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(54) **Granular detergent compositions containing mixed polymer additive system.**

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Description

This invention relates to granular detergent compositions which are free of or with reduced levels of phosphorus -containing builders containing a mixed polymer additive system. The polymer system comprises specific homopolymeric polyacrylates and copolymeric carboxylates whereby the homopolymeric species are characterized by a molecular weight below 3 000. The preferred copolymeric component is prepared from an ethylenically unsaturated carboxylic acid, most preferably maleic acid, and (meth)-acrylic acid monomers. Particularly preferred polyacrylates herein are represented by substantially equiponderant mixtures of polyacrylates having molecular weights of around 1 000 and 2 000 respectively.

The polymer additive system provides unpredictable and significant textile cleaning benefits expressed, for example, in terms of whiteness and whiteness maintenance after multiple washes as compared to identical granular detergents containing same total level of either the individual polymers or mixtures of various conventional detergent polymers. The claimed technology is especially beneficial in granular detergent compositions containing reduced levels of polyphosphate builders such as from 8 % to 20 % by weight of the composition. As is well-known, the polyphosphate builder level reduction leads to performance deficiencies which cannot be cured in a fully acceptable manner with the sole aid of a conventional detergent additive such as a polymeric carboxylate.

The individual components of the polymer additive system are well-known in detergent technology and may have found commercial application.

The copolymeric ingredient is known from European Patent 0 025 551, BASF AG, which discloses such material in an incrustation inhibitor functionality in detergent compositions.

The detergent art is also possessed of combinations of the copolymeric ingredient and conventional detergent additives. FR-A-2 388 045, The PROCTER & GAMBLE Company, is representative of this general knowledge. It discloses detergent compositions containing surface-active agents, builders, and a binary system of additive levels of a polyphosphonate and a polymeric ingredient which latter ingredient can be represented by copolymers of (meth)-acrylic acid and maleic anhydride.

The detergent utilization of the copolymeric ingredient is also known from European Patent Application 0 066 915. In detail, this reference discloses the utilization of the copolymeric ingredient in combination with detergent performance additives inclusive of hydrocarbon detergent suds regulants, photoactivators, amine or oxidized amine soil release agents, silicone detergent suds regulants and bleach activators/peracids.

The detergent utilization of polyacrylates, having a molecular weight in the range of from 1 000 to 5 000, is known from U.K. Patent Application 2,097,419, Colgate-Palmolive. Detergent compositions are disclosed containing high levels of difficultly processable components inclusive of sodium carbonate, sodium bi-carbonate, detergent zeolites, and bentonites. It is said that the polyacrylates are added in a processing aid functionality to ensure uniform mixing of the crutcher mix component. Comparable disclosures are known from U.K. Patent Application 2 095 274, Colgate-Palmolive. Detergent compositions containing substantial levels of water-insoluble ingredients inclusive of zeolite builders, and bentonites, carbonates and bi-carbonates are processed into beads whereby physical and detergent properties are controlled with the aid of polyacrylates having molecular weight e. g. in the range from 1 000 to 5 000.

The detergent utilization of mixed polymer systems is known from German Patent Application 29 10 133, BASF AG ; German Patent Application 26 25 444, CIBA-GEIGY AG ; and Belgian Patent 881 488, SENZORA B. V. The BASF '133 reference relates to the utilization of detergent builder mixtures consisting of a copolymeric ingredient and polymaleic acid. The CIBA-GEIGY '444 citation refers to the use of low molecular weight polymer mixtures, namely combinations of hydrolized polymaleic anhydride, having a molecular weight in the range from 300 to 5 000, in combination with a hydrolized copolymer of maleic anhydride and an ethylenically unsaturated monomer whereby the molecular weight of the copolymeric species is below 1 000. The SENZORA '488 reference refers to the partial or total replacement of polyphosphate detergent builders by a ternary combination consisting of polyvalent substituted carboxylic acids, a copolymer of methyl vinyl ether and maleic anhydride ; and a polyacrylic acid having a molecular weight in the range of from 12 000 to 20 000.

The total prior art is consistently and unequivocally confirmatory of a standing desire for improving and enhancing textile laundry performance of granular detergent compositions containing no or reduced levels of conventional polyphosphate builders with the aid of carboxylates. While prior art attempts for solving the problem have yielded some benefits, frequently processing advantages, the claimed system procures significant textile laundry benefits and can constitute basis for superior commercial detergent executions.

It is a major object of this invention to formulate granular detergent compositions having no or reduced level of phosphorus-containing builders capable of providing textile cleaning performance comparable to phosphate built compositions.

It is a further object of this invention to formulate granular detergent compositions capable of providing superior textile cleaning benefits over a broad range of laundry conditions particularly in up to the boil washing operations.

Brief description of the invention

It has now been discovered that significantly enhanced textile cleaning can be obtained from the use of granular detergent compositions which do not contain or contain reduced level of conventional phosphorus (P)-containing detergent builders. In more detail, it has been discovered that such benefits are derived from the utilization of granular detergent compositions containing no or reduced levels of P-containing builders, and further containing surface-active agents, polymeric carboxylates and, if desired, conventional detergent additives including non-phosphorus detergent builders, characterized in, that the compositions contain :

a) from 0.5 % to 15 % by weight of a polyacrylate homopolymer having a molecular weight below 3 000 ; and

b) from 0.5 % to 15 % by weight of a copolymer which consists of an ethylenically unsaturated monocarboxylic acid monomer having not more than 5 carbon atoms, and an ethylenically unsaturated dicarboxylic acid monomer having not more than 6 carbon atoms, whereby the molar ratio of the monomers is from 1 : 4 to 4 : 1 ; and

whereby the weight ratio of the homopolymeric ingredient to the copolymeric ingredient is in the range from 4 : 1 to 1 : 4.

In a preferred aspect of this invention, the compositions herein comprise reduced (vs. current practice) levels of polyphosphate builders such as corresponding to phosphorus levels in the range of from 2 % to 5 % by weight. The latter P-levels, if e. g. calculated on basis of sodiumtripolyphosphate amount to from 8 % to 20 % by weight.

Detailed description of the invention

The invention herein comprises a granular detergent composition containing a binary polymer system containing a homopolymeric polyacrylate having a low molecular weight and a copolymeric polycarboxylate with a given monomers ratio and whereby further the weight ratio of homopolymer to copolymer can be varied within narrowly set conditions. The major parameters of the invention are described in more detail hereinafter.

Unless indicated to the contrary, the « percent » indications represent « percent by weight » indications.

The detergent matrix comprises a surface-active agent, a detergent builder, preferably reduced level of tripolyphosphate, and a series of optional, but frequently desirable, components such as an oxygen-bleach component, possibly an activator therefore, a suds regulant frequently based on silicones, and further usual additives in the art established level for their known functionality.

Qualitatively and quantitatively suitable surface-active agents for use herein are disclosed in U.S.-PS 4,192,761, column 3, line 49 to column 5, line 42.

Qualitative and quantitative indications concerning suitable detergent builder materials for use herein are found in U.S.-PS 4,192,761, column 8, line 56 to column 9, line 68.

The compositions herein unexpectedly provide superior laundry cleaning performance, as compared to commercial phosphate built detergent compositions, in the absence of or with reduced level of phosphate builder, especially detergent compositions containing phosphate builder levels representing from 2-5 % of phosphorus. The latter limit, in terms of sodium tripolyphosphate, amounts to from 8 % to 20 %. The detergent builder can be represented by non-phosphorus containing builders, by mixtures of such non-phosphorus containing builders and phosphorus-containing builders, or by reduced levels (vs. current levels) of P-containing builders alone, such as sodium tripolyphosphate. The total level of the detergent builder ingredients can vary within broad limits well-known in the detergent art. Importantly, the inventive technology is particularly adapted for use in combination with a detergent composition containing a phosphorus-containing detergent builder in a level, calculated as phosphorus, from 2 % to 5 %.

Suitable non-phosphorus containing detergent builders can be represented by conventional species inclusive of but not limited to detergent zeolites such as zeolite A, zeolite X and zeolite P, most preferably zeolite A, having a particle size in the range from 1-10 μm as e. g. described in DE-B-24 22 655. Additional builders for use herein include nitrilotriacetic acids or the water-soluble alkali salts thereof, sodium carbonate, sodium citrate, sodium silicates and fatty acid soaps e. g. sodium or potassium soaps.

The total level of the detergent builder can vary within broad ranges. The builder usually represents from 5 % to 70 %, but frequently, and depending upon the selection of the builder, is in the range from 10 % to 50 %.

The compositions herein contain as an essential detergent component a mixture of a polyacrylic homopolymer and a copolymeric ingredient.

The polyacrylate homopolymer has a molecular weight below 3 000 and is utilized in levels of from 0.5 % to 15 %. In a preferred execution, the homopolymeric polyacrylate is represented by a mixture of two different polyacrylates, one having a molecular weight of about 2 000 and a second one having a

molecular weight of about 1 000, whereby these species are used in a weight ratio of 2 : 1 to 1 : 2, most preferably 1 : 1. The polyacrylate component is well-known in detergent technology. The molecular weight of the polyacrylate polymer is determined with the aid of known techniques inclusive of intrinsic viscosity measurements.

5 The level of the polyacrylate homopolymer can vary as pointed out above and depending upon the nature of the detergent matrix components. Particularly relevant in this respect are variations in the qualitative and quantitative parameters of the builder system. Reduced levels of polyphosphate e. g. between 8-12 % by weight will require a relatively higher level of the homopolymer as compared to what is needed for levels of sodium tripolyphosphate in the range of from e. g. 15 %-18 %.

10 A further essential component for use herein is a copolymer of an unsaturated monocarboxylic acid and an unsaturated di-carboxylic acid. This copolymeric ingredient is used in levels from 0.5 % to 15 %. The copolymeric ingredient consists of an ethylenically unsaturated monocarboxylic acid monomer having not more than 5, preferably 3 or 4, carbon atoms, and an ethylenically unsaturated dicarboxylic acid monomer having not more than 6, preferably 4 carbon atoms, whereby the molar ratio of the monomers is in the range from 1 : 4 to 4 : 1, most preferably 1 : 1. Suitable examples of the monocarboxylic acid monomer are : acrylic acid, methacrylic acid and vinyl acetic acid. Acrylic and methacrylic acids are preferred. Suitable examples of the dicarboxylic acid monomers are : maleic acid ; fumaric acid ; citraconic acid ; itaconic acid ; and mesaconic acid. Preferred dicarboxylic acids are maleic acid, citraconic acid, and itaconic acid.

20 The copolymeric ingredient can be further defined with the aid of the calcium sequestration value. These values can be measured by nephelometric titration methods (as described in literature

— S. Chaberek and A.E. Martell, Organic Sequestering Agents, Wiley, New York, 1959 ;

— R.L. Smith, The Sequestration of Metals, Chapman and Hall, London, 1959) :

a calcium nitrate solution is added to a solution containing sequestrant and sodium oxalate until turbidity is produced ; the titration is being carried out at constant pH = 10 and room temperature.

The sequestration value is expressed in mgCaCO₃/gram of copolymeric ingredient.

The calcium sequestration value of the copolymeric ingredient is preferably higher than 200 mg CaCO₃/g.

30 The weight ratio of the homopolymeric ingredient to the copolymeric ingredient is in the range from 1 : 4 to 4 : 1 and preferably from 2 : 1 to 1 : 2. While the quantitative levels of the individual homopolymer and the individual copolymer can vary from 0.5 % to 15 % provided their weight ratio is from 4 : 1 to 1 : 4, the level selection of these individual polymers will vary depending upon the major detergent matrix ingredients, particularly the detergent builder. The homopolymer and copolymer are preferably used in levels of 0.5 % to 4 % each when incorporated in built detergent compositions containing from 2 % to 5 % phosphorus in another embodiment the detergent compositions herein preferably contain from 2 % to 8 % of the homopolymeric ingredient and from 2 % to 8 % of the copolymeric ingredient if the phosphorous based builder/sequestrant is present in a level, expressed as phosphorus of below 2 %.

40 The detergent compositions herein can comprise, in addition to the essential components, a series of supplementary substances to perfect and augment the performance benefits. The additional components are represented by known ingredients which have already found application in detergency, for their known functionality in the art established levels. Examples of the like components include peroxygen bleaches, such as perborate mono-or tetrahydrate and percarbonate, oxygen bleach activators such as tetraacetyl ethylene diamine, oxygen bleach regulants such as a copolymer of maleic anhydride and methylvinylether, detergent enzymes such as proteases, amylases, lipases and mixtures thereof, and stabilizing agents for the like enzymes. Other optional components include soil suspending agents such as the sodium salt of carboxymethylcellulose and the sodium salt of methylhydroxypropyl cellulose ; through-the-wash softening smectite clays such as alkali montmorillonites, saponites and hectorites, having an ion-exchange capacity of at least 50 m.eq./100 g, and photoactivators, for example, sulfonated metal phthalocyanines such as zinc and aluminium phthalocyanines.

50 The subject compositions further can comprise suds regulants e. g. those of U.S. Patent 4,192,761 and more in general suds regulants based on silicones, silica, waterinsoluble hydrocarbons, either individually or optimized mixtures thereof, and renewable textile soil release agents such as described in European Patent Applications 0,042,187 and 0,042,188. Preferred soil release agents include N-hydrogenated tallow C₁₆-C₁₈-N,N',N'-tri-(2-hydroxyethyl)-propylene-1,3-diamine and N-C₁₂-C₁₄-coconutalkyl-N,N-dimethyl-N-amine oxide and can be utilized in levels of from 0.1-1.5 %. The claimed compositions also can contain brighteners, perfumes, dyes, bactericidal agents, antioxidants and fillers. A preferred additive system is comprised of a combination of a tertiary amine and an impalpable smectite clay as described in European Patent Application 0 011 340.

The following examples illustrate the invention and highlight the benefits derivable therefrom.

60 The abbreviations for the individual ingredients have the following meaning :

LAS : Sodium salt of linear dodecyl benzene sulfonate

TAS : Sodium salt of tallow alcohol sulfate

α-OS : Sodium salt of α-olefin (C₁₂₋₁₈) sulfonate

65 FAE₃S : Sodium salt of fatty alcohol (C₁₂₋₁₈) (ethoxy)₃ sulfate

- AO : C₁₂₋₁₄ alkyl dimethylamine oxide
TAE₁₁ : Tallow alcohol ethoxylated with about 11 moles of ethylene oxide
FA₂₅E_X : Fatty alcohol (C₁₂-C₁₅) ethoxylated with X moles of ethylene oxide
DTMA : Ditalow methyl amine
5 CFA : C₁₂₋₁₄ coconut fatty acid
HFA : Hydrogenated C₁₆₋₂₂ fatty acid
STPP : Sodium tripolyphosphate
Zeolite A : Sodium salt of zeolite 4A (average particle size between 2-6 μ m)
NTA : Sodium salt of nitrilotriacetate
10 Copolymer : AA⁴⁰/MA⁶⁰ = copolymer of acrylic acid 40 % mol. % and maleic acid 60 % mol. %
CMC : Sodium salt of carboxymethyl cellulose
Clay : Sodium montmorillonite
Silicate 1.6 : Sodium silicate SiO₂/Na₂O = 1.6
Silicate 1.0 : Sodium metasilicate
15 STS : Sodium salt of toluene sulfonate
EDTA : Sodium salt of ethylene diamine tetra-acetate
Perborate : NaBO₂ · H₂O₂ · 3H₂O
P.A. : Photoactivator sulfonated Zn phthalocyanine Antioxidant : 4,4'-thiobis(6-tertiary butyl-3-m-cresol)

20 The following granular detergent compositions were prepared by conventional spray-drying of slurry of most of the individual ingredients and subsequent dry-mixing of the spray-dried powder with spray-drying sensitive ingredients, namely perborate enzyme photoactivator and suds regulant.

25 Compositions (% by weight)

30		EXAMPLES				
		<u>I</u>	<u>A</u>	<u>B</u>	<u>II</u>	<u>C</u>
	LAS	5.0	5.0	5.0	5.0	5.0
	TAS	3.0	3.0	3.0	3.0	3.0
35	TAE	1.0	1.0	1.0	1.0	1.0
	HFA	1.0	1.0	1.0	1.0	1.0
	STPP	18.0	18.0	18.0	18.0	18.0
40	Copolymer MA ⁶⁰ /AA ⁴⁰	2.0	2.0	4.0	1.0	1.0
	Polyacrylate MW 1000	1.0	-	-	-	-
	" MW 2000	1.0	-	-	2.0	-
	" MW 4500	-	2.0	-	-	-
45	" MW 200 000	-	-	-	-	2.0
	P.A	0.004	0.004	0.004	0.004	0.004
	CMC	1.0	1.0	1.0	1.0	1.0
50	Silicate 1.6	8.0	8.0	6.0	8.0	8.0
	MgSO ₄	0.5	0.5	0.5	0.5	0.5
	EDTA	0.2	0.2	0.2	0.2	0.2
55	Perborate	24.0	24.0	24.0	24.0	24.0
	Enzyme	0.6	0.6	0.6	0.6	0.6
	Suds regulant (1)	1.0	1.0	1.0	1.0	1.0
60	Brightener/Perfume/Water/ Sodium Sulfate	balance to 100				

65 (1) Prilled suds regulant system consisting of : 77.5 % sodiumtripolyphosphate and 22.5 % active consisting of : 13.5 % paraffin oil ; 6 % paraffin wax (m. p. 70 °C) ; and 3 % amorphous hydrophobic silica.

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The compositions of Examples I (invention), A and B (prior art) were compared under the following conditions. The variations were expressed as whiteness maintenance :

- minidrums testing apparatus ;
- 0.6 % product concentration in wash liquor ;
- 0.3 g/l (18 grains/US gallon) water hardness (3 : 1 Ca/Mg ratio) ;
- heating up from 15 °C to 90 °C ; + 20 min at 90 °C ;
- fabrics : terry tracers ;
- 4 cumulative cycles ;
- whiteness readings under standard daylight : visual grading by two judges working independently. 0 to 4 scale (0 = no difference, 1 = probable difference, 2 = consistent small difference, 3 = clear difference, 4 = big difference).

The testing results were as follows :

Composition I	vs.	Composition A
standard		- 1.7
Composition I	vs.	Composition B
standard		- 0.4

These results show the significant performance benefits derivable from inventive Composition I vs. closely related prior art compositions A and B.

The compositions of Examples II and C were compared as described hereinbefore except for the following conditions.

- commercial washing machine ;
- 1 % product concentration ;
- 0.2 g/l (12 grains/US gallon) water hardness (3 : 1 Ca/Mg ratio) ;
- 90 °C prewash + mainwash cycle ;
- 8 cumulative washes.

The whiteness maintenance results were as follows :

Composition II	vs.	Composition C
standard		- 1.1

The performance superiority of the claimed technology vs. identical compositions containing high molecular weight polyacrylates is confirmed.

An additional composition of this invention III and closely related prior art compositions were spray-dried/drymixed as described above, the sole difference being the levels of polymers as follows :

EXAMPLES				
	III	D	E	F
Copolymer MA ⁶⁰ /AA ⁴⁰	1.5	1.0	3.0	-
Polyacrylate MW 1000	0.75	-	-	1.5
" MW 2000	0.75	-	-	1.5
" MW 4500	-	2.0	-	-

The compositions of Examples III, D, and E were compared for whiteness maintenance under the conditions recited for Examples II and C, except that the water hardness was 0.3 g/l (18 grains/US gallon).

The results were as follows :

Composition III	vs.	Composition D
standard		- 2.6
Composition III	vs.	Composition E
standard		- 2.1

The inventive composition is again markedly superior over the art.

Compositions III and F were compared for soil antiredeposition, measured as whiteness, thereby using the following testing conditions :

tubes testing apparatus ;

0.3 % to 1.0 % product concentrations ;

5 0.4 g/l (25 grains/US gallon) water hardness (3 : 1 Ca/Mg ratio) ;

heating up from 15 °C to 90 °C + 30 min at 90 °C ;

fabrics : terry tracers.

The whiteness readings were done with a Zeiss-spectrophotometer. The results were as follows :

	<u>EXAMPLE</u>	
	<u>III</u>	<u>F</u>
% of soil deposition avoided at:		
15 0.3% prod. concentration	70.3	70.4
0.4% "	71.1	71.0
0.5% "	71.2	63.9
20 0.6% "	72.3	61.2
0.7% "	71.9	70.9
0.8% "	72.5	72.3
25 0.9% "	72.6	72.7
1.0% "	73.0	72.9

30 These results show that the combined utilization of the copolymeric and the homopolymeric ingredients is a requisite for obtaining the inventive benefits.

Additional detergents of this invention are prepared having the following composition.

	INGREDIENT	<u>EXAMPLES</u> (% by weight)			
		IV	V	VI	VII
40	LAS	5.0	5.0	-	5.0
	TAS	3.0	-	2.5	3.0
	α -OS	-	-	5.0	-
45	Coconut-trimethyl-quaternary ammonium chloride	-	2.0	-	-
	TAE ₁₁	1.0	2.5	-	1.0
	FA ₂₅ E ₇	-	-	4.0	-
50	DTMA	-	5.5	-	-
	CFA	-	-	4.0	-
	HFA	-	0.5	-	-
55	STPP	20.0	20.0	16.0	28.0
	Zeolite A	-	-	16.0	-
	NTA	6.0	-	-	-
	Na ₃ Citrate	-	5.0	-	-
60	Copolymer AA ⁴⁰ /MA ⁶⁰	1.5	2.0	2.0	1.0
	Polyacrylate MW 1000	1.0	1.5	1.0	0.5
	Polyacrylate MW 2000	1.0	1.5	1.0	0.5
65	CMC	0.8	-	1.0	0.8

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(Continued)

5	INGREDIENT	EXAMPLES (% by weight)			
		IV	V	VI	VII
10	Montmorillonite	-	8.0	-	-
	Silicate 1.6	6.0	6.0	2.0	6.0
	MgSO ₄	0.5	-	0.5	1.0
	NaOH	0.8	1.3	0.95	0.75
15	EDTA	0.2	0.2	0.3	0.2
	Perborate	32.0	-	28.0	28.0
	Suds regulant (1)	1.0	2.7	1.5	1.2
20	Enzyme (proteolytic)	0.2	0.6	0.3	0.2
	Brightener, perfume, water/ sodium sulfate	balance to 100			

25 (1) See Example I

30	INGREDIENTS	EXAMPLES (% by weight)		
		VIII	IX	X
	LAS	10.0	5.0	7.0
35	TAS	-	3.0	-
	FAE ₃ S	3.0	-	-
	TAE ₁₁	1.0	1.0	2.7
	HFA	-	4.0	3.5
40	STPP	-	24.0	10.0
	NTA	6.0	-	4.0
	Na ₂ CO ₃	20.0	-	10.0
45	Copolymer MAA ⁵⁰ /MA ⁵⁰	7.7	1.4	3.3
	CMC	1.0	1.0	0.8
	Polyacrylates 1:1(MW1000/2000)	7.7	1.0	3.3
50	Silicate solids 1.6	4.0	3.0	8.0
	MgSO ₄	1.0	-	0.5
	NaOH	1.1	0.9	0.2
55	STS	1.4	-	-
	EDTA	0.2	0.3	0.3
	Perborate	25.0	-	30.0
	P.A.	0.007	0.003	0.002
60	Enzyme (proteolytic)	0.3	0.6	0.2
	Brightener, perfume, H ₂ O/ sulfate	balance to 100		

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	INGREDIENT	EXAMPLES (% by weight)			
		XI	XII	XIII	XIV
5	LAS	7.0	4.5	7.0	4.5
	TAS	-	2.5	-	2.5
10	A.O.	0.5	0.3	0.8	1.0
	TAE ₁₁	2.7	-	2.7	-
	FA ₂₅ E ₇	-	2.0	-	2.0
	CFA	-	2.0	-	2.0
15	HFA	3.5	4.0	3.5	4.0
	STPP	4.0	24.0	16.0	8.0
	Zeolite A	-	-	16.0	-
20	NTA	-	4.0	-	6.0
	Copolymer AA ⁶⁰ /MA ⁴⁰	5.0	1.0	2.0	3.0
	Polyacrylate MW 1000	2.0	1.0	1.5	1.0
25	Polyacrylate MW 2000	2.0	0.5	1.5	2.0
	CMC	0.8	0.8	1.0	1.0
	Silicate 1.6	5.0	5.0	2.0	2.0
	MgSO ₄	-	0.5	0.5	1.0
30	Na ₂ CO ₃	10.0	-	6.0	10.0
	Ethylenediamine tetramethyl- phosphonate Na-salt	1.3	-	0.8	-
35	EDTA	0.2	0.3	0.3	0.2
	Perborate	32.0	28.0	30.0	28.0
	Enzyme (proteolytic)	0.2	0.2	0.3	0.2
40	Brightener, perfume, water, sulfate		balance	to	100

	INGREDIENTS	EXAMPLES (% by weight)		
		XV	XVI	XVII
50	LAS	4.0	4.0	-
	α-OS	-	-	4.5
	FA ₂₅ E ₇	12.0	10.0	6.0
	CFA	-	2.0	6.0
55	HFA	0.5	-	0.5
	STPP	12.0	20.0	18.0
	Zeolite A	-	-	20.0
60	Na ₃ Citrate	-	10.0	-
	Copolymer AA ⁷⁵ /MA ²⁵	2.0	1.0	1.3
65	Polyacrylates 1:1 mix (MW 1000 and 2000)	4.0	1.0	2.5

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5	INGREDIENTS	EXAMPLES (% by weight)		
		XV	XVI	XVII
	CMC	0.8	1.0	0.8
	Silicate 1.6	6.0	6.0	2.0
10	MgSO ₄	0.5	-	1.0
	Sodium carbonate	5.0	5.0	-
	NaOH	1.3	0.8	0.8
15	EDTA	0.2	0.2	0.3
	Perborate	24.0	10.0	28.0
	Antioxidant	0.01	0.01	0.01
20	Silicone suds regulant of Example I	1.6	2.1	1.3
	Brightener, perfume, H ₂ O, sulfate		balance to 100	

		EXAMPLES			
		(% by weight)			
	INGREDIENT	XVIII	XIX	XX	XXI
30	LAS	7.0	5.0	15.0	4.0
	TAS	-	3.0	-	-
	TAE ₁₁	2.7	-	2.5	-
35	FA ₂₅ E ₇	-	2.0	-	12.0
	CFA	-	2.0	-	-
	HFA	3.5	-	0.5	0.5
40	STPP	20.0	16.0	25.0	24.0
	Zeolite A	-	16.0	-	-
	Copolymer AA ⁶⁰ /MA ⁴⁰	2.0	2.0	1.0	1.0
	Polyacrylate MW 1000	1.0	1.5	0.5	1.0
45	Polyacrylate MW 3000	1.0	1.5	0.5	0.5
	CMC	0.8	1.2	1.0	1.0
	Silicate solids 1.6	5.0	2.0	5.0	6.0
50	Silicate solids 1.0	1.0	-	-	-
	MgSO ₄	0.5	1.0	0.5	1.0
	Sodium carbonate	6.0	-	6.0	6.0
	NaOH	0.75	0.50	0.95	1.1
55	TAED	3.0	2.5	4.0	2.5
	Perborate	24.0	20.0	8.0	2.0
	Antioxidant	-	-	-	0.01
60	Enzyme (proteolytic)	0.3	0.6	0.6	0.3
	Suds regulant silicone	-	0.5	1.3	0.16
	Brightener, perfume, water, sulfate		balance	to	100
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Claims

1. A granular detergent composition containing no or reduced levels of P-containing builders, and further containing surface-active agents, polymeric carboxylates and, if desired, conventional detergent additives including non-phosphorus detergent builders, characterized in, that the composition contains
 - a) from 0.5 % to 15 % by weight of a polyacrylate homopolymer having a molecular weight below 3 000 ;
 - b) from 0.5 % to 15 % by weight of a copolymer which consists of an ethylenically unsaturated monocarboxylic acid monomer having not more than 5 carbon atoms, and an ethylenically unsaturated dicarboxylic acid monomer having not more than 6 carbon atoms, whereby the molar ratio of the monomers is from 1 : 4 to 4 : 1, and, whereby the weight ratio of the homopolymeric ingredient to the copolymeric ingredient is in the range from 4 : 1 to 1 : 4.
2. The composition in accordance with Claim 1 wherein the copolymeric ingredient is comprised of (meth)-acrylic acid and maleic acid monomers.
3. The composition in accordance with Claim 1 wherein, for a detergent composition containing P-builders in a level, expressed as phosphorus, of from 2 % to 5 % by weight, the homopolymeric ingredient represents from 0.5 to 4 % by weight and the copolymeric ingredient represents from 0.5 % to 4 % by weight.
4. The composition in accordance with Claim 1 wherein, for a detergent composition containing P-builders in a level, expressed as phosphorus, below 2 % by weight, the homopolymeric ingredient represents from 2 % to 8 % by weight and the copolymeric ingredient from 2 % to 8 % by weight.
5. The composition in accordance with Claims 1, 3 and 4 wherein the weight ratio of the copolymeric ingredient to the homopolymeric ingredient is from 2 : 1 to 1 : 2.
6. The composition in accordance with Claim 1 wherein the homopolymeric ingredient is comprised of a polyacrylate having a molecular weight of 2 000 and a polyacrylate of a molecular weight of 1 000 in a weight ratio of 2 : 1 to 1 : 2.
7. The detergent composition in accordance with Claims 1 and 6 wherein the homopolymer is represented by a 1 : 1 weight ratio mixture of polyacrylates having molecular weights of 1 000 and 2 000 respectively.

Patentansprüche

1. Eine granuliert Detergengzusammensetzung, die keine oder verringerte Mengen an P-hältigen Gerüststoffen enthält, und die weiterhin oberflächenaktive Mittel, polymere Carboxylate und, gewünschtenfalls, übliche Detergengzusätze, darunter Nicht-Phosphor-Detergenggerüststoffe, enthält, dadurch gekennzeichnet, daß die Zusammensetzung
 - a) 0,5 Gew.-% bis 15 Gew.-% eines Polyacrylathomopolymers mit einem Molekulargewicht unter 3 000 ; und
 - b) 0,5 Gew.-% bis 15 Gew.-% eines Copolymers enthält, welches aus einem ethylenisch ungesättigten Monocarbonsäuremonomer mit nicht mehr als 5 Kohlenstoffatomen und einem ethylenisch ungesättigten Dicarbonsäuremonomer mit nicht mehr als 6 Kohlenstoffatomen, wobei das Molverhältnis der Monomere 1 : 4 bis 4 : 1 beträgt, besteht, und wobei das Gewichtsverhältnis des homopolymeren Bestandteils zu dem copolymeren Bestandteil im Bereich von 4 : 1 bis 1 : 4 liegt.
2. Die Zusammensetzung nach Anspruch 1, in der der copolymeren Bestandteil aus (Meth)-acrylsäure- und Maleinsäuremonomeren zusammengesetzt ist.
3. Die Zusammensetzung nach Anspruch 1, in der für eine Detergengzusammensetzung, die P-Gerüststoffe in einer Menge, ausgedrückt als Phosphor, von 2 Gew.-% bis 5 Gew.-% enthält, der homopolymeren Bestandteil 0,5 Gew.-% bis 4 Gew.-% ausmacht und der copolymeren Bestandteil 0,5 Gew.-% bis 4 Gew.-% ausmacht.
4. Die Zusammensetzung nach Anspruch 1, in der für eine Detergengzusammensetzung, die P-Gerüststoffe in einer Menge, ausgedrückt als Phosphor, unter 2 Gew.-% enthält, der homopolymeren Bestandteil 2 Gew.-% bis 8 Gew.-% und der copolymeren Bestandteil 2 Gew.-% bis 8 Gew.-% ausmacht.
5. Die Zusammensetzung nach den Ansprüchen 1, 3 und 4, in der das Gewichtsverhältnis des copolymeren Bestandteils zum homopolymeren Bestandteil 2 : 1 bis 1 : 2 beträgt.
6. Die Zusammensetzung nach Anspruch 1, in der der homopolymeren Bestandteil aus einem Polyacrylat mit einem Molekulargewicht von 2 000 und einem Polyacrylat mit einem Molekulargewicht von 1 000 in einem Gewichtsverhältnis von 2 : 1 bis 1 : 2 zusammengesetzt ist.
7. Die Detergengzusammensetzung nach den Ansprüchen 1 und 6, in der das Homopolymer durch ein Gemisch von Polyacrylaten, die Molekulargewichte von 1 000 bzw. 2 000 aufweisen, in einem Gewichtsverhältnis 1 : 1 verkörpert wird.

Revendications

1. Composition détergente granulaire ayant une teneur nulle ou une teneur réduite en adjuvants

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contenant P et qui contient en outre des agents tensio-actifs, des carboxylates polymères et, si on le désire, des additifs pour détergents classiques y compris des adjuvants de détergence ne contenant pas de phosphore, composition caractérisée en ce qu'elle contient :

5 a) 0,5 à 15 % en poids d'un homopolymère polyacrylate ayant un poids moléculaire inférieur à 3 000 ;

b) 0,5 à 15 % en poids d'un copolymère constitué d'un monomère d'un monoacide carboxylique à insaturation éthylénique n'ayant pas plus de 5 atomes de carbone et d'un monomère d'un diacide carboxylique à insaturation éthylénique n'ayant pas plus de 6 atomes de carbone, le rapport molaire des monomères étant de 1 : 4 à 4 : 1 et le rapport pondéral de l'ingrédient homopolymère à l'ingrédient copolymère étant dans l'intervalle de 4 : 1 à 1 : 4.

10 2. Composition selon la revendication 1, dans laquelle l'ingrédient copolymère est constitué de monomères d'acide (méth)-acrylique et d'acide maléique.

3. Composition selon la revendication 1, dans laquelle, pour une composition détergente contenant des adjuvants contenant P à une teneur, exprimée en phosphore, de 2 % à 5 % en poids, l'ingrédient homopolymère représente 0,5 à 4 % en poids et l'ingrédient copolymère représente 0,5 à 4 % en poids.

15 4. Composition selon la revendication 1, dans laquelle, pour une composition détergente comprenant des adjuvants contenant P à une teneur, exprimée en phosphore, inférieure à 2 % en poids, l'ingrédient homopolymère représente 2 % à 8 % en poids et l'ingrédient copolymère représente 2 à 8 % en poids.

20 5. Composition selon les revendications 1, 3 et 4, dans laquelle le rapport pondéral de l'ingrédient copolymère à l'ingrédient homopolymère est de 2 : 1 à 1 : 2.

6. Composition selon la revendication 1, dans laquelle l'ingrédient homopolymère est constitué d'un polyacrylate ayant un poids moléculaire de 2 000 et d'un polyacrylate ayant un poids moléculaire de 1 000 dans un rapport pondéral de 2 : 1 à 1 : 2.

25 7. Composition détergente selon les revendications 1 et 6, dans laquelle l'homopolymère est représenté par un mélange dans un rapport pondéral de 1 : 1 de polyacrylates ayant des poids moléculaires de 1 000 et de 2 000 respectivement.

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