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(54) A process for enhancing the bleaching effect at washing and use of certain amphoteric compounds in a detergent composition for enhancing the bleaching effect.

(57) The bleaching effect at washing in the presence of perborates is enhanced by using a detergent composition containing perborate and up to 4.5 per cent by weight of an amphoteric compound according to the formula

$$R - [N(B) - (CHR_1)_x]_y - N(B) - Q$$

wherein R is a hydrocarbon group having 7 to 22 carbon atoms, R_1 is hydrogen or alkyl with 1 to 6 carbon atoms, x is 2 or 3, y is 0 or an integer of 1 to 4 and Q is (R_2-COOM) where R_2 is alkylene with 1 to 6 carbon atoms, M is H, an alkali metal, an alkaline earth metal, an ammonium or a substituted ammonium ion, and B is hydrogen or is defined according to Q. Alternatively the composition contains at least one amine oxide of a compound of the above definition. Compounds as defined are used in detergent compositions containing perborate in order to enhance the bleaching effect at washing with the compositions.

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A PROCESS FOR ENHANCING THE BLEACHING EFFECT AT WASHING AND USE OF CERTAIN AMPHOTERIC COMPOUNDS IN A DETERGENT COMPOSITION FOR ENHANCING THE BLEACHING EFFECT

The invention relates to a method for enhancing the bleaching effect at washing in the presence of perborates. The bleaching effect is enhanced by using certain amphoteric compounds, or amine oxides of these, and the invention also relates to the use of such compounds in detergent compositions containing perborates.

Commercial detergent compositions usually contain perborates which in alkaline aqueous solutions release hydrogen peroxide. This is decomposed into H^+ and HO_2^-, which has a bleaching effect at washing. However, the hydrogen peroxide is to a high degree decomposed into free radicals, which do not have a bleaching effect, in the presence of metal ions which are commonly present in the wash water such as calcium, magnesium, copper, iron and manganese. A common method for preventing the decomposition into free radicals is the addition of complexing agents, such as phosphonates and EDTA, to the detergent composition. Despite additions of complexing agents part of the hydrogen peroxide is anyhow decomposed to free radicals at the washing. Several of these complexing agents are also doubtful with regard to environment.

Amphoteric compounds of the type which can be characterized by the general formula

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

wherein R is a higher hydrocarbon group, R_1 is hydrogen or a lower alkyl group, x is 2 or 3, y is 0 to 4, Q is a group —R_2COOM wherein R_2 is an alkylene group and M is hydrogen or another cation and B is hydrogen or a group Q are per se known. Compounds of this type are disclosed in the European patent applications 160507, 162600 and 214868. The compounds are used in detergent and shampoo compositions for surface activity and for their antimicrobial properties. From the European patent application 314648 it is also known to use amphoteric compounds of this type in combination with zeolites in detergent compositions since it has been found that they show a synergistic effect at softening of water. It is also evident from this application that the detergent compositions may contain perborates as bleaching agents. However, the amphoteric compound should be present in fairly high amounts to give the desired effect. Further, it is advised against the use of the amphoteric compounds in detergent compositions containing anionic tensides.

It has now surprisingly been found that certain amphoteric compounds, or amine oxides of these, enhance the bleaching effect at washing in the presence of perborates. The amphoteric compounds and their amine oxides can inhibit the decomposition of hydrogen peroxide to free radicals at washing, which probably depends on their complexing ability.

The invention thus relates to a process for enhancing the bleaching effect at washing under alkaline conditions in the presence of perborates as defined in the patent claims. The washing is carried out under alkaline conditions using a detergent composition containing perborate and up to 4.5 per cent by weight of at least one amphoteric compound of the general formula (I)

$$R - [\underset{\underset{B}{|}}{N} - (CHR_1)_x]_y - \underset{\underset{B}{|}}{N} - Q \quad (I)$$

wherein R is a hydrocarbon group having 7 to 22 carbon atoms, R_1 is hydrogen or alkyl with 1 to 6 carbon atoms, x is 2 or 3, y is 0 or an integer of 1 to 4 and Q is (R_2-COOM) where R_2 is alkylene with 1 to 6 carbon atoms, M is H, an alkali metal, an alkaline earth metal, an ammonium or a substituted ammonium ion, and B is hydrogen or is defined according to Q, or a detergent composition containing perborate and up to 4.5 per cent by weight of at least one amine oxide of the defined amphoteric compound.

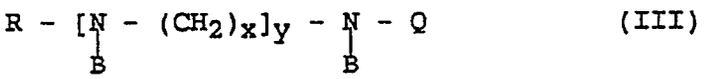
The composition can thus contain corresponding amounts of at least one amine oxide of amphoteric compound as above defined. One or several of the nitrogen groups in the amphoteric compounds can be oxidized. Useful compounds can be defined by the general formula (II)

$$R - [\overset{O}{\uparrow}\underset{\underset{B}{|}}{N} - (CHR_1)_x]_y - \overset{O}{\uparrow}\underset{\underset{B}{|}}{N} - Q \quad (II)$$

wherein R, R_1, x, y, Q, R_2, M and B have the above given definitions. However, the term amine oxide is used to include also compounds wherein only some of the amine groups have been oxidized. The amine oxides of the defined amphoteric compounds are new compounds and can also be used for the same purposes as the previously known amphoteric compounds of formula (I), ie as tensides, antimicrobial agents or take part in softening of water.

In the above given formulae the hydrocarbon group R can be straight or branched, saturated or unsaturated, and may contain substituents such as hydroxyl groups or carbonyl groups. R is preferably an alkyl or alkenyl group, but can also be a cycloalkyl-alkyl group, an aralkyl or aralkenyl group where the alkyl or alkenyl group contains at least 6 carbon atoms. R suitably contains 12 to 22 carbon atoms, preferably 12 to 20 carbon atoms. In particular it is preferred that R is a hydrocarbon group originating from natural fatty acids and particularly from tallow or coco fatty acid. R_1 is hydrogen or a lower alkyl group, suitably with 1 to 6 carbon atoms and preferably hydrogen or a methyl group. x is 2 or 3 and y is suitably 1, 2, 3 or 4 and preferably 1, 2 or 3. The group R_2 is suitably a methylene or ethylene group, preferably a methylene group. M is hydrogen or an ion from the groups alkali metals, alkaline earth metals, ammonium or substituted ammonium such as for example mono-, di- or trihydroxyethylammonium. M is preferably alkali metal, especially sodium. It is particularly preferred that all groups B in the compounds of the above given general formulae are groups Q.

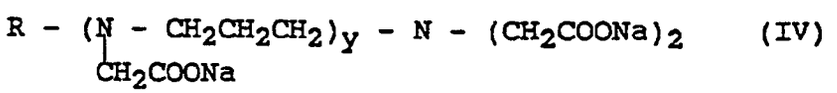
Especially preferred compounds according to formula (I) are included in formula (III)



(III)

wherein Q is CH_2-COOM or CH_2CH_2-COOM, y is 1, 2 or 3 and M, R, x and B are as earlier defined, or an amine oxide of a compound of this formula. Preferably all groups B are groups Q.

In particular compounds according to formula (III) included in formula (IV) are preferred



(IV)

wherein y is 1, 2 or 3 and R is as earlier defined or an amine oxide of a compound of this formula. Mixtures of compounds with different values for y can also be used. It is especially preferred that R originates from tallow fatty acid.

Amphoteric compounds which can be used according to the present invention are per se previously known, for example from the earlier mentioned patent applications. They are also commercially available under the trade name Ampholak(R). Amine oxides can be prepared by allowing one of the earlier known amphoteric compounds to react with a per-compound, such as peracid or hydrogen peroxide, under acid conditions. The detergent composition suitably contains from 0.5 per cent by weight and preferably from 0.5 to 3 per cent by weight of the amphoteric compound and/or amine oxide of this.

The perborate can be present as mono- or tetrahydrate with an alkali metal, such as for example sodium, as positive counter ion. Suitable amounts in the composition is within the range of from 6 to 25 per cent by weight, preferably from 10 to 20 per cent by weight.

The invention also relates to the use of amphoteric compounds as above defined or amine oxides of these in detergent compositions containing perborates to enhance the bleaching effect at washing with the compositions. The compositions contain up to 4.5 per cent by weight, suitably from 0.5 per cent by weight and preferably from 0.5 to 3 per cent by weight of at least one of the defined amphoteric compounds, or an amine oxide of this. Suitable amounts of perborates in the compositions are within the range of from 6 to 25 per cent by weight, preferably from 10 to 20 per cent by weight.

The combination according to the invention of perborate and amphoteric compound, or amine oxide of the amphoteric compound, can be used in otherwise conventional detergent compositions intended at first hand for laundering. The detergent compositions are suitably in powder form and can be prepared in a conventional manner, such as by dry blending, agglomeration or spray drying a slurry of the components.

In the detergent compositions tensides are also present, preferably anionic and/or nonionic tensides and/or soaps. The anionic tensides are suitably present in an amount of from 6 to 20 per cent by weight and can for example comprise linear alkylbenzene sulfonate, secondary alkane sulfonate, alcohol-ethoxy sulfate or alpha-olefin sulfonate. The nonionic tensides are suitably present in an amount of from 2 to 8 per cent by weight and can for example comprise alkoxylated compounds, such as fatty alcohols, alkyl phenols and alkyl amines. The soaps are suitably present in amounts of from 2 to 4 per cent by weight and can for example comprise sodium—

or potassium salts of tallow. The compositions can moreover comprise per se known components such as water glass, enzymes, builders such as phosphates or zeolites, fillers such as sodium sulfate, carbonates and bicarbonates, bleach activators such as TAED (tetraacetylethylene diamine) or TAGU (tetraacetylglucoluril), diperoxy acids, foam regulators, perfumes and colorants.

A detergent composition containing perborate and amphoteric compounds, or amine oxides, can for example contain the following main components up to 100%.

Compounds as according to the invention	0.5 - 4.5	per cent by weight
Perborates	6 - 25	"
Anionic tensides	6 - 20	"
Nonionic tensides	2 - 8	"
Soaps	2 - 4	"
Fillers	10 - 50	"
Phosphates	10 - 30	"

As alternative to the phosphates 10 to 30 per cent by weight of zeolites and 3 to 10 per cent by weight of polycarboxylates can be used.

The invention is further illustrated in the following examples which, however, are not intended to limit the same. All amounts are given in per cent by weight, unless otherwise stated.

Example 1

An amine oxide according to the invention was prepared by mixing 100 g of Ampholak 7TX(R) (corresponds to formula (III) above and is a mixture of compounds with different values for y from 1 to 3 and wherein R originates from tallow fatty acid) with 10 g of H_2O_2 (35%) and heating at 70°C for 1 hour. The mixture was allowed to cool and was then freeze dried.

Example 2

In order to investigate the effect of an amphoteric compound according to the invention the following detergent compositions were used ;

A : 15% LAS sulfosoft(R) (linear alkylbenzenesulfonate)
2% Berol 25 - 3(R) (nonionic ethoxylate)
6% Berol 25 - 7(R) (nonionic fatty alcohol ethoxylate)
6% disilicate
20% sodium perborate tetrahydrate
20% sodium tripolyphosphate
30% sodium sulphate
1% Ampholak 7TX(R)

B : The same formulation as in A, with the exception that the detergent composition contained 1% of the amine oxide of Example 1 instead of Ampholak 7TX.

C. The same formulation as in A, with the exception that the detergent did not contain any amphoteric compound or amine oxide as according to the invention.

In all tests water with a hardness of 25° dH with regard to Ca/Mg in the ratio 3 :1 was used. Further 3 ppm metal ions were added according to the following :

2.5 ppm Fe^{3+}
0.25 ppm Cu^{2+}
0.25 ppm Mn^{2+}

10 g detergent composition per liter of water were used. The solutions, with a pH of 9.5, were stored for 60 minutes at 60°C. They were then titrated with sodium thiosulfate in order to determine remaining content of active oxygen. The results are shown in Table 1.

TABLE 1

Test No.	Amount of sample (g)	Active oxygen (g)	Yield (%)
A1	38.260	0.0824	80
A2	43.260	0.0812	79
A3	39.160	0.0754	78
A4	41.330	0.0806	78
B1	36.587	0.0960	93
B2	41.780	0.0945	92
B3	38.340	0.0986	96
B4	40.190	0.0969	94
C1	39.908	0.0724	70
C2	39.720	0.0678	66
C3	38.532	0.0710	69
C4	41.130	0.0683	66

The tests show that if no compound as according to the invention is used (according to tests C) on an average about 68% of the active oxygen remain after 60 minutes at 60°C. The compositions according to the invention (tests A and B) give a corresponding yield of 79% and 94% respectively. The better results for the detergent with amine oxide might be due to the fact that part of the hydrogen peroxide in the tests according to A is consumed in the oxidation of nitrogen groups in the amphoteric compound.

Example 3

Pieces of cloth were immersed in tea and red wine respectively and then allowed to dry. The reflectance was then measured at 460 nm, and then the pieces were washed in a washing machine at 60°C for about 60 minutes in the same type of water as used in Example 2. 10 g detergent, formulated according to Example 2A and 2C respectively, were added per liter of water. The reflectance was then measured again and the difference in relation to the reflectance before the washing was calculated. The results are shown in Table 2.

TABLE 2

Detergent	Stains	Difference in reflectance
A	Wine	19.6
A	Tea	5.1
C	Wine	7.3
C	Tea	0.0

The tests show a considerable improvement in the bleaching effect with the detergent composition according to the invention.

Claims

1. A process for enhancing the bleaching effect at washing under alkaline conditions in the presence of perborates, characterized in that the washing is carried out using a detergent composition containing perborate and up to 4.5 per cent by weight of at least one amphoteric compound of the general formula (I)

$$R - [N(B) - (CHR_1)_x)]_y - N(B) - Q \qquad (I)$$

wherein R is a hydrocarbon group having 7 to 22 carbon atoms, R_1 is hydrogen or alkyl with 1 to 6 carbon atoms, x is 2 or 3, y is 0 or an integer of 1 to 4 and Q is (R_2-COOM) where R_2 is alkylene with 1 to 6 carbon atoms, M is H, an alkali metal, an alkaline earth metal, an ammonium or a substituted ammonium ion, and B is hydrogen or is defined according to Q, and/or that the detergent composition contains up to 4.5 per cent by weight of at least one amine oxide of the defined amphoteric compound.

2. A process according to claim 1, characterized in that the amphoteric compound has the general formula (III)

$$R - [N(B) - (CH_2)_x]_y - N(B) - Q \qquad (III)$$

where Q is CH_2-COOM or CH_2CH_2-COOM, y is 1, 2 or 3, and M, R, x and B are defined as in claim 1.

3. A process according to claim 2, characterized in that the amphoteric compound has the general formula (IV)

$$R - (N(CH_2COONa) - CH_2CH_2CH_2)_y - N - (CH_2COONa)_2 \qquad (IV)$$

wherein y is 1, 2 or 3 and R is as defined in claim 1.

4. A process according to any of claims 1 to 3, characterized in that the amphoteric compound is present in an amount of from 0.5 to 3 per cent by weight.

5. A process according to any of the preceding claims, characterized in that the perborate is present in an amount of from 6 to 25 per cent by weight.

6. Use of up to 4.5 per cent by weight of at least one amphoteric compound of the general formula (I)

$$R - [N(B) - (CHR_1)_x)]_y - N(B) - Q \qquad (I)$$

wherein R is a hydrocarbon group having 7 to 22 carbon atoms, R_1 is hydrogen or alkyl with 1 to 6 carbon atoms, x is 2 or 3, y is 0 or an integer of 1 to 4 and Q is (R_2-COOM) where R_2 is alkylene with 1 to 6 carbon atoms, M is H, an alkali metal, an alkaline earth metal, an ammonium or a substituted ammonium ion, and B is hydrogen or is defined according to Q, and/or at least one amine oxide of the defined amphoteric compound, in detergent compositions containing perborate to enhance the bleaching effect at washing with the compositions.

7. Use according to claim 6, whereby the amphoteric compound has the general formula (III)

$$R - [N(B) - (CH_2)_x]_y - N(B) - Q \qquad (III)$$

where Q is CH_2-COOM or CH_2CH_2 -COOM, y is 1, 2 or 3, and M, R, x and B are defined as in claim 6.

8. Use according to claim 7, whereby the amphoteric compound has the general formula (IV)

$$R - (N(CH_2COONa) - CH_2CH_2CH_2)_y - N - (CH_2COONa)_2 \qquad (IV)$$

wherein y is 1, 2 or 3 and R is as defined in claim 6.

9. Use according to any of claims 6 to 8, whereby the amphoteric compound is present in an amount of from 0.5 to 3 per cent by weight.

10. Use according to any of claims 6 to 9, whereby the detergent compositions contain from 6 to 25 per cent by weight of perborate.

11. Use according to any of claims 6 to 11, whereby the detergent compositions contain at least one anionic tenside.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT

EP 90850401.2

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP - A2 - 0 314 648 (KENOBEL) * Claims 1-3; page 3, lines 33,34,37-53 *	1-3, 5-8, 10,11	C 11 D 1/88 C 11 D 3/395 C 11 D 1/94
A	EP - A2 - 0 160 507 (FISHLOCK LOMAX) * Claims 1,7 *	1,6,11	
A	EP - A1 - 0 162 600 (FISHLOCK LOMAX) * Claim 1 *	1,6	
A	EP - A2 - 0 325 124 (COLGATE PALMOLIVE) * Page 3, line 40 - page 4, line 9; abstract; example *	1,5,6	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 11 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	20-02-1991	WILFLINGER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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