

REPLACED SHEETS		SG
☒	Description : paged 01 to paged 09	
☒	Claim(s) : paged 10 to paged 12	
☐	Drawing(s) : paged — to paged —	
☒	Abstract : paged — to paged 13	

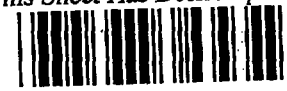
STORAGED STABILIZED WASHING AGENT WITH BOOSTED BLEACH ACTION

5 The present invention relates to a storage-stabilized washing agent with a boosted bleach action, in particular a domestic washing agent for heavy laundry, white laundry and colored laundry, containing 2 to 20% by weight of detergents and conventional washing auxiliaries, including fillers, 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 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 tripolyphosphate, 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 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
15 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 which has an improved storage stability and a boosted bleach action, and maintains the "soft handle" in the washed material.

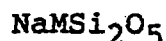
25 Surprisingly, it has been found that a storage-stabilized washing agent with a boosted bleach action is obtained when it contains 10 to 50% by weight, in particular 20 to 35% by weight, of a crystalline



layered silicate as the builder and 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.

5

A crystalline layered silicate of the general formula



where M = Na or H,

has proved particularly suitable.

10

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

15

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 ,

25

b) the crystalline layered silicate has an ion 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 (NTA) 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.

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.

25 Even though all the crystalline layered silicates listed in US-A-4,664,839 can be employed in the washing agent according to the invention, it has been found that δ - $\text{Na}_2\text{Si}_2\text{O}_5$ is to be preferred if a boosted bleach



action during the washing process is important.

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.

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.

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)

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



condition 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 $0.4 \text{ g/m}^2 \times \text{h}$.

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, 2 commercially available washing agents based on zeolite and sodium tri-
polyphosphate were included in Table 2. The degradation of bleach, in particular that of sodium percarbonate,
15 is very high in the presence of zeolite.

Washing results:

The washing agent formulations 2 and 4 were tested in accordance with DIN 44983 and calculated according to
20 equation I. The washing power (bleach action) of washing agent 2 was 30.0%, and that of washing agent 4 according to the invention was 36.5%.

The assessment of handle by a panel of experts gave a
25 markedly "softer handle" of the washed material, which had been washed with the washing agent 4 according to the invention, as compared with the washed material which had been washed with the zeolite-containing

This Sheet Has Been Replaced



- 7 -

washing agent 2.



-Table 1
Washing agent formulations

Ingredients (% by weight)	Washing agent 1	Washing agent 2	Washing agent 3 ^{x)}	Washing agent 4 ^{x)}
$\text{S}^- \text{Na}_2\text{Si}_2\text{O}_5$	-	-	21.5	21.5
Zeolite	21.5	21.5	-	-
Na_2CO_3	7.5	7.5	-	-
Anionic surfactants	6.5	6.5	6.5	6.5
Nonionic surfactants	4.5	4.5	4.5	4.5
Soap	5.5	5.5	5.5	5.5
Soil carriers	1.5	1.5	1.5	1.5
Polycarboxylates	2.5	2.5	2.5	2.5
EDTA	0.2	0.2	0.2	0.2
Optical brighteners	0.2	0.2	0.2	0.2
Enzymes	0.25	0.25	0.25	0.25
$\text{NaBO}_3 \times \text{H}_2\text{O}$	-	10.0	-	10.0
$2 \text{Na}_2\text{CO}_3 \times 3 \text{H}_2\text{O}$	18.0	-	18.0	-
Mg silicate	2.0	2.0	2.0	2.0
Na silicate	5.0	5.0	-	-
Na_2SO_4			to 100%	

x) washing agent according to the invention .



Table 2
AVOX degradation

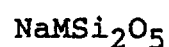
Washing agent	AVOX degradation in %			
	1 week	2 weeks	4 weeks	
1	33	50	86	
2	18	34	35	
3 ^{x)}	0	4	8	
4 ^{x)}	0	12	13	
Zeolite-based commercial material	16	22	37	
Na ₅ P ₃ O ₁₀ -based commercial material	0	16	21	

x) washing agent according to the invention

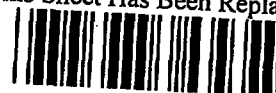


We claim:

1. A storage-stabilized washing agent with a boosted bleach action, with 2 to 20% by weight of detergents and conventional washing auxiliaries, including fillers, containing 10 to 50% by weight of a crystalline layered silicate as the builder 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.
2. The storage-stabilized washing agent as claimed in claim 1, containing 20 to 35% by weight of a crystalline layered silicate as the builder.
3. The storage-stabilized washing agent as claimed in claim 1, 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.
4. The storage-stabilized washing agent as claimed in claim 1, wherein the crystalline layered silicate is of the general formula



where M = Na or H.



5. The storage-stabilized washing agent as claimed in claim 1, wherein the crystalline layered silicate corresponds to the δ -modification of $\text{Na}_2\text{Si}_2\text{O}_5$.
6. The storage-stabilized washing agent as claimed in claim 1, wherein the crystalline layered silicate has a particle diameter from 0.01 to 1,000 μm .
7. The storage-stabilized washing agent as claimed in claim 1, wherein the crystalline layered silicate has a particle diameter from 1 to 20 μm .
8. The storage-stabilized washing agent as claimed in claim 1, wherein the crystalline layered silicate has an ion exchange capacity from 400 to 1,200 mmol of Na^+ /100 g of dry matter.
9. The storage-stabilized washing agent as claimed in claim 1, 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.
10. The storage-stabilized washing agent as claimed in claim 1, composed of agglomerate particles having a particle size in the range from 0.25 to 2.5 mm





-12-

This Sheet Has Been Replaced



and obtained by means of a spray-mist mixing process.

11. The storage-stabilized washing agent as claimed in claim 1, wherein the bleach is sodium perborate tetrahydrate, sodium perborate monohydrate, sodium percarbonate or mixtures thereof.



Storage-stabilized washing agent with
boosted bleach action

Abstract of the disclosure:

The invention relates to storage-stabilized washing agents with a boosted bleach action, containing 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 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.

REPLACEMENT SHEETS SG

- ☒ Description : paged 2 to paged 9
☒ Claim(s) : paged 10 to paged 11
☐ Drawing(s) : paged 12 to paged 13
☒ Abstract : paged 14 to paged 15

DATE OF RECEIPT 12/02/1996

- 1 -

This is the replacement sheet

Date: 13 FEB 1996

Storage-stabilized washing agent with boosted bleach
action

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The present invention relates to a storage-stabilized washing agent with a boosted bleach action, in particular a domestic washing agent for heavy laundry, white laundry and colored laundry, containing 2 to 20% by weight of detergents and conventional washing auxiliaries, including fillers, 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.

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 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.

Polymeric phosphates, in particular sodium tripolyphosphate, are regarded as excellent builders. Because of

Date: 13 FEB 1996

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
10 of the washing agent, the washing agent loses part of 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
15 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
20 thereby.

It is the object of the invention to provide a washing agent which has an improved storage stability and a boosted bleach action, and maintains the "soft handle"
25 in the washed material.

Surprisingly, it has been found that a storage-stabilized washing agent with a boosted bleach action

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 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.

A crystalline layered silicate of the general formula



where M = Na or H,
has proved particularly suitable.

Very particularly good results are obtained when the crystalline layered silicate corresponds to the -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

- a) the crystalline layered silicate has a particle diameter from 0.01 to 1,000 m, in particular from 1 to 20 m,
- b) the crystalline layered silicate has an ion exchange capacity from 400 to 1,200 mmol of Na^+ /100 g of dry matter,

Date: 13 FEB 1996

- 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 (NTA) 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. Even though all the crystalline layered silicates

Date: 13 FEB 1966

listed in DE-34 13 571 A1 can be employed in the washing agent according to the invention, it has been found that $\text{-Na}_2\text{Si}_2\text{O}_5$ is to be preferred if a boosted bleach action during the washing process is important.

5

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.

15

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.

20

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

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

25

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

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

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

Date: 13 FEB 1988

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

5 The washing agent to be investigated was stored in a condition 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 g/m² x h.

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

15 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, 2 commercially available washing agents based on zeolite and sodium tri-polyphosphate were included in Table 2. The degradation of bleach, in particular that of sodium percarbonate, is very high in the presence of zeolite.

20 Washing results:

25 The washing agent formulations 2 and 4 were tested in accordance with DIN 44983 and calculated according to equation I. The washing power (bleach action) of washing agent 2 was 30.0%, and that of washing agent 4 according to the invention was 36.5%.

The assessment of handle by a panel of experts gave a markedly "softer handle" of the washed material, which

This is the replacement sheet.

- .7 -

Date: 13 FEB 1995

had been washed with the washing agent 4 according to the invention, as compared with the washed material which had been washed with the zeolite-containing washing agent

Date: 13 FEB 1996

Table 1
Washing agent formulations

Ingredients (% by weight)	Washing agent 1	Washing agent 2	Washing agent 3 ^{x)}	Washing agent 4 ^{x)}
$\text{C-Na}_2\text{Si}_2\text{O}_5$	-	-	21.5	21.5
Zeolite	21.5	21.5	-	-
Na_2CO_3	7.5	7.5	-	-
Anionic surfactants	6.5	6.5	6.5	6.5
Nonionic surfactants	4.5	4.5	4.5	4.5
Soap	5.5	5.5	5.5	5.5
Soil carriers	1.5	1.5	1.5	1.5
Polycarboxylates	2.5	2.5	2.5	2.5
EDTA	0.2	0.2	0.2	0.2
Optical brighteners	0.2	0.2	0.2	0.2
Enzymes	0.25	0.25	0.25	0.25
$\text{NaBO}_3 \times \text{H}_2\text{O}$	-	10.0	-	10.0
$2 \text{Na}_2\text{CO}_3 \times 3 \text{H}_2\text{O}_2$	18.0	-	18.0	-
Mg silicate	2.0	2.0	2.0	2.0
Na silicate	5.0	5.0	-	-
Na_2SO_4				
			to 100%	

x) washing agent according to the invention

This is the replacement sheet

Date: 13 FEB 1996

Table 2
AVOX degradation

Washing agent	AVOX degradation in %			
	1 week	2 weeks	4 weeks	
1	33	50	86	
2	18	34	35	
3 ^{x)}	0	4	8	
4 ^{x)}	0	12	13	
Zeolite-based commercial material	16	22	37	
Na ₅ P ₃ O ₁₀ -based commercial material	0	16	21	

x) washing agent according to the invention



Date: 73 FEB 1998

Storage-stabilized washing agent

with boosted bleach action

5 Patent claims:

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

2. The storage-stabilized washing agent as claimed in
claim 1, wherein the crystalline layered silicate
20 is of the general formula



where M = Na or H.

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



This is the replacement sheet

- 11 -

Date: 11 3 FEB 1996

4. The storage-stabilized washing agent as claimed in one of claims 1 to 3, wherein the crystalline layered silicate has a particle diameter from 0.01 to 1,000 m, in particular from 1 to 20 μm .

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5. The storage-stabilized 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.

10

6. The storage-stabilized 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.

15

7. The storage-stabilized washing agent as claimed in one of claims 1 to 6, which contains inorganic and/or organic phosphates, borates, citrates, gluconates, nitrilotriacetic acid (NTA) and/or iminodiacetates as additional builders in quantities of up to 20% by weight.

20

8. The storage-stabilized 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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Date: 19 FEB 1996

Storage-stabilized washing agent with
boosted bleach action

5

Abstract:

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