

- 1 -

DESCRIPTION

DETERGENT COMPOSITION

[Technical Field to which the Invention Belongs]

This invention relates to a detergent composition in powder for clothes.

[Prior Art]

Detergents for clothes are composed of surfactants which solubilize stains on fibers and thus dissolve or disperse the same in the washing liquor, sequestering agents for removing, for example, calcium and magnesium which deteriorate the performance of the surfactants, alkalis promoting the decomposition and solubilization of stains, high-molecular weight compounds for dispersing stains and other detergent builders.

One of the actions of detergent builders is to inhibit the redeposition of soils once removed from clothes. Examples of builders exhibiting this effect include sodium tripolyphosphate, polyacrylic acid and polyethylene glycol. As an example of the prior art with the use of these builders, citation may be made of "Detergent composition having improved physical properties and solubility in cold water" (containing surfactants, sodium tripolyphosphate, polyethylene glycol and polyacrylic acid) disclosed in U.S. Patent No. 4657693. However, this composition is insufficient in the performance

of inhibiting the redeposition of solid stains.

[Disclosure of the Invention]

The present inventors have conducted extensive studies to solve the above-mentioned problem. As a result, they have found out that the above-mentioned problem can be solved by blending an inorganic phosphate, polyethylene glycol, a copolymer of acrylic acid and maleic acid and Glauber's salt at a specific ratio and further adding a surfactant and an alkali thereto.

Accordingly, the present invention provides a detergent composition in powder containing 15 to 30 wt. % of an inorganic phosphate, 0.05 to 2.0 wt. % of a copolymer of acrylic acid and maleic acid, 0.05 to 2.0 wt. % of polyethylene glycol, 15 to 40 wt. % of Glauber's salt, a surfactant and an alkali.

In other words, the invention is directed to a detergent composition in powder comprising a surfactant and an alkali, characterized by further comprising 15 to 30 wt. % of an inorganic phosphate, 0.05 to 2.0 wt. % of a copolymer of acrylic acid and maleic acid, 0.05 to 2.0 wt. % of polyethylene glycol and 15 to 40 wt. % of Glauber's salt or sodium sulfate.

It is preferable that the detergent composition of the present invention further contains 0.1 to 5 wt. % of a crystalline silicate which gives a maximum pH value of 11 or above, when dispersed in deionized water at 20°C at a rate of

0.1 wt. %, and such an alkalinity that at least 5 ml of a 0.1 N aqueous solution of HCl is needed in lowering the pH value of 1 l of the above-mentioned aqueous dispersion to 10.

The detergent composition of the present invention preferably contains 10 to 40 wt. % of the surfactant and 10 to 30 wt. % of the alkali.

It is preferable that the inorganic phosphate is a tripolyphosphate, an orthophosphate or a pyrophosphate and the counter ion of the salt is an alkali metal.

Particular examples of the copolymer of acrylic acid and maleic acid include acrylic acid/maleic acid copolymers, acrylic acid/maleic anhydride copolymers and partial salts thereof.

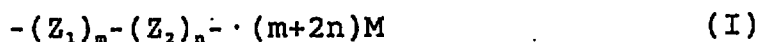
According to the present invention, a phosphorus-containing detergent containing a surfactant, an alkali, an inorganic phosphate and Glauber's salt is improved by adding a copolymer of acrylic acid and maleic acid and polyethylene glycol thereto.

[Detailed Description of the Invention]

Preferable examples of the inorganic phosphate to be used in the present invention are orthophosphates and pyrophosphates, in addition to tripolyphosphates. It is appropriate that the content of sodium tripolyphosphate in the whole phosphates is at least 80 wt. %, while the contents of

orthophosphoric acid and pyrophosphoric acid range respectively from 1 to 5 wt. % and from 2 to 5 wt. % (content: in terms of dry matters). As the counter ion, alkali metals are preferable and sodium and/or potassium are still preferable therefor. The content of the inorganic phosphate(s) in the detergent composition is 15 to 30 wt. %, preferably 17 to 25 wt. % (content: in terms of dry matters).

In addition to the sequestering effect, the copolymer of acrylic acid and maleic acid to be used in the present invention further exhibits an effect of dispersing solid stain particles from the clothes into the washing bath and another effect of inhibiting the redeposition (re-staining) of these particles onto the clothes. It is preferable for this purpose to blend a copolymer having a molecular weight of from hundreds to one hundred thousand and represented by the following formula (I). In general, the copolymer is prepared by random polymerization.



in the above formula, Z_1 represents a monomeric unit originating in acrylic acid; Z_2 is another monomeric unit originating in maleic acid or maleic anhydride; m and n are numbers capable of giving a molecular weight $(m+n)$ of hundreds to one hundred thousand and a ratio $m:n$ of 8 : 2 to 5 : 5; and M is Na, K, NH_4 or H. This copolymer may be in the form of

a partial salt. Ms in one molecule are a mixture of Na, K or NH₄ with H.

The content of the copolymer of the formula (I) in the detergent composition is 0.05 to 2 wt. %. The molecular weight of this polymer preferably ranges from 200 to 100,000.

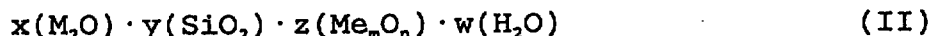
It is preferable that the polyethylene glycol to be used in the present invention is one having an average molecular weight of 5,000 to 15,000. The content of polyethylene glycol in the composition is 0.05 to 2.0 wt. %, preferably 0.1 to 1.0 wt. %.

Glauber's salt to be used in the present invention, which is a generic name of sodium sulfate, has effects of enhancing the salt strength of the washing bath and forming, similar to other alkalis, the skeleton of the detergent particle after drying. It is preferable that the content of Glauber's salt in the composition is 15 to 40 wt. %, still preferably 18 to 35 wt. % (content: in terms of dry matters).

In the present invention, the detergency of the composition can be further improved by adding a crystalline silicate. The crystalline silicate to be used in the present invention is one which gives a maximum pH value of 11 or above, when dispersed in deionized water at 20°C at a rate of 0.1 wt. %, and such an excellent alkalinity that 5 ml of a 0.1 N aqueous solution of HCl is needed for lowering the pH value of 1 l of

the above-mentioned aqueous dispersion to 10. Such a crystalline silicate is distinguished from crystalline aluminosilicates.

Particularly preferable examples of the crystalline silicate are those having the following composition:



wherein M represents an element of the group Ia in the periodic table, particularly preferably K and/or Na; Me represents one or more elements selected from among those of the groups IIa, IIb, IIIa, IVa and VIII in the periodic table, preferably Mg and/or Ca; y/x is 0.5 to 2.6; z/x is 0.01 to 0.9; w is 0 to 20; and n/m is 0.5 to 2.0.

The crystalline silicate represented by the general formula (II) can be produced by reference to JP-A 7-89712.

Also, crystalline silicates having the following composition can be appropriately employed:



wherein M represents an alkali metal, particularly preferably K and/or Na; x' is 1.5 to 2.6; and y' is 0 to 20, particularly preferably 0 substantially.

The crystalline silicates of the general formula (III) are described in JP-A 60-227895, Phys. Chem. Glasses. 7, 127-138 (1966), Z. Kristallogr., 129, p. 396 - p. 404 (1969), etc. Also, powdery or granular products are available as

"Na-SKS-6TM" (δ -Na₂Si₂O₅) from Hoechst AG. In the present invention, it is preferable to use the crystalline silicate in an amount of 0 to 5 wt. %, preferably 0.1 to 5 wt. %, in the composition.

As the surfactant to be employed in the present invention, use is made of one containing an anionic surfactant as the main component. It is particularly preferable in the present invention to use linear alkylbenzenesulfonates having 12 to 14 carbon atoms in the alkyl chain or alkyl sulfates having 12 to 18 carbon atoms. As the counter ion, alkali metals are preferable and sodium and/or potassium are still preferable. In addition thereto, it may contain a small amount of fatty acid salts originating in beef tallow or coconut.

In the present invention, the content of the anionic surfactant ranges from 10 to 40 wt. %, preferably 15 to 30 wt. %.

As the alkali to be used in the present invention, it is preferable to add conventionally known alkali(s) in addition to the crystalline silicate and inorganic phosphate as described above. Examples of such alkalis include alkali metal carbonates such as sodium carbonate generally called dense ash or light ash, and amorphous alkali metal silicates such as JIS No. 1, No. 2 and No. 3. These inorganic alkalis are effective in the formation of the particle skeleton in the step of drying the detergent and thus ensure the provision of

relatively hard and highly flowable detergents. The content of the alkali in the composition preferably ranges from 10 to 30 wt. %, still preferably from 15 to 25 wt. %.

In addition to the above-mentioned components, the detergent composition of the present invention may contain publicly known components each at a publicly known ratio, for example, surfactants such as nonionic surfactants such as polyoxyethylene alkyl ethers, cationic surfactants and ampholytic surfactants; sequestering agents such as crystalline aluminosilicate called zeolite and crystalline silicates described in JP-A 7-89712 and JP-A 60-227895; organic sequestering agents such as ethylenediamine-tetraacetic acid (EDTA) and citrates; dispersants or color-transfer inhibitors such as carboxymethylcellulose (CMC), polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA); bleaching agents such as sodium percarbonate; bleaching activators such as organic peracid precursors described in JP-A 6-316700 and tetraacetythylenediamine (TAED); enzymes such as protease, cellulase, amylase and lipase; enzyme stabilizers such as boron compounds and sodium sulfite; fluorescent dyes of biphenyl or stilbene type; defoaming agents of silicone/ silica type, etc.; antioxidants; blueing agents; and perfumes. More particularly, those described in JP-A 8-218093 can be used as the above-mentioned additives.

The detergent composition may be produced by publicly known methods. The appropriate production conditions can be easily selected by those skilled in the art depending on the composition.

The composition of the present invention has a high detergency and, moreover, an excellent performance of inhibiting the redeposition of solid stains.

[Mode for Carrying Out the Invention]

Examples 1 and 2 and Comparative Examples 1 to 4

An aqueous slurry having a solid content of 60 % was prepared from 20 kg of LAS, 0.5 kg of an AA-MA copolymer, 0.5 kg of polyethylene glycol, 20 kg of sodium tripolyphosphate, 10 kg of sodium silicate JIS No. 2, 14.9 g of soda ash, 20 kg of Glauber's salt and 0.3 kg of a fluorescent dye. After spray drying the slurry, the powder thus obtained was fed into a vertical blender. After further adding 3 kg of zeolite, 1.5 kg of a crystalline silicate and 1 kg of enzymes, the blend was mixed to thereby give the detergent composition in powder (bulk density: 0.35 g/ml, average particle size: 400 μ m) of Example 1 as shown in Table 1. The compositions of Example 2 and Comparative Examples 1 to 4 were prepared in the same manner.

Each of the compositions thus obtained was subjected to a detergency test and an anti-redeposition test by the

following methods. Table 1 summarizes the results.

<Detergency test>

(Preparation of artificially stained cloth)

A cloth was artificially stained with an artificial staining solution of the following composition. Staining was effected by printing the cloth with the artificial staining solution by using a gravure roll coater with a cell capacity of 58 cm³/m² at a coating rate of 1.0 m/min and then drying at 100°C for 1 minute. As the cloth, use was made of a shirting cotton cloth 2003 (mfd. by Tanigashira Shoten).

[Composition of artificial staining solution]

lauric acid	0.44 wt. %
myristic acid	3.09 wt. %
pentadecanoic acid	2.31 wt. %
palmitic acid	6.18 wt. %
heptadecanoic acid	0.44 wt. %
stearic acid	1.57 wt. %
oleic acid	7.75 wt. %
trioleic acid	13.06 wt. %
n-hexadecyl palmitate	2.18 wt. %
squalene	6.53 wt. %
egg lecithin, liquid crystal form	1.94 wt. %
red-colored soil (Kanuma)	8.11 wt. %
carbon black	0.01 wt. %

tap water

the balance.

(Washing conditions and evaluation method)

Five pieces of the artificially stained cloth (10 cm x 10 cm) were put into 1 litre of an aqueous solution of the detergent to be evaluated and washed at 100 rpm with a Terg-O-Tometer under the following conditions.

Washing condition:

washing time	10 min
detergent concentration	0.133 %
water hardness	5° DH
water temperature	25°C
rinsing	with tap water for 5 min

The detergency was evaluated by measuring the reflectances at 550 nm of the starting cloth and the stained cloth before and after washing with a self colorimeter (mfd. by Shimadzu Corporation) and calculating the detergency (%) in accordance with the following formula. The detergency is expressed in the average of the data of five cloth pieces.

$$\text{detergency (\%)} = \frac{\text{reflectance after washing} - \text{reflectance before washing}}{\text{reflectance of starting cloth} - \text{reflectance before washing}} \times 100.$$

<Anti-redeposition test>

As the cloth, use was made of a shirting cotton cloth 2003 (mfd. by Tanigashira Shoten). After washing with a marketed detergent Attack™ (mfd. by Kao Corporation), this cloth was cut into pieces (10 × 10 cm). To 1 litre of an aqueous solution of the detergent to be evaluated was added 2.5 g of red-colored soil (Kanuma), which was dried and dressed through a 150-mesh sieve. Then five pieces of the above cloth were put thereinto and washed at 100 rpm with a Terg-O-Tometer under the following conditions.

Washing condition:

washing time	10 min
detergent concentration	0.133%
water hardness	5° DH
water temperature	25°C
rinsing	with tap water for 5 min

The anti-redeposition ratio was evaluated by measuring the reflectances at 550 nm of the starting cloth before staining and the cloth after washing with a self colorimeter (mfd. by Shimadzu Corporation) and calculating the anti-redeposition ratio (%) in accordance with the following formula. The anti-redeposition ratio is expressed in the average of the data of five cloth pieces.

$$\begin{array}{lcl} \text{Anti-redeposition} & \text{reflectance after washing} & \\ \text{ratio (\%)} & = \frac{\quad}{\text{reflectance of starting cloth}} & \times 100. \end{array}$$

Table 1

Component(wt%)	Exam ple										Comp. Example			
	1	2	3	4	5	6	1	2	3	4				
LAS	20	18	20	20	27	20	25	20	20	20				
AA-MA copolymer	0.5	0.5	0.5	0.5	0.07	1.9	0.5	-	0.5	-				
polyacrylic acid	-	-	-	-	-	-	-	-	-	-				
polyethylene glycol	0.5	0.5	0.5	0.5	0.07	1.9	0.5	0.5	0.5	-				
STPP	20	20	29	16	20	20	10	20	20	20				
soda ash	14.9	14.9	9.9	1.9	8.76	12.1	14.9	14.9	14.9	14.9				
sodium silicate	10	10	10	10	10	10	10	10	10	10				
crystalline silicate	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5				
zeolite	3	3	3	3	3	3	18	3.5	3.5	3				
Glauber's salt	20	22	16	37	20	20	10	20	20	20				
enzyme	1	1	1	1	1	1	1	1	1	1				
fluorescent dye	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3				
perfume	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3				
water	8	8	8	8	8	8	8	8	8	8				
detergency(%)	70	68	70	66	68	70	72	71	71	70				
anti-redeposition ratio(%)	80	78	80	78	75	82	68	67	69	69				

Note:

LAS: sodium linear-alkyl(C_{12})benzenesulfonate.

AA-MA copolymer: sodium salt of acrylic acid/maleic acid
(molar ratio 7/3) copolymer with average M.W. of 70,000.

Polyacrylic acid: polysodium acrylate with average M.W. of
6,000.

Polyethylene glycol: with average M.W. of 7,000.

STPP: sodium tripolyphosphate.

Sodium silicate: sodium silicate JIS No. 2.

Crystalline silicate: composition $M_2O \cdot 1.8SiO_2 \cdot 0.02M'O$ (M: Na,
K. $K/Na = 0.03$, $M' = Ca, Mg$, $Mg/Ca = 0.01$).
ion exchange capacity: 290 $CaCO_3$ mg/g, average particle
size: 30 μm [crystalline silicate represented by general
formula (II)].

Zeolite: composition $M_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, average particle
size: 4 μm , ion exchange capacity: 290 $CaCO_3$ mg/g.

Enzyme: protease (Savinase 12.0TW, mfd. by Novo Nordisk),
lipase (Lipolase 100T, mfd. by Novo Nordisk), cellulase
(Celluzyme 0.1T, mfd. by Novo Nordisk), amylase
(Termamyl 60T, mfd. by Novo Nordisk), mixed at a wt. ratio
of 2 : 1 : 1 : 1.

Fluorescent dye: Tinopal CBS (mfd. by Ciba-Geigy)/Whitex SA
(mfd. by Sumitomo Chemical Co., Ltd.) mixed at a wt.
ratio of 1/1.



Claims

1. A detergent composition in powder comprising a surfactant and an alkali, characterized by further comprising 15 to 30 wt. % of an inorganic phosphate, 0.05 to 2.0 wt. % of a copolymer of acrylic acid and maleic acid, 0.05 to 2.0 wt. % of polyethylene glycol and 15 to 40 wt. % of Glauber's salt or sodium sulfate.
2. The composition as set forth in Claim 1, which further contains 0.1 to 5 wt. % of a crystalline silicate which gives a maximum pH value of 11 or above, when dispersed in deionized water at 20°C at a rate of 0.1 wt. %, and such an alkalinity that at least 5 ml of a 0.1 N aqueous solution of HCl is needed in lowering the pH value of 11 of the above-mentioned aqueous dispersion to 10.
3. The composition as set forth in Claim 1, which contains 10 to 40 wt. % of said surfactant and 10 to 30 wt. % of said alkali.
4. The composition as set forth in Claim 1, wherein said inorganic phosphate is a tripolyphosphate, an orthophosphate or a pyrophosphate and the counter ion of the salt is an alkali metal.
5. The composition as set forth in Claim 1, wherein said copolymer of acrylic acid and maleic acid is an acrylic acid/maleic acid copolymer, an acrylic acid/maleic anhydride



-17-

copolymer or a partial salt thereof.