements have taken place recently, the problem of the stability of these formulations has not yet been solved in a satisfactory manner.

In addition, for certain uses, mainly in the field of detergents, the water-based formulations are not desirable.

At present, the manufacturing of detergents is going through an evolutionary phase, in fact, there is a tendency towards the production of detergents which are more and more concentrated in active substance (the so-called "compacts"). Moreover, in order to save energy in the heating of the washing water, the new detergents have to be active and effective at low temperatures, even at room temperature.

So as to achieve good efficiency at low temperatures, the amount of perborate in the detergent composition must be increased, and a perborate activator must even be added, if the desired activity at room temperature is to be attained.

The optical bleachers usually employed in detergents, when perborate is present, undergo a rather marked degradation depending on the amount of perborate, the amount of water still present in the formulation when the optical bleacher is added and the operating temperature.

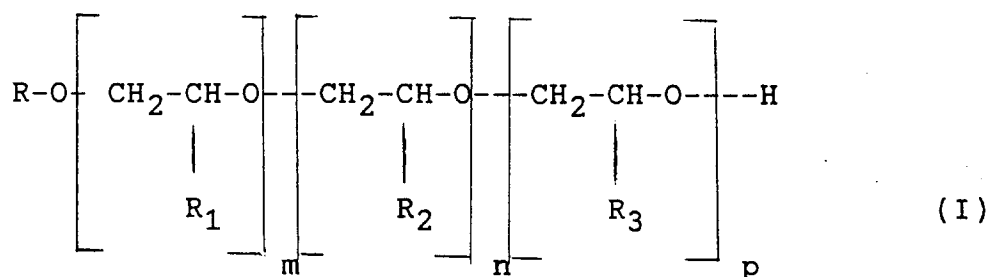
In order to avoid or reduce to a minimum the loss in the optical bleacher due to perborate-induced degradation, the present state-of-the-art provides for the addition of the optical bleacher as the last component in the final phase of the process, that is when the formulation is almost ready and it contains no water at all or a minimum amount.

Recently, new types of detergents in the form of granules, also spherical in shape (pearls), have appeared on the market.

These new formulations are prepared by mixing the different components, virtually in the absence of water and, in this case too, to avoid partial degradation, the optical bleacher is added last to the pre-formed water-free granules. Obviously, the optical bleacher must be of such a form that enables it to be deposited, mixed and distributed evenly on the surface of the granules and pearls to which it adheres firmly.

It is clear from what has been described above that, in order that the optical bleacher formulations may be employed without problems, the new types of detergents must be anhydrous or contain water in a minimum amount.

Surprisingly, formulations of optical bleachers which fully meet these new technological requirements have been found. They are solutions or dispersions, containing from 5 to 60% of optical bleachers, preferably anionic, anhydrous or containing at most 10% water, and comprising as a solvent or dispersing phase a compound of formula I:



in which R is hydrogen, C₁-C₁₈ straight or branched alkyl, aryl or aryl substituted with one or two C₁-C₉ alkyl groups, R₁, R₂ and R₃ can be the same or different and are hydrogen or methyl, m, n and p can have values ranging from 0 to 80, with the proviso that the sum of m+n+p is at least 1 and at most 100.

Examples of C₁-C₁₈ alkyl are methyl, ethyl, propyl, isopropyl, hexyl, octyl, 4-methylheptyl, nonyl, dodecyl, tetradecyl, hexadecyl, octadecyl. Examples of aryl and substituted aryl groups are phenyl, methylphenyl, dimethylphenyl, 4-tert-butylphenyl, 4-tert-octylphenyl, 2,4-di-tert-butylphenyl, 4-nonylphenyl.

Preferred polyethers of formula I are those wherein R is hydrogen or a C₁-C₁₈ alkyl group and the sum of m+n+p ranges from 1 to 60.

These formulations are fluid, anhydrous or contain at most of 10% water; they are ready to use, stable during storage and easily handled.

The oxyethylene-oxypropylene condensation compounds of formula I constituting the dispersing or solvent phase of the formulations according to the present invention have been known for some time and already widely used in numerous industrial fields (see for example: Nickolas Schoenfeldt: Grenzflächenaktive Äthylenoxide-Addukte-Wissenschaftliche Verlagsgesellschaft GmbH Stuttgart 1976; CTFA Cosmetic Ingredient Handbook First Edition-Editor Joanne M. Mikitakis pages 71-91).

The compounds of formula I have also been widely employed for some time in the detergent industry both as auxiliaries and as active substances depending on their chemical structure.

The process for the preparation of the dispersions according to the present invention has the advantage of simplicity. The optical bleacher is added to the compounds of formula I under stirring and stirring is continued until a solution or an homogeneous dispersion is obtained.

The attainment of a solution or of a dispersion depends mainly on the chemical nature of the optical bleacher and/or from the structure of the compounds of formula I.

Generally speaking, using anionic stilbene optical bleachers, solutions are obtained when R is hydrogen, methyl or R₁ and R₃ are hydrogen and the sum of m+n+p is lower than 10, whereas dispersions are obtained in the other cases.

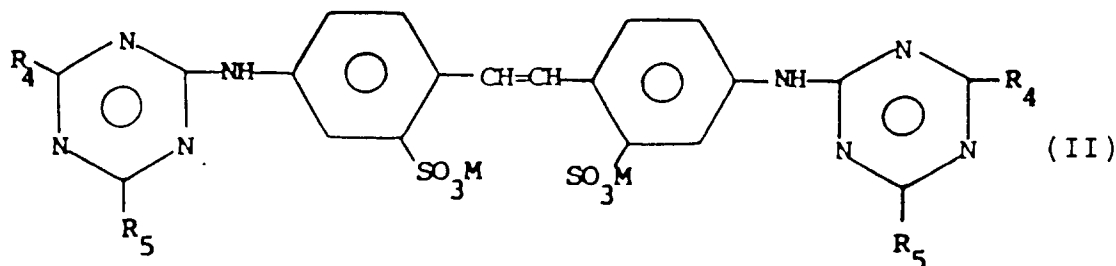
The viscosity of the solutions or dispersions depends on the nature of the condensate of formula I. The concentration may vary within wide ranges, normally between 5 and 60%, preferably between 10 and 40%, so as to avoid very low concentration formulations, which are not economical or very viscous formulations which are difficult to use.

By using this approach solutions or dispersions with satisfactory stability and with a viscosity generally varying between 10² and 10⁴ mPas are obtained.

A further object of the present invention is the use of the above mentioned fluid formulations in the preparation of detergents, especially those which are "compact" or "Mega-Pearls".

As has already been described, the formulations according to the present invention contain, preferably, anionic optical bleachers, containing in their chemical structure at least one sulfonic group.

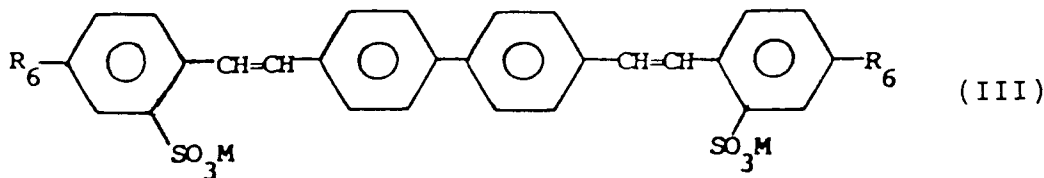
For example, stilbene optical bleachers of formula II



in which R₄ and R₅ can be the same or different and are phenylamino, morpholino, C₁-C₄ alkylamino or hydroxyalkylamino groups, M is hydrogen or a cation.

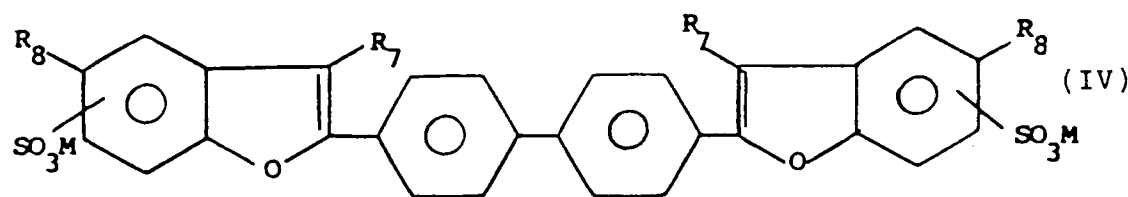
Preferred compounds of formula II are those in which R₄ is phenylamino, R₅ is morpholino or ethylamino and M is an alkali metal.

Or distyryl bleachers of formula III

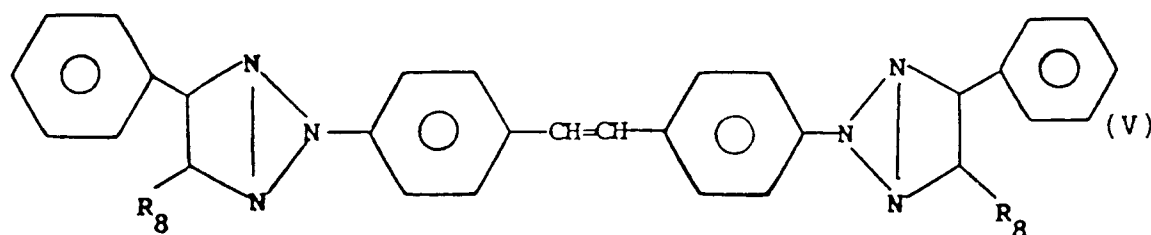


in which R₆ is hydrogen or chlorine and M is an alkali metal.

Or difuran compounds of formula IV



in which R_7 and R_8 can be the same or different and are hydrogen or the methyl group, M is an alkali metal or triazole compounds of formula V



in which R_8 and M have the meanings defined above.

The formulations according to the present invention preferably contain from 10 to 40% of a compound of formula II-V or of mixtures thereof.

They are prepared, as described previously, by simply adding the compounds of formula II-V in powder form to the condensates of formula I and by stirring until dissolution or homogeneity.

Where the optical bleachers of formula II-V contain large amounts of inorganic salts (for example, sodium chloride or sodium sulfate), before the preparation of the suspensions, they must preferably be removed or reduced to a minimum with respect to content. On the other hand, when a solution is to be prepared, any salt that may be present in the optical bleacher may be removed from the solution obtained by means of simple filtration.

The formulations according to the present invention can also be prepared from moist cakes of the optical bleachers derived from isolation by means of the filtration of these products. In this case, the moist cake is suspended or dissolved and water is successively eliminated through distillation, optionally under vacuum, completely or to a predetermined minimum residue.

Example 1

To 700 g of diethylene glycol (Formula I, $R = R_1 = H$, $m = 2$, n and $p = 0$), 305 g of optical bleacher of formula II ($R_4 = \text{morpholino}$, $R_5 = \text{anilino}$, $M = Na$) containing 1.6% of sodium chloride are added, stirring until dissolution. The undissolved salt is filtered off, to obtain a clear amber solution containing 30% of optical bleacher.

Example 2

To 390 g of diethylene glycol, 112.5 g of compound of formula II ($R_4 = \text{ethylamino}$, $R_5 = \text{anilino}$, $M = Na$) are added, stirring until dissolution. The undissolved sodium chloride is filtered off. A yellow-brown solution is obtained, containing 22% of optical bleacher.

Example 3

To 650 g of diethylene glycol, 575 g of moist cake of the optical bleacher of Example 1, containing 43.5% of active substance and 1.8% of sodium chloride. The mixture is heated slowly to 150°C , distilling the water contained in the moist cake, to obtain a turbid solution. When the water content in the solution reaches 10%, distillation is stopped and the mixture is cooled and any insolubles are filtered off.

A clear amber solution is obtained, containing 25% of optical bleacher.

Example 4

To 400 g of diethylene glycol monomethyl ether (Formula I, $R = CH_3$, $R_1 = H$, $m = 2$, n and $p = 0$), 106.3 g of optical bleacher of formula III ($R_6 = H$, $M = Na$) containing 6% of sodium chloride are added, stirring until dissolution. The undissolved sodium chloride is filtered off, to obtain a nearly colourless clear solution.

Example 5

To 300 g of diethylene glycol, 211.4 g of the moist cake of the optical bleacher of Example 2, containing 47.3% of active substance and 2.5% of sodium chloride, are added. The mixture is heated slowly to 150°C distilling the water from the moist cake, continuing distillation (optionally under a slight vacuum) until the water content of the solution is below 0.5%, then the mixture is cooled and filtered.

A yellow-brown solution is obtained.

Example 6

To 452 g of compound of formula I ($R = \text{alkyl } C_{12}-C_{14}$, $R_1 = H$, $m = 4$, n and $p = 0$), 248 g of the optical bleacher of Example 1, containing 1.2% of sodium chloride, are added, stirring until obtaining a fluid dispersion containing 35% of the active substance.

Example 7

To 225 g of diethylene glycol monomethyl ether, 77.5 g of optical bleacher of formula V ($R_8 = H$, $M = Na$) containing 3% of sodium chloride, are added, stirring until dissolution. The undissolved salt is filtered off to obtain a clear light yellow solution 25% of the active substance.

Example 8

To 257 g of dipropylene glycol monomethyl ether (Formula I, $R = R_1 = CH_3$, $m = 2$, n and $p = 0$) 143 g of the optical bleacher of Example 1, containing 2.2% of sodium chloride, are added, stirring until homogeneity. A fluid dispersion containing 35% of the active substance is obtained.

Example 9

33.3 g of a solution of the optical bleacher of Example 1 are added to 9000 g of a slurry of a detergent formulation consisting of water, sodium bicarbonate, sodium dodecylbenzenesulfonate, sodium silicate and sodium sulfate. After stirring for 30 minutes, the mixture is spray-dried.

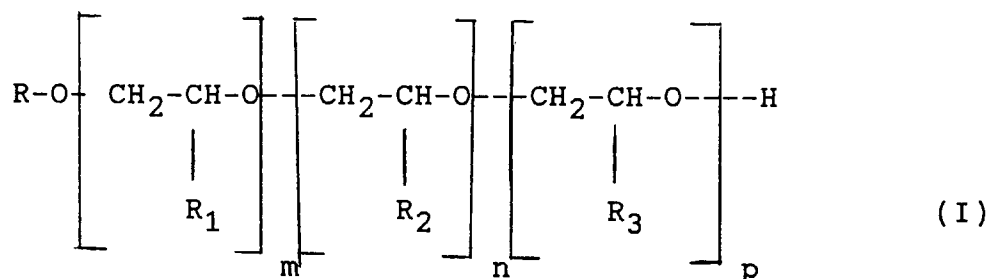
About 4000 g of a detergent in the form of a white powder are obtained.

Example 10

4 g of a solution of the optical bleacher of Example 5 are added to 500 g of a detergent formulation in granules (pearls), mixing in a suitable mixer until homogeneity.

Claims

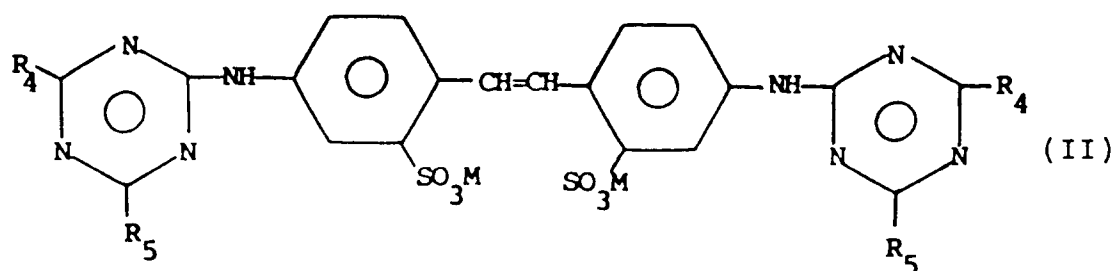
1. Fluid formulations consisting of 10-40% of anionic optical bleachers containing at least one sulfonic group and 90-60% of a compound or a mixture of compounds of formula I



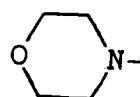
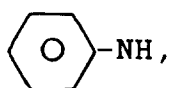
in which R is hydrogen, C₁-C₁₈ straight or branched alkyl, aryl or aryl substituted with one or two C₁-C₉ alkyl groups, R₁, R₂ and R₃ can be the same or different and are hydrogen or methyl, m, n and p can have values ranging from 0 to 80, with the proviso that the sum of m+n+p is at least 1 and at most 100.

2. Formulations according to claim 1, wherein the sum of m+n+p ranges from 1 to 80.

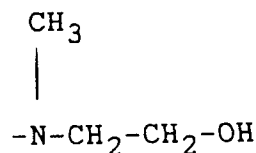
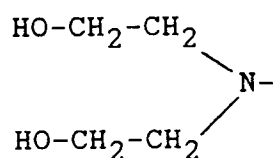
3. Formulations according to claim 1 wherein the optical bleachers have formula II:



wherein R₄ and R₅ are the same or different and are one of the following groups
C₂H₅-NH,

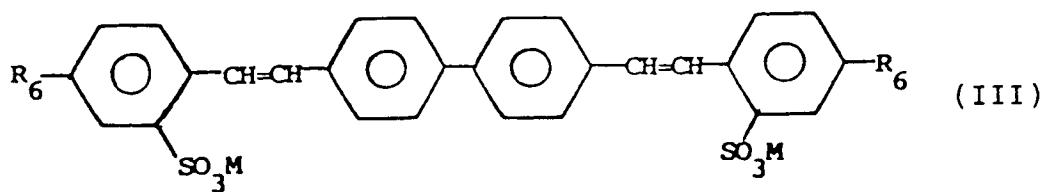


HO-CH₂-CH₂-NH-



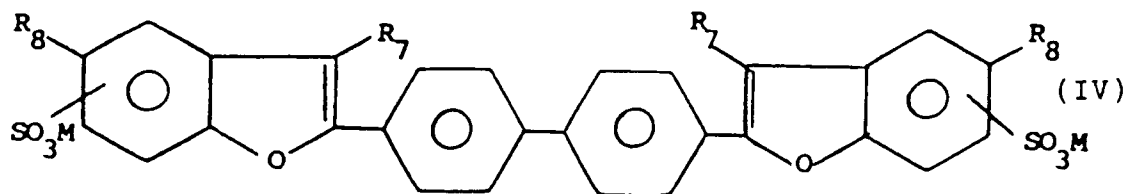
and M is sodium or potassium.

4. Formulations according to claim 1 wherein the optical bleachers have formula III



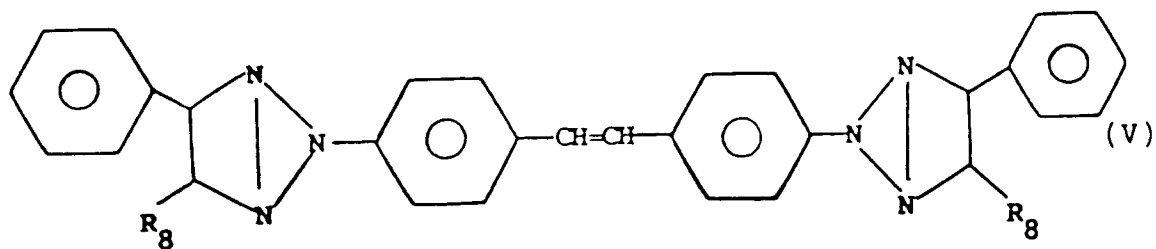
10 wherein R_6 is hydrogen or chlorine and M is sodium or potassium.

5. Formulations according to claim 1, wherein the optical bleachers have formula IV



25 wherein R_7 and R_8 can be the same or different and are hydrogen or methyl, M is sodium or potassium.

6. Formulations according to claim 1, wherein the optical bleachers have formula (V):



wherein R_8 is hydrogen or methyl and M is sodium or potassium.

- 40 7. The use of the formulations according to claims 1-6 for the preparation of detergents.