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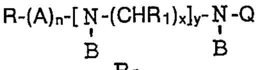
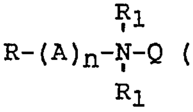
(54) A method for washing and a product for increasing the bleaching performance at washing.

(57) The bleaching effect at washing is increased by carrying out the washing in a wash water containing a hydrogen peroxide source and a bleach activator compound of the general formula


$R\text{-}(A)_n\text{-}[\underset{B}{N}\text{-}(CHR_1)_x]_y\text{-}\underset{B}{N}\text{-}Q$ (I) or


$R\text{-}(A)_n\text{-}\overset{R_1}{\underset{R_1}{N}}\text{-}Q$ (II)

wherein R is a higher hydrocarbon group and Q is a group $-R_2\text{-}S(O)_2\text{-}O\text{-}M$. A bleaching system contains these compounds and a hydrogen peroxide source, preferably a perborate. The bleach activator compounds give decomposition products which are surface active compounds.

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Description

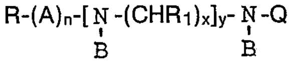
A method for washing and a product for increasing the bleaching performance at washing

The present invention relates to a method for washing using certain sulfonated compounds as bleach activators and to a product including these compounds and a hydrogen peroxide source.

Bleaching agents are used in washing in order to enhance the whiteness of the laundry. Perborates are among the most common bleaching agents and in the wash liquor these are decomposed to hydrogen peroxide which gives the actual bleaching effect. The bleaching effect of hydrogen peroxide starts at about 60° C and the full effect is reached at about 90° C. Washing at this temperature involves both a high energy consumption and an unnecessary wear of the laundry. As a consequence of this, so-called bleach activators have been developed in later years. Bleach activators are compounds which react further with the hydrogen peroxide during the wash-process and form peroxicarbonic acids which give the bleaching at lower temperatures. One example of such a bleach activator is the commercial product TAED, tetraacetylethylene diamine, which gives good bleaching effect at about 60° C.

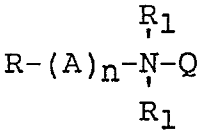
According to the present invention it has been found that certain sulfonated compounds which are characteristic in that they contain a sulfonic group, $-S(O)_2-O-$, nitrogen and a long-chain hydrocarbon group can be used as bleach activators and enhance the bleaching effect at washing. These compounds are advantageous in that they in the reaction with hydrogen peroxide give decomposition products which are amphoteric compounds which have surface activity. The bleaching effect of the sulfonated compounds begins to appear at about 40° C and is very good at temperatures of about 60° C.

The present invention thus relates to a method for increasing the bleaching effect at washing according to which method the washing is carried out in a wash liquor containing a hydrogen peroxide source and a compound which can be characterized by the general formula



$$R-(A)_n-[\underset{B}{N}-(CHR_1)_x]_y-\underset{B}{N}-Q$$

(I) or



$$R-(A)_n-\overset{R_1}{\underset{R_1}{N}}-Q$$

(II)

wherein R is a hydrocarbon group having from 7 to 22 carbon atoms, A is the group (C(O) or the group (OCH_2CH_2) and n is 0 or 1, R_1 is hydrogen or a lower alkyl group, whereby at least one group R_1 is a lower alkyl group for compounds of formula II, x is 2 or 3, y is an integer of 0 to 4, and Q is the group $-R_2-S(O)_2-O-M$ where R_2 is an alkylene group having 1 to 6 carbon atoms, which can contain a hydroxy group, and M is hydrogen, an ion from the groups alkali metals, alkaline earth metals, ammonium or substituted ammonium or a group $-C(O)R_3$, wherein R_3 is an alkyl group, and B is hydrogen or a group Q as defined.

As hydrogen peroxide source any known such compound can be used, for example perborates or percarbonates. It is preferred that the hydrogen peroxide releasing compound is sodium perborate, in the form of its monohydrate or tetrahydrate.

By the combination of the hydrogen peroxide source and the sulfonated compounds according to the above given formulae I and II which is used in the method of the present invention the latter compounds will react with HO_2^- ion from the hydrogen peroxide source and persulfonic acid derivatives with bleaching performance are formed in situ in the wash liquor. As decomposition product after the bleach reaction the corresponding amphoteric compounds are obtained and these compounds are surface active and thus contribute actively to an improved detergency performance.

In the compounds of the above given formulae R is a hydrocarbon group having 7 to 22 carbon atoms, and suitably from 12 to 20 carbon atoms. The hydrocarbon group R can be straight or branched, saturated or unsaturated and can also be a cycloalkyl-alkyl group, an arylalkyl or arylalkenyl group where the alkyl or alkenyl group contains at least 6 carbon atoms. It is preferred that R is an alkyl or alkenyl group. Compounds wherein A is a carbonyl group and compounds wherein n is 0 are preferred to those wherein A is the group (OCH_2CH_2). R_1 is hydrogen or a lower alkyl group, suitably having from 1 to 6 carbon atoms and preferably hydrogen or a methyl group, x is 2 or 3 and y is suitably 1, 2 or 3. The group R_2 is suitably an ethylene, propylene, 2-hydroxypropylene or a butylene group. M is hydrogen, an ion as defined above and hereby substituted ammonium should be understood as for example mono-, di- or trihydroxyalkylammonium, such as mono-, di or trihydroxyethylammonium, or the group $-C(O)R_3$. M is preferably hydrogen, sodium or magnesium or the group $-C(O)R_3$ wherein R_3 can have from 1 to 18 carbon atoms, suitably from 1 to 10. R_3 preferably has from 1 to 5 carbon atoms and is most preferably a methyl group.

The most preferred compounds are those of formula I wherein n is 0, R_1 is hydrogen, x is 3, y is 1 or 2, preferably 1, and all groups B are groups Q. R_2 in the groups Q are then preferably butylene groups and M is preferably a sodium ion or the group $-C(O)R_3$ wherein R_3 is a lower alkyl group, preferably a methyl group. The hydrocarbon group R in these compounds is most preferably a C12 to C18 alkyl or alkenyl group, or mixtures of these.

The compounds according to the formula II are, when being acids or salts, per se known and for surface activity used sulfobetaines. Derivatives of sulfobetaines wherein M is the group $-C(O)R_3$ are new compounds and can be prepared by reaction of sulfobetain with the acid anhydride which gives the group -C(O)R$_3$, eg acetic acid anhydride. Most of the compounds of formula I are also new compounds and these are suitably prepared starting from a mono-, di- or polyamine with the general formula R-(A)$_n$-[NH-(CHR$_1$)$_x$]$_y$-NH$_2$, wherein R, A, R$_1$, n, x and y have the previously given meanings. Preparation of compounds with the group -R$_2$-S(O)$_2$-O-M wherein R$_2$ is a methylene group can be carried out by reaction between the amine and chloromethanesulfonic acid, while compounds wherein R$_2$ is an ethylene group can be prepared by reaction between the amine and for example dichloroethane or dibromoethane and subsequent reaction with a sulfite reagent. Compounds wherein R$_2$ is an alkylene group with 3 or more carbon atoms are preferred, and most preferably R$_2$ is a propylene or butylene group, and these compounds are prepared by reaction between the amine and the corresponding alkylsultone. The reaction is here suitably carried out in water and at a temperature of from about 60 to about 90°C during times up to about 24 hours. It is suitable to use a molar excess of the sultone with regard to the amine, up to about 10 per cent. The compounds can subsequently be converted to salts or to compounds containing the group -C(O)R$_3$ by reaction with the desired acid anhydride.

Washing with the present bleaching enhancing and wash effect enhancing combination is carried out in a conventional manner with selection of temperature with regard to the textile material which is laundered and a good bleaching effect is obtained already at temperatures of about 40°C. The pH of the wash liquor should suitably be above 8. As the bleach activator compounds give a surface active effect comparatively high amounts of them can be used. The weight ratio of the compounds which according to the present invention are used as bleach activators to the hydrogen peroxide source should suitably be within the range of from 1:2 to 4:1, preferably within the range of from 1:1 to 3:1 and most preferably within the range of from 2:1 to 3:1. The term washing is herein used primarily for washing of textiles, ie laundering, but other industrial or household applications where the bleaching effect at washing according to the invention can be useful are of course also conceivable.

The present invention also relates to a bleaching product which comprises at least one hydrogen peroxide source and at least one bleach activator characterized by the given formulae I and II and having the for these formulae given definitions. The bleaching system of the invention contains as a hydrogen peroxide source any known such agent. The hydrogen peroxide source is suitably a perborate or a percarbonate and preferably sodium perborate in the form of its monohydrate or tetrahydrate. The weight ratio of bleach activator to hydrogen peroxide source in the combination should suitably be within the range of from 1:2 to 4:1, preferably within the range of from 1:1 to 3:1 and most preferably within the range of from 2:1 to 3:1.

The bleaching composition of the invention can be used in per se known detergent compositions in powder form. In these compositions can be included surface active compounds such as nonionic, anionic, amphoteric and cationic tensides, builders such as polyphosphates, zeolites and NTA, optical brighteners, foam regulators, perfumes and colouring agents etc. Other bleach activators and/or bleaching agents can of course also be included. The bleaching system of the invention is suitably present in an amount of from 10 to 40 per cent by weight, based on dry detergent composition, and preferably in an amount of from 20 to 35 per cent by weight.

The invention is further illustrated in the following examples which, however, are not intended to limit the same. Parts and per cent relate to parts by weight and per cent by weight unless otherwise stated.

Example

The bleaching effect of the following compounds was investigated:

1. Sulfobetaine according to formula II wherein R was an alkyl residue from coco fatty acid, ie with a hydrocarbon chain length distribution of essentially C12/C14, the groups R$_1$ were methyl groups and R$_2$ was a butylene group.

2. A compound with the formula R-NQ-(CH$_2$)$_3$-NQ$_2$ wherein R was an alkyl residue from coco fatty acid, ie with a hydrocarbon chain length distribution of essentially C12/C14, and the groups Q were groups -(CH$_2$)$_4$S(O)$_2$OH. This compound had been prepared according to the following: The corresponding diamine was reacted with butanesultone. 20.0 g (84.5 mmoles) of the diamine, 34.5 g (253.5 mmoles) of 1,4-butanesultone and 80 ml of water were charged to a 250 ml two-neck flask equipped with reflux condenser and a thermometer. The reaction was allowed to proceed for 21 hours under nitrogen atmosphere. During the process the from the beginning turbid emulsion became clear. The product was recrystallized three times by dissolving it in decanol at +70 to +90°C and was then, at a lower temperature, precipitated with petroleum ether. 27.6 g of the product was obtained and this corresponds to a yield of 51%. The product was analyzed by IR and gave two characteristic peaks for -S(O)$_2$- at 1195-1170 cm^{-1} and 1040 cm^{-1} respectively and a characteristic peak for -S-O- at 605 cm^{-1}, which is entirely in accordance with data given in literature.

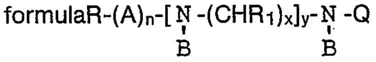
The products are also surface active agents and this is shown by their surface tension. The surface tension for the products was measured according to Du Noüi's ring at 25°C in 0.1% solution. The surface tension of compound 1 was measured to 40 mNm^{-1} and that of compound 2 to 48mNm^{-1} These values can be compared with that of water which is 72 mNm^{-1} and that of the well known surface active agent laurylalkylsulfonate which is 37 mNm^{-1}.

The bleaching effect of the compounds 1 and 2 in combination with a hydrogen peroxide source was investigated according to the following: A solution was prepared containing 0.5 g of tannin, 5 g of sodium hydrogencarbonate and 1.68 g of sodium metaborate (NABO$_2$.4H$_2$O) per liter. The pH of the solution was adjusted to about 10.5 with sodium hydroxide. For each test 100 ml of this solution was used and to this 50 mg of sodium perboratmonohydrate were added and 63 mg of compound 1, for solution 1, and, respectively, 113 mg of compound 2 for solution 2. The bleaching preformance was evaluated by following the decolouring of the solution by means of UV-spectrophotometry. The tests were carried out at a temperature of +60°C and the wave length was 450 nm. The results are given as UV-absorbency after the indicated time and the difference between the values at the start and the end. As a comparison is shown the results with solution 3 which was 100 ml of the above base solution with addition of solely 50 mg sodium perboratemonohydrate and solution 4 which was 100 ml of the base solution with addition of 50 mg sodium perborate and 20 mg of the commercial bleach activator TAED.

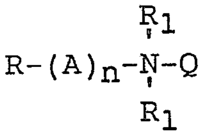
Solution	UV absorbency after given number of minutes					
	0	10	20	30	40	δ
1	1.368	1.106	1.029	0.947	0.888	0.480
2	1.274	0.969	0.822	0.771	0.743	0.531
3 ref	1.314	1.110	1.010	0.964	0.916	0.398
4 ref	1.336	0.999	0.854	0.772	0.721	0.615

Claims

1. A method for enhancing the bleaching effect at washing, characterized in that the washing is carried out in a wash liquor containing a hydrogen peroxide source and a bleach activator compound having the general formula



$R\text{-}(A)_n\text{-}[\underset{B}{N}\text{-}(CHR_1)_x]_y\text{-}\underset{B}{N}\text{-}Q$ (I) or



$R\text{-}(A)_n\text{-}\overset{R_1}{\underset{R_1}{N}}\text{-}Q$ (II)

wherein R is a hydrocarbon group having from 7 to 22 carbon atoms, A is the group (C(O)) or the group (OCH_2CH_2) and n is 0 or 1, R_1 is hydrogen or a lower alkyl group, whereby at least one group R_1 is a lower alkyl group for compounds of formula II, x is 2 or 3, y is an integer of 0 to 4, and Q is the group $-R_2\text{-}S(O)_2\text{-}O\text{-}M$ where R_2 is an alkylene group having 1 to 6 carbon atoms, which can contain a hydroxy group, and M is hydrogen, an ion from the groups alkali metals, alkaline earth metals, ammonium or substituted ammonium or a group $-C(O)R_3$, wherein R_3 is an alkyl group, and B is hydrogen or a group Q as defined.

2. A method according to claim 1, characterized in that the bleach activator is a compound in which n is 0 or A is the group (C(O)), R is an alkyl or alkenyl group having from 7 to 22 carbon atoms, R_1 is hydrogen or a methyl group and y is 1, 2 or 3.

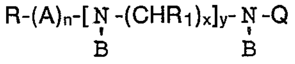
3. A method according to claim 1 or 2, characterized in that bleach activator is a compound in which R_2 is an ethylene, propylene, hydroxypropylene or butylene group.

4. A method according to claim 1, 2 or 3, characterized in that the bleach activator is a compound in which M is hydrogen, sodium, magnesium or the group $-C(O)R_3$ wherein R_3 is an alkyl group having from 1 to 5 carbon atoms.

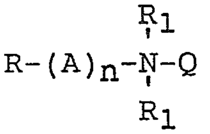
5. A method according to any of the preceding claims, characterized in that the bleach activator is a compound of formula I wherein all groups B are $-R_2\text{-}S(O)_2\text{-}O\text{-}M$ groups.

6. A method according to any of the preceding claims, characterized in that the hydrogen peroxide source is a perborate.

7. A bleaching system comprising a hydrogen peroxide source and a bleach activator, characterized in that the bleach activator is a compound of the general formula



$R\text{-}(A)_n\text{-}[\underset{B}{N}\text{-}(CHR_1)_x]_y\text{-}\underset{B}{N}\text{-}Q$ (I) or



$R\text{-}(A)_n\text{-}\overset{R_1}{\underset{R_1}{N}}\text{-}Q$ (II)

wherein R is a hydrocarbon group having from 7 to 22 carbon atoms, A is the group (C(O)) or the group (OCH_2CH_2) and n is 0 or 1, R_1 is hydrogen or a lower alkyl group, whereby at least one group R_1 is a lower alkyl group for compounds of formula II, x is 2 or 3, y is an integer of 0 to 4, and Q is the group $-R_2\text{-}S(O)_2\text{-}O\text{-}M$ where R_2 is an alkylene group having 1 to 6 carbon atoms, which can contain a hydroxy group, and M is hydrogen, an ion from the groups alkali metals, alkaline earth metals, ammonium or substituted ammonium or a group -C(O)R_3, wherein R_3 is an alkyl group, and B is hydrogen or a group Q as defined.

8. A bleaching system according to claim 7, characterized in that bleach activator is a compound wherein n is 0 or A is the group (C(O)), R is an alkyl or alkenyl group having from 7 to 22 carbon atoms, R_1 is hydrogen or a methyl group and y is 1, 2 or 3 and R_2 is an ethylene, propylene, hydroxypropylene or butylene group.

9. A bleaching system according to claim 7 or 8, characterized in that the hydrogen peroxide source is a perborate.

10. A bleaching system according to claim 7, 8 or 9, characterized in that the weight ratio of bleach activator to hydrogen peroxide source is within the range of from 1:2 to 4:1.