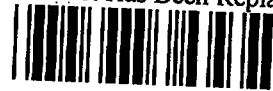


REPLACED SHEETS		SG
☒ Description	: paged 01 to paged 10	
☒ Claim(s)	: paged 11 to paged 13	
☐ Drawing(s)	: paged to paged	
☒ Abstract	: paged to paged 14	

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-1-

WASHING AGENT WITH STORED STABILIZED BLEACH SYSTEM

- 5 The present invention relates to a washing agent with a storage-stabilized bleach system and 2 to 20% by weight of detergents and conventional washing auxiliaries, including fillers, in particular to a domestic washing agent for heavy laundry, white laundry and colored laundry, as is used in washing machines.
- 10 Due to the increasingly wide use of domestic washing machines, the washing agent must be adapted to the changed washing conditions.
- 15 Modern washing agents are therefore composed of a combination of detergents as the washing-active substances, bleaches and additives which boost the washing power, the so-called builders which, on the one hand, eliminate the hardness of the washing liquor and, on
- 20 the other hand, prevent depositions of inorganic salts on the material being washed and thereby ensure a "soft handle" of the washed material after the washing process.
- 25 Polymeric phosphates, in particular sodium triphosphate, are regarded as excellent builders. Because of the danger of eutrophication of rivers and lakes by the phosphate content in domestic effluents, the use of



zeolites as a builder has been proposed.

It has been found that the use of zeolites as a builder has the disadvantages that the washed material loses the desired "soft handle" in the course of a plurality of washing steps. A further point is that, during the storage time between the production and the consumption of the washing agent, the washing agent loses part of its washing power by decomposition of the bleach.

10

DE 3416,669 A1
It has therefore been proposed in US-A-4,728,443 to add to the washing agent an additional 1 to 20% by weight of a crystalline layered silicate or alkali metal silicate. In this way, it was possible to achieve a "soft handle" of the washed material even if zeolites were used as the builders; however, the storage stability of the washing agent was not affected thereby.

15

It is the object of the invention to provide a washing agent with a storage-stabilized bleach system, which has a boosted bleach action on the washed material and maintains the "soft handle" in the washed material.

20

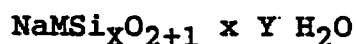
Surprisingly, it has been found that a washing agent with a storage-stabilized bleach system is obtained when it contains 10 to 50% by weight, in particular 20 to 35% by weight, of a crystalline layered silicate as the builder and 1 to 5% by weight, in particular 2.0 to

25



3.0% by weight, of tetraacetylenediamine (TAED) and a bleach, the quantity of bleach being such that 0.5 to 4% by weight, in particular 1.0 to 2.5% by weight, of washing-active oxygen (AVOX) is present in
5 the washing agent.

A crystalline layered silicate of the general formula



where

10 X = 1.9 to 4.0,

M = Na or H and

Y = 0 to 20

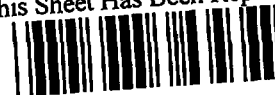
has proved particularly suitable. Very particularly good results are obtained when the crystalline layered
15 silicate corresponds to the δ -modification of $\text{Na}_2\text{Si}_2\text{O}_5$.

Further preferred and selective features of the washing agent according to the invention can be that

20 a) the crystalline layered silicate has a particle diameter from 0.01 to 1,000 μm , in particular from 1 to 20 μm ,

b) the crystalline layered silicate has an ion
25 exchange capacity from 400 to 1,200 mmol of Na^+ /100 g of dry matter,

c) the bleach is sodium perborate tetrahydrate,



sodium perborate monohydrate and/or sodium percarbonate,

- 5 d) it contains inorganic and/or organic phosphates, borates, citrates, gluconates, nitrilotriacetic acid and/or iminodiacetates as additional builders in quantities of up to 20% by weight,
- 10 e) it is composed of agglomerate particles having a particle size in the range from 0.25 to 2.5 mm and was obtained by a spray-mist mixing process,
- 15 f) it contains, as the detergent, alkali metal salts of alkylbenzenesulfonates, higher alkylsulfonates and/or higher fatty alcohol polyethoxylate-sulfates, in particular with alkyl radicals having 10 to 18 carbon atoms on average in the alkyl group, and
- 20 g) it contains carboxymethylcellulose, carboxymethyl starch and/or methylcellulose in quantities of up to 10% by weight as a washing auxiliary.

25 The crystalline layered silicates used in the production of the washing agent according to the invention can be prepared according to US-A-4,664,839.

DE 3413571 A1

The washing-active oxygen (AVOX) of the bleach and of



the washing agent was determined in accordance with the instructions by Dr. E. Heinerth, Tenside 2 (1965) 180. The sodium perborate tetrahydrate ($\text{NaBO}_3 \times 4 \text{H}_2\text{O}$) investigated had an AVOX number of 10% by weight; 5 sodium perborate monohydrate ($\text{NaBO}_3 \times \text{H}_2\text{O}$) had an AVOX number of 15% by weight and sodium percarbonate ($2 \text{Na}_2\text{CO}_3 \times 3 \text{H}_2\text{O}_2$) had an AVOX number of 13.5% by weight.

10 The washing power (bleach action) of the washing agent was determined as the whiteness of the test fabrics (WFK polyester/cotton soiled by tea, order code 20 G) according to DIN 44983.

15 The washing power (bleach action) of the washing liquor was determined by the difference method which follows from equation I

$$\% \text{WK} = \% \text{WG}_g - \% \text{WG}_b$$

where: $\% \text{WK}$ = % washing power (bleach action)

20 $\% \text{WG}_g$ = % whiteness of the washed material

$\% \text{WG}_b$ = % whiteness of the unwashed material.

The storage tests were carried out under the following forced test conditions:

25 The washing agent to be investigated was stored in a conditioned cabinet at a relative atmospheric humidity of 70% at a temperature of 37°C . During the test, the washing agent was packed in a waxed carton. The water



vapor permeability of the packaging was $0.4 \text{ g/m}^2 \times \text{h}$.

The tested washing agent formulations are listed in Table 1.

5

The degradation values of the bleach as a function of the time after the forced storage test conditions are compiled in Table 2. In addition, two commercially available washing agents based on zeolite and sodium tripolyphosphate were included in Table 2. The degradation of bleach, in particular that of sodium percarbonate, is very high in the presence of zeolite.

10

The test results according to DIN 44983 for the various washing agent formulations, as determined in accordance with equation I, are listed in Table 3.

15

The test values show that the bleach action is enhanced when a crystalline layered silicate is used as the builder in place of zeolite. In the presence of TAED, the washing power (bleach action) of the washing agent is boosted synergistically.

20

The assessment of handle by a panel of experts gave a markedly "softer handle" of the washed material, which had been washed with the washing agents according to the invention in accordance with Examples 2 and 3, as

25



compared with the washed material which had been washed with the zeolite-containing washing agent in accordance with Examples 1 and 4.

T A B L E 1
Washing agent formulations

Ingredients (% by weight)	Example 1	Example 2 *)	Example 3 *)	Example 4	Example 5
Anionic surfactants	6.5	6.5	6.5	6.5	6.5
Nonionic surfactants	3.5	3.5	3.5	3.5	3.5
Soap	4.5	4.5	4.5	4.5	4.5
Zeolite A	21.5	-	-	21.5	-
δ - $\text{Na}_2\text{Si}_2\text{O}_5$	-	21.5	21.5	-	21.5
Soda	7.5	-	-	7.5	-
$\text{NaOH} \times \text{H}_2\text{O}$	10.0	10.0	-	-	-
IAED	2.5	2.5	2.5	-	-
$2 \text{Na}_2\text{CO}_3 \times 3 \text{H}_2\text{O}$	-	-	18.0	18.0	18.0
Optical brighteners	0.2	0.2	0.2	0.2	0.2
Soil carriers	1.5	1.5	1.5	1.5	1.5
Enzymes	0.3	0.3	0.3	0.3	0.3
Dispersants (polycarboxylates)	4.0	2.0	-	4.0	2.0
Na silicate	5.0	-	-	5.0	-
Extender (Na_2SO_4)		to 100%			

*) washing agent according to the invention



T A B L E 2
AVOX degradation

Example	AVOX degradation in %		
	1 week	2 weeks	3 weeks
1	14	29	32
2 *)	0	9	11
3 *)	0	5	9
4	33	50	86
5	0	4	8
Zeolite-based commercial material	16	22	37
Na ₅ P ₃ O ₁₀ -based commercial material	0	16	21

*) washing agent according to the invention

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T A B L E 3
Bleach action, determined in accordance with
equation I

Example	% Washing power
1	37.5
2 *)	43.0
3 *)	42.0
4	31.5
5	38.5

*)washing agent according to the invention

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We claim:



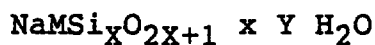
1. A washing agent with a storage-stabilized bleach system, with 2 to 20% by weight of detergents and conventional washing auxiliaries, including fillers, containing 10 to 50% by weight ^{in particular} of a crystalline layered silicate as the builder and 1 to 5% by weight ^{in particular} of tetraacetythylenediamine (TAED) and a bleach, the quantity of bleach being such that 0.5 to 4% by weight ^{in particular} of washing-active oxygen (AVOX) is present in the washing agent.
- (diff) 2. The washing agent as claimed in claim 1, containing 20 to 35% by weight of a crystalline layered silicate as the builder.
- (diff) 3. The washing agent as claimed in claim 1, ^{wherein} containing 2.0 to 3.0% by weight of tetraacetyl-ethylenediamine (TAED).
- (diff) 4. The washing agent as claimed in claim 1, ^{crystal} wherein the bleach quantity is such that 1.0 to 2.5% by weight of washing-active oxygen (AVOX) is present in the washing agent.

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5. (2) The washing agent as claimed in claim 1, wherein the crystalline layered silicate is of the formula



where

X = 1.9 to 4.0

M = Na or H and

Y = 0 to 20.

6. (3) The washing agent as claimed in claim 1, wherein the crystalline layered silicate corresponds to the δ -modification of $\text{Na}_2\text{Si}_2\text{O}_5$.

7. (4) The washing agent as claimed in claim 1, wherein the crystalline layered silicate has a particle diameter from 0.01 to 1,000 μm .

8. (4?) The washing agent as claimed in claim 7, wherein the crystalline layered silicate has a particle diameter from 1 to 20 μm .

9. (5) The washing agent as claimed in claim 1, ^{2,3,4} wherein the crystalline layered silicate has an ion exchange capacity from 400 to 1,200 mmol of Na^+ /100 g of dry matter.

10. (7) The washing agent as claimed in claim 1, ^(1st) containing inorganic phosphates, organic





phosphates, borates, citrates, gluconates, nitrilotriacetic acid (NTA), iminodiacetates or mixtures thereof as additional builders in quantities of up to 20% by weight.

11. The washing agent as claimed in claim 1, ^(1 to 7) composed
(8) of agglomerate particles having a particle size in the range from 0.25 to 2.5 mm and obtained by means of a spray-mist mixing process.

12. The washing agent as claimed in claim 1, ^(1 to 5) wherein
(6) the bleach is sodium perborate tetrahydrate, sodium perborate monohydrate, sodium percarbonate or mixtures thereof.

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Washing agent with storage-
stabilized bleach system

Abstract of the disclosure:

The invention relates to a washing agent with a storage-stabilized bleach system and 2 to 20% by weight of detergents and conventional washing auxiliaries, including fillers, the washing agent containing 10 to 50% by weight of a crystalline layered silicate as a builder as well as 1 to 5% by weight of tetraacetylenediamine (TAED) and a bleach, the quantity of bleach being such that 0.5 to 4% by weight of washing-active oxygen (AVOX) is present in the washing agent.

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Date: 3 FEB 1996

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☐	Drawing(s)	: paged 14 to paged 15
☒	Abstract	: paged 16 to paged 17
DATE OF RECEIPT		13/02/96

Washing agent with storage-stabilized
bleach system

5 The present invention relates to a washing agent with a
storage-stabilized bleach system and 2 to 20% by weight
of detergents and conventional washing auxiliaries,
including fillers, in particular to a domestic washing
agent for heavy laundry, white laundry and colored
10 laundry, as is used in washing machines.

Owing to the increasingly wide use of domestic washing
machines, the washing agent must be adapted to the
changed washing conditions.

15

Modern washing agents are therefore composed of a com-
bination of detergents as the washing-active sub-
stances, bleaches and additives which boost the washing
power, the so-called builders which, on the one hand,
20 eliminate the hardness of the washing liquor and, on
the other hand, prevent depositions of inorganic salts
on the material being washed and thereby ensure a "soft
handle" of the washed material after the washing
process.

25

Polymeric phosphates, in particular sodium triphospho-
phate, are regarded as excellent builders. Because of
the danger of eutrophication of rivers and lakes by the

phosphate content in domestic effluents, the use of zeolites as a builder has been proposed.

5 It has been found that the use of zeolites as a builder has the disadvantages that the washed material loses the desired "soft handle" in the course of a plurality of washing steps. A further point is that, during the storage time between the production and the consumption of the washing agent, the washing agent loses part of
10 its washing power by decomposition of the bleach.

It has therefore been proposed in DE-34 16 669 A1 to add to the washing agent an additional 1 to 20% by weight of a crystalline layered silicate or alkali
15 metal silicate. In this way, it was possible to achieve a "soft handle" of the washed material even if zeolites were used as the builders; however, the storage stability of the washing agent was not affected thereby.

20

It is the object of the invention to provide a washing agent with a storage-stabilized bleach system, which has a boosted bleach action on the washed material and maintains the "soft handle" in the washed material.

25

Surprisingly, it has been found that a washing agent with a storage-stabilized bleach system is obtained when it contains 10 to 50% by weight, in particular 20

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to 35% by weight, of a crystalline layered silicate as the builder and 1 to 5% by weight, in particular 2.0 to 3.0% by weight, of tetraacetylenediamine (TAED) and a bleach, the quantity of bleach being such that
5 0.5 to 4% by weight, in particular 1.0 to 2.5% by weight, of washing-active oxygen (AVOX) is present in the washing agent.

A crystalline layered silicate of the general formula
10
$$\text{NaMSi}_x\text{O}_{2+1} \times Y \text{ H}_2\text{O}$$

where

$x = 1.9$ to 4.0 ,

$M = \text{Na}$ or H and

$Y = 0$ to 20

15 has proved particularly suitable. Very particularly good results are obtained when the crystalline layered silicate corresponds to the δ -modification of $\text{Na}_2\text{Si}_2\text{O}_5$.

Further preferred and selective features of the washing
20 agent according to the invention can be that

a) the crystalline layered silicate has a particle diameter from 0.01 to $1,000 \mu\text{m}$, in particular from 1 to $20 \mu\text{m}$,

25

b) the crystalline layered silicate has an ion exchange capacity from 400 to $1,200 \text{ mmol}$ of Na^+ /100 g of dry matter,

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c) the bleach is sodium perborate tetrahydrate, sodium perborate monohydrate and/or sodium percarbonate,

5

d) it contains inorganic and/or organic phosphates, borates, citrates, gluconates, nitrilotriacetic acid and/or iminodiacetates as additional builders in quantities of up to 20% by weight,

10

e) it is composed of agglomerate particles having a particle size in the range from 0.25 to 2.5 mm and was obtained by a spray-mist mixing process,

15 f) it contains, as the detergent, alkali metal salts of alkylbenzenesulfonates, higher alkylsulfonates and/or higher fatty alcohol polyethoxylate-sulfates, in particular with alkyl radicals having 10 to 18 carbon atoms on average in the alkyl group, and

20

g) it contains carboxymethylcellulose, carboxymethyl starch and/or methylcellulose in quantities of up to 10% by weight as a washing auxiliary.

25

The crystalline layered silicates used in the production of the washing agent according to the invention can be prepared according to DE-34 13 571 A1.

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The washing-active oxygen (AVOX) of the bleach and of the washing agent was determined in accordance with the instructions by Dr. E. Heinerth, Tenside 2 (1965) 180. The sodium perborate tetrahydrate ($\text{NaBO}_3 \times 4 \text{H}_2\text{O}$) investigated had an AVOX number of 10% by weight; sodium perborate monohydrate ($\text{NaBO}_3 \times \text{H}_2\text{O}$) had an AVOX number of 15% by weight and sodium percarbonate ($2 \text{Na}_2\text{CO}_3 \times 3 \text{H}_2\text{O}_2$) had an AVOX number of 13.5% by weight.

10

The washing power (bleach action) of the washing agent was determined as the whiteness of the test fabrics (WFK polyester/cotton soiled by tea, order code 20 G) according to DIN 44983.

15

The washing power (bleach action) of the washing liquor was determined by the difference method which follows from equation I

$$\% \text{WK} = \% \text{WG}_g - \% \text{WG}_b$$

20

where: $\% \text{WK}$ = % washing power (bleach action)

$\% \text{WG}_g$ = % whiteness of the washed material

$\% \text{WG}_b$ = % whiteness of the unwashed material.

25

The storage tests were carried out under the following forced test conditions:

The washing agent to be investigated was stored in a conditioned cabinet at a relative atmospheric humidity of 70% at a temperature of 37°C. During the test, the

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washing agent was packed in a waxed carton. The water vapor permeability of the packaging was $0.4 \text{ g/m}^2 \times \text{h}$.

5 The tested washing agent formulations are listed in Table 1.

10 The degradation values of the bleach as a function of the time after the forced storage test conditions are compiled in Table 2. In addition, two commercially available washing agents based on zeolite and sodium tripolyphosphate were included in Table 2. The degradation of bleach, in particular that of sodium percarbonate, is very high in the presence of zeolite.

15 The test results according to DIN 44983 for the various washing agent formulations, as determined in accordance with equation I, are listed in Table 3.

20 The test values show that the bleach action is enhanced when a crystalline layered silicate is used as the builder in place of zeolite. In the presence of TAED, the washing power (bleach action) of the washing agent is boosted synergistically.

25 The assessment of handle by a panel of experts gave a markedly "softer handle" of the washed material, which had been washed with the washing agents according to the invention in accordance with Examples 2 and 3, as

compared with the washed material which had been washed with the zeolite-containing washing agent in accordance with Examples 1 and 4.

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T A B L E 1
Washing agent formulations

Ingredients (% by weight)	Example 1	Example 2 *)	Example 3 *)	Example 4	Example 5
Anionic surfactants	6.5	6.5	6.5	6.5	6.5
Nonionic surfactants	3.5	3.5	3.5	3.5	3.5
Soap	4.5	4.5	4.5	4.5	4.5
Zeolite A	21.5	-	-	21.5	-
δ - $\text{Na}_2\text{Si}_2\text{O}_5$	-	21.5	21.5	-	21.5
Soda	7.5	-	-	7.5	-
$\text{NaBO}_3 \times \text{H}_2\text{O}$	10.0	10.0	-	-	-
IAED	2.5	2.5	2.5	-	-
$2 \text{Na}_2\text{CO}_3 \times 3 \text{H}_2\text{O}$	-	-	18.0	18.0	18.0
Optical brighteners	0.2	0.2	0.2	0.2	0.2
Soil carriers	1.5	1.5	1.5	1.5	1.5
Enzymes	0.3	0.3	0.3	0.3	0.3
Dispersants (polycarboxylates)	4.0	2.0	-	4.0	2.0
Na silicate	5.0	-	-	5.0	-
Extender (Na_2SO_4)		to 100%			

*) washing agent according to the invention

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TABLE 2
AVOX degradation

Example	AVOX degradation in %		
	1 week	2 weeks	3 weeks
1	14	29	32
2 *)	0	9	11
3 *)	0	5	9
4	33	50	86
5	0	4	8
Zeolite-based commercial material	16	22	37
Na ₅ P ₃ O ₁₀ -based commercial material	0	16	21

*) washing agent according to the invention

This is the replacement sheet

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T A B L E 3
Bleach action, determined in accordance with
equation 1

Example	% Washing power
1	37.5
2 *)	43.0
3 *)	42.0
4	31.5
5	38.5

*) washing agent according to the invention



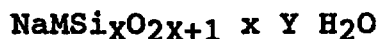
Date: 3 FEB 1996

Washing agent with storage-stabilized
bleach system

5 Patent claims:

1. A washing agent with a storage-stabilized bleach system, with 2 to 20% by weight of detergents and conventional washing auxiliaries, including fillers, which contains 10 to 50% by weight, in particular 20 to 35% by weight, of a crystalline layered silicate as the builder and 1 to 5% by weight, in particular 2.0 to 3.0% by weight, of tetraacetythylenediamine (TAED) and a bleach, the quantity of bleach being such that 0.5 to 4% by weight, in particular 1.0 to 2.5% by weight, of washing-active oxygen (AVOX) is present in the washing agent.

2. The washing agent as claimed in claim 1, wherein the crystalline layered silicate is of the formula



where

25 $x = 1.9 \text{ to } 4.0$

$M = \text{Na or H and}$

$y = 0 \text{ to } 20.$



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3. The washing agent as claimed in claim 1, wherein the crystalline layered silicate corresponds to the δ -modification of $\text{Na}_2\text{Si}_2\text{O}_5$.
- 5 4. The washing agent as claimed in claim 1, wherein the crystalline layered silicate has a particle diameter from 0.01 to 1,000 μm , in particular from 1 to 20 μm .
- 10 5. The washing agent as claimed in one of claims 1 to 4, wherein the crystalline layered silicate has an ion exchange capacity from 400 to 1,200 mmol of Na^+ /100 g of dry matter.
- 15 6. The washing agent as claimed in one of claims 1 to 5, wherein the bleach is sodium perborate tetrahydrate, sodium perborate monohydrate and/or sodium percarbonate.
- 20 7. The washing agent as claimed in one of claims 1 to 6, which contains inorganic and/or organic phosphates, borates, citrates, gluconates, nitrilotriacetic acid and/or iminodiacetates as additional builders in quantities of up to 20% by weight.
- 25 8. The washing agent as claimed in one of claims 1 to 7, which is composed of agglomerate particles



having a particle size in the range from 0.25 to 2.5 mm and has been obtained by means of a spray-mist mixing process.

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Washing agent with storage-
stabilized bleach system

Abstract:

The invention relates to a washing agent with a storage-stabilized bleach system and 2 to 20% by weight of detergents and conventional washing auxiliaries, including fillers, the washing agent containing 10 to 50% by weight of a crystalline layered silicate as a builder as well as 1 to 5% by weight of tetraacetylenediamine (TAED) and a bleach, the quantity of bleach being such that 0.5 to 4% by weight of washing-active oxygen (AVOX) is present in the washing agent.