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54 **Builder system suitable for cleaning agent.**

57 The invention relates to a builder system suitable for use in a cleansing agent, comprising porous beads of at least partially hydrated soda, into the pores of which a solution of a soluble calcium salt has been incorporated, to a method for the manufacture thereof and to a cleansing agent containing such a builder system

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The invention relates to a builder system suitable for use in a cleansing agent, to a process for the manufacture thereof, and to a cleansing agent containing such a builder.

5 Cleansing agents and more particularly (main wash) detergents contain a number of groups of raw materials. The most important among them are the surface-active substances or surfactants, which serve to reduce the surface tension of the water, and the builders, which serve to neutralize the hardness of the water. Often, such cleansing agents further contain bleaching agents for removing colored soil components through oxidation, and additives such as perfume, optical bleaches, corrosion inhibitors and the like.

10 In the past, for reducing the hardness of the washing water, use was mainly made of phosphates. Although these phosphates exhibit optimum effectiveness in terms of detergency, the use thereof is less desirable with regard to eutrophication and excessive algal growth. Accordingly, alternatives to the use of phosphates have been searched for. Known alternative builders are nitrilotriacetate, ethylene tetracetate, citrate and zeolites. Soda has also been used in detergents on account of its calcium-binding activity. The presence of soda in detergents leads to the formation of insoluble calcium carbonate, often designated as calcite.

15 The mains water that is used in the washing process must first be softened on account of the negative influence of hard water on the cleaning power of the suds system. When a detergent goes into solution, the hardness of the suds system is reduced by the activity of the builders. This improves the detergency. The fact is there appears to be a virtually linear relation between the logarithm of the residual hardness and the cleaning power. In the times when mainly phosphates were used, the residual hardness was approximately 20 0.01° dH. At that value the negative influence of the calcium hardness is minimal.

It appears that with the builders utilized in the current situation, the residual hardness in suds systems of modern detergents is approximately 3° dH. This has an adverse effect on the detergency.

25 Soda could be an attractive alternative as a builder, since it is capable of reducing the residual hardness to the same level as was formerly achieved by the phosphates and other builders which are no longer desired for environmental reasons. Soda moreover does not have any disadvantages from an environmental point of view. A major drawback of the use of soda, which has to date prevented the large-scale application thereof, is the fact that the seed formation proceeds particularly slowly, so that it may take a very long time for the suds to be softened.

30 Much research has already been done into the promotion of the calcite seed formation in detergents. An example thereof is the co-spraying of calcium salts in the spray-drying of detergents. It was found, however, that nevertheless the softening process in the suds could hardly be influenced.

35 Another possibility which was considered was the addition of fine calcite particles to detergents. It is a particularly expensive process to generate very small seeds and further it appeared that these seeds were inactivated during storage. Since moreover in many detergents phosphonates were used to bind traces of metal so as to optimize the bleaching process, a rapid deactivation of the seeds occurred. The fact is that phosphonates are particularly good poisons for calcite seeds. Accordingly, the presence of phosphonates appears to prevent the growth of calcite seeds extremely effectively. This partly explains why the residual hardness of modern detergents cannot be reduced to below approx. 3° dH despite the presence of soda.

40 It has also been proposed to add ground calcite to detergents, but it was found that these particles are much too coarse to soften the detergent really effectively.

The object of the invention is to provide a builder system that is based on soda, does not possess the disadvantages of the known agents and yet does give rise to a very effective seed formation.

45 The invention accordingly relates to a builder system which is suitable for use in a cleansing agent, and in particular in a main wash detergent, comprising porous beads of soda, preferably at least partially hydrated soda, into the pores of which beads an aqueous solution of a soluble metal salt, in particular a calcium salt, has been incorporated with the aid of an additive.

50 Surprisingly, it has been found that if a, preferably saturated, aqueous solution of a soluble metal salt, preferably a calcium salt, such as calcium chloride, calcium nitrate or calcium acetate, is incorporated into the pores of porous soda beads with the aid of an additive, the resultant product, as a builder system in main wash detergents, gives a particularly fast softening of the suds system.

The principle of the present invention is not entirely clear. On the one hand, it is possible that during the impregnation of the calcium salt solution in the pores a conversion of the soda to the fully hydrated form occurs, with the calcium salt precipitating on the pore wall. On the other hand, it is also possible that a reaction of the calcium ions and the carbonate ions occurs in the builder system giving rise already to the precipitation of calcium carbonate on the pore wall, which particles could then be so fine as to start functioning as seeds directly upon dissolution of the soda. Another possibility is that a combination of these two mechanisms plays a part. In view of the necessary presence of an additive, such as a non-ionic surface-active substance (non-ionic), in the system, it is also possible that upon the dissolution of soda in

the washing water a rapid formation of fine seeds occurs, which seeds are responsible for the rapid reduction of the hardness.

It has been found in any event that irrespective of the nature of the theory, the use of the present calcium salt-impregnated porous soda as a builder system in a powder detergent gives a particularly good and effective softening of the suds system. Both the time period within which and the degree to which softening occurs is clearly superior to the current builder systems.

According to the invention, use is made of porous soda beads which preferably have an average particle size of between 0.2 and 1.0 mm. The porosity of the soda, determined with mercury porosimetry, is such that 50 to 85 vol.% of the pores have a diameter of from 0.1 to 0.7 μm , while the rest of the pores substantially have a smaller diameter. The average pore size of the beads is preferably between 0.05 and 3 μm , more particularly between 0.1 and 0.7 μm .

The impregnation of the soda beads with the, preferably saturated, salt solution in combination with an additive, preferably takes place in such a manner that the metal ion content, drawn to the weight of the beads, is between 0.5 and 10 wt.% and more preferentially between 0.5 and 5 wt.%. This impregnation preferably takes place in such a manner that the volume of the liquid employed for impregnation is not more than the total pore volume of the soda beads. This provides the advantage that eventually a dry product is obtained which can be further processed in a main wash detergent in the conventional manner.

A particularly effective method for impregnating soda beads with the aqueous salt solution consists in the use of an emulsion of the calcium-salt solution in a non-ionic surface-active substance, such as an alkyl ethoxylate (3 to 20 EO) or an alkyl(poly) glucoside (1 or more glucoside), as additive. Instead of using a non-ionic as additive, it is also possible to use an oil or another compound through the effect of which the aqueous solution of the metal salt is incorporated into the soda and which gives rise to rapid formation of small seeds in the washing water.

Accordingly, the invention also relates to a method for manufacturing such builder particles, comprising impregnating porous beads of soda with an emulsion of a saturated solution of a calcium salt in a non-ionic surface-active substance, the amount of the emulsion being not greater than the pore volume of the soda beads.

The invention also relates to a detergent comprising, in addition to the customary components, at least one builder system as described hereinabove.

In addition to the builder system referred to, the main wash detergent comprises conventional components for powdered detergents, such as surfactants, optionally one or more other builders or additives such as bleaches, perfume, corrosion-inhibitors, anti-redeposition agents and the like.

It is observed that the use of phosphonates can inhibit the seed formation, but, on the other hand, the use of phosphonates is not strictly necessary in a system utilizing the builders according to the present invention because the builder according to the invention has at least partially the same activity as the phosphonates utilized according to the prior art.

According to the invention, a powdered detergent comprises the builder system as described within the concept of the invention, optionally in combination with other conventional builder components, such as untreated soda, bicarbonate, NAS, zeolite, co(polymer) and the like, at least one surface-active substance (non-ionic and/or anionic), optionally bleachers, such as perborate, additives, such as magnesium stearate and sodium sulfate, as well as the so-called "minors", optical white, perfume, anti-redeposition agents and corrosion-inhibitors.

Generally, a powdered detergent according to the invention comprises, on a weight basis, 10 to 50% surface-active substance, 25 to 90% builder system, at least partially consisting of the porous soda impregnated with the metal salt, 0 to 25% bleaching agent and further additives and minors in an amount which is dependent on the nature of the additives and minors, but which will generally not exceed 60%. The amount of the builder system according to the invention that can be utilized in the detergents varies from 2.5 to 50 wt.%, more particularly between 5 and 25 wt.%. The amount depends at least partly on the amount of metal ion present in the builder system. In the light of the effectiveness of the system, it is generally not necessary to utilize more than 25 wt.%, drawn to the weight of the washing powder. In this connection it should further be observed that the detergent should not contain any appreciable amounts of components which adversely affect the effectiveness of the builder system. This relates particularly to complexing agents for calcium.

The invention will now be further explained in and by some examples.

In order to compare the activity of the builder system according to the invention and soda, a number of experiments were performed. On the basis of soda of an average pore diameter of from 0.1 to 0.7 μm , a number of builder systems were prepared.

A untreated soda

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- B Soda impregnated with 9 wt.% tallow fatty alcohol.5 EO
- C Soda impregnated with 1.4 wt.% CaCl₂, in saturated solution
- D Soda impregnated with a suspension of 1.4 wt.% solids CaCl₂, in 9 wt.% tallow fatty alcohol.5 EO
- E Soda impregnated with an emulsion of 1.4 wt.% CaCl₂ as saturated solution in 9 wt.% tallow fatty alcohol.5 EO.

These systems were added to water of a temperature of 25 °C and a Ca hardness of 2.5° dH (2.1 g builder system per liter water), the hardness being measured as a function of time.

The results of the experiments are shown in the following Table.

Table 1

System	Hardness after 4 minutes °DH	10 minutes °DH	20 minutes °DH
A	0.35	0.038	0.036
B	0.31	0.041	0.039
C	0.34	0.040	0.037
D	0.32	0.042	0.040
E	0.03	0.004	0.004

From these data it clearly appears that a fast and effective softening can only be obtained if the system according to the invention is used.

On the basis of builder system E, two detergents were formulated, which contain lauryl ethoxylate.6 EO, perborate and optionally sodium citrate. The dose per liter was 2.1 g builder system, 0.8 g lauryl ethoxylate.6 EO, 0.6 perborate and 0 (exp. 1) and 0.1 g (exp. 2) sodium citrate, respectively. The results are shown in Table 2.

Table 2

Experiment	Hardness after 0 minutes °DH	4 minutes °DH	10 minutes °DH	20 minutes °DH
1	15	0.05	0.004	0.003
2	15	0.08	0.005	0.003

Claims

1. A builder system suitable for use in a cleansing agent, comprising porous soda beads, into the pores of which a solution of a soluble metal salt has been incorporated with the aid of an additive.
2. A builder system according to claim 1, characterized in that an emulsion of the solution of the metal salt and a surface-active substance is incorporated into the pores.
3. A builder system according to claim 1 or 2, characterized in that, as metal salt, a calcium salt, more particularly calcium chloride, calcium nitrate, or calcium acetate, is used.
4. A builder system according to claims 1-3, characterized in that an at least partially hydrated soda is used.
5. A builder system according to claim 3 or 4, characterized in that the amount of calcium, drawn to the weight of the beads, is between 0.5 and 10, preferably between 0.5 and 5 wt.%.
6. A builder system according to claims 1-5, characterized in that a saturated solution of the salt is used.
7. A builder system according to claims 1-6, characterized in that the average bead size is between 0.1 and 3 mm, preferably between 0.3 and 1.0 mm.

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8. A builder system according to claims 1-7, characterized in that the average pore size of the original soda beads is between 0.05 and 3 μm , preferably between 0.1 and 0.7 μm .
- 5 9. A method for manufacturing a builder system according to claims 1-8, comprising impregnating porous beads of soda with an emulsion of a saturated solution of a metal salt in a non-ionic surface-active substance, the amount of the emulsion being not greater than the pore volume of the soda beads.
- 10 10. A cleansing agent comprising, in addition to the customary components, at least one builder system according to claims 1-8.

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EUROPEAN SEARCH REPORT

Application Number

EP 93 20 1846

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-5 198 145 (W. LOBUNEZ ET AL) * claims 1-3 * ---	1-10	C11D3/10
A	EP-A-0 221 776 (UNILEVER PLC ET AL) * abstract * * claims 1-2,16-20 * ---	1-10	
A	US-A-4 992 079 (C. W. LUTZ) * abstract * ---	1-10	
A	EP-A-0 266 863 (UNILEVER PLC ET AL.) * claims 1-14 * -----	1-10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C11D
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 15 DECEMBER 1993	Examiner SIATOU E.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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