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This paper comprises:

Annex 1 (Patent Application)

The present invention relates to a powdery detergent composition, which contains a sodium percarbonate bleaching agent having improved storage stability.

Detergent compositions are complex formulations principally comprising a surfactant, a builder and a bleaching agent, each of them fulfilling a different function.

Detergent builders play a central role in the course of the washing process. Their function is largely that of supporting detergent action and of water softening, i.e., eliminating calcium and magnesium ions, which arise from the water and from soil. They can be selected among several types of materials such as complexing agents like sodium triphosphate and ion exchangers, such as zeolites. For environmental reasons phosphates are preferably replaced by zeolites.

Surfactants constitute the most important group of detergent components, and they are present in all types of detergents. Generally, surfactants are water-soluble surface-active agents comprised of a hydrophobic portion attached to hydrophilic or solubility-enhancing functional groups. The surfactant is responsible for the cleaning effect.

Chemical bleaching is employed for the removal of coloured non-washable soils and stains adhering to fibres. The bleaching component preferably contains a source of peroxygen, which is needed for giving bleaching action to the detergent composition. For a number of years, oxygen-based bleaches, such as sodium perborate, have mainly been used. An increasing awareness of the potential environmental hazard of these boron-containing bleaches has, however, intensified the interest in other oxygen-based bleaches.

Particular attention is here attached to sodium percarbonate which is dissolved qu
water and which in addition to its bleaching effect also has an alkaline effect supportin
and intensifying the washing effect. A drawback of sodium percarbonate is, however, its poor stability, which presents a limiting factor for its use in detergent compositions, especially those containing zeolite. Factors adversely affecting the stability are especially the presence of moisture and temperatures exceeding 28 °C to 30 °C.

Numerous attempts have been made to improve the stability of sodium percarbonate. However, none of these have led to a material, which has a shelf life that is long enough for use in detergent compositions. Several coated percarbonates have been proposed. Most of these products have coatings comprising materials, which are not desirable in view of environmental concerns. Furthermore, these coating materials need to be present in large amounts; this means that less active oxygen is available per gram of coated product, since active oxygen is only present in the percarbonate and not in the coating material. Active oxygen is the amount of oxygen that will be liberated as oxygen on decomposition of the percarbonate.

It is thus an object of the present invention to improve the stability of sodium percarbonate, especially in the presence of moisture and temperatures exceeding 28 °C to 30 °C, as to obtain a shelf life that is long enough for use in zeolite-containing detergent compositions.

We have now found that the stability of sodium percarbonate in the detergent composition can be improved to a satisfactory degree by adding an alkali metal salt of a carboxylic acid to the detergent composition or by coating the sodium percarbonate particles with said alkali metal carboxylic acid salt.

The carboxylic acid salts used for obtaining a stabilizing effect are commercially available. They are selected from the group consisting of:

(1) Alkali metal salts of aliphatic monocarboxylic acids of formula $CH_3(CH_2)_nCOOH$ (I), wherein n is at least 2. The aliphatic monocarboxylic acids are for example butanoic acid (n = 2), pentanoic acid (n = 3), hexanoic acid (n = 4), heptanoic acid (n = 5), octanoic acid (n = 6), nonanoic acid (n = 7), decanoic acid (n = 8), undecanoic acid (n = 9) or dodecanoic acid (n = 10).

(2) Alkali metal salts of aliphatic dicarboxylic acids of formula $HOOC(CH_2)_mCOOH$ (II) wherein m is from 2 to 12. Preferred dicarboxylic acids are butanedioic acid ($HOOC-(CH_2)_2-COOH$) and hexanedioic acid ($HOOC-(CH_2)_4-COOH$).

(3) Alkali metal salts of hydroxycarboxylic acids (i.e. alkali metal salts of carboxylic acids bearing at least one –OH substituent) such as:

(3.1) monocarboxylic acids substituted with at least one -OH group, for example hydracrylic acid $HOCH_2-CH_2-COOH$, hydroxybutyric acid $HOCH_2-CH_2\ CH_2-COOH$ or glyceric acid $HOCH_2-CHOH-COOH$.

(3.2) dicarboxylic acids substituted with at least one -OH group, for example tartronic acid $HOOC-CHOH-COOH$ or tartaric acid $HOOC-CHOH-CHOH-COOH$.

(3.3) Tricarboxylic acids substituted with one -OH group such as citric acid $HOOC-CH_2\ C(OH)(COOH)CH_2-COOH$ or agaricic acid $HOOC-CH_2-C(OH)(COOH)-CH(COOH)-(CH_2)_{15}\ CH_3$.

The best results are obtained with the alkali metal salts of the unsubstituted aliphatic dicarboxylic acids of formula (II). The reason for this is not known yet. Suitable stability is also achieved with the alkali metal salts of carboxylic acids bearing at least one –OH substituent (i.e. hydroxycarboxylic acids described in (3)).

Preferably, the carboxylic acid salt is coated on the sodium percarbonate bleaching agent. Alternatively, it can be added as a separate additive to the detergent composition already comprising the sodium percarbonate bleaching agent. The alkali metal carboxylic salts according to the present invention improve the stability of sodium percarbonate, especially in moist and warm surroundings.

The coated sodium percarbonate according to the invention have a further advantage in that the coating material i.e. the carboxylic acid salt by itself is a good detergent builder, therefore reducing the use of other builders in the detergent composition.

The coating of the sodium percarbonate can be obtained by any of the conventional coating techniques known in the art such as, for example, spraying percarbonate particles in a pan-granulator or a rotating drum, followed by drying. However, best results have been obtained using a fluid bed drier, wherein coating and drying are effected in one step. When coated in a fluid bed drier, an extremely stable product is obtained.

When the alkali metal carboxylic acid salt is not present as a coating on the surface of sodium percarbonate, but is added as a separate additive to the detergent composition comprising sodium percarbonate, any conventional technique for incorporating additives in detergent compositions can be used.

The amount of carboxylic acid salt can be varied over quite a wide range. A level of at least 1 %, based on the weight of sodium percarbonate, is necessary to get any stabilizing effect, however. Since the carboxylic acid salt is water-soluble and a useful builder component in detergent compositions there is no specific limitation for the upper level, though 50 % by weight based on sodium percarbonate may be taken as the practical upper level. An amount for the carboxylic acid salt from 5 % to 15 % by weight based on the amount of sodium percarbonate is, however, preferably employed.

Sodium percarbonate is used in a conventional amount, i.e. between 1 and 25 % by weight based on the detergent composition.

The detergent compositions may also contain conventional additional ingredients. The precise nature of these additional ingredients, and levels of incorporation thereof will depend on the precise nature of the washing operation for which it is to be used. Examples of those conventional ingredients are acid sources, enzymes, suds suppressors, dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors.

Example 1

(a) Sodium percarbonate was coated, in a fluid bed drier, with a solution of sodium citrate (i.e. the sodium salt of citric acid) to give coatings of 5 and 10 % by weight (based on the weight of sodium percarbonate). These coated percarbonates were stored in a spray-dried zeolite containing base detergent powder in sealed bottles at 35 °C. All samples contained 2.0 g sodium percarbonate (amount before coating) and 8.0 g base powder detergent.

(b) The same base detergent powder, but containing an admixture of sodium citrate and sodium percarbonate in the same amounts as above, was also tested.

(c) The same base detergent powder comprising the same amount of sodium percarbonate but no carboxylic acid salt was stored under the same conditions and used as a control.

Percarbonate decomposition was monitored by measuring available oxygen (permanganate titration) at regular intervals. The stabilities of sodium percarbonate in these detergent compositions is indicated in the following tables.

Table 1:

Amount of peroxygen (in %) remaining as a function of the number of days stored at 35 °C and of the amount of carboxylic acid salt (coated/in admixture)

Time (days)	No carboxylic salt	sodium citrate 5 % coated	sodium citrate 10 % coated	sodium citrate 5 % in admixture	sodium citrate 10 % in admixture
7	89.1	97.0	97.7	95.3	95.4
14	87.1	93.4	95.4	91.7	93.2
28	61.4	91.5	91.5	80.3	83.4
42	57.1	77.4	89.2	65.4	69.2
56	46.8	76.6	86.0	59.6	65.9
70	46.1	74.6	84.7	56.2	64.1

These results clearly show the benefit of the sodium citrate compound in the detergent composition for improving the storage stability of sodium percarbonate. It is noted that the stabilizing effect is at best when sodium citrate is coated on the sodium percarbonate bleaching agent particles.

Example 2

Several different carboxylic acid salts were also used to stabilize sodium percarbonate. They were tested in amount of 5 % by weight based on the weight of sodium percarbonate. These stabilized percarbonates were stored in a spray-dried zeolite containing base powder in sealed bottles at 35 °C as in example 1. The stabilities of these coated products can be seen in table 2.

Table 2:

Amount of peroxygen remaining (%) as a function of the carboxylic acid salt ; 5 % coating or admixture; stored at 35 °C for 28 and 70 days. The second left-hand column indicates the carboxylic acid on which the sodium salt is based.

Carboxylic acid sodium salts		28 days coated	28 days admixture	70 days coated	70 days admixture
No carboxylic acid salt (comparative example)		61.4		46.1	
Sodium salts of $CH_3(CH_2)_nCOOH$	Hexanoic acid n = 4	82.5	67.4	69.3	57.9
	Decanoic acid n = 8	88.6	73.6	73.5	62.1
	Dodecanedioic acid n = 10	78.7	62.4	60.8	51.2
Sodium salts of $HOOC(CH_2)_mCOOH$	Butanedioic acid m = 2	96.2	92.3	87.2	83.1
	Hexanedioic acid m = 4	91.4	86.7	82.1	75.4
	Tetradecanedioic acid m = 12	77.2	70.1	63.3	59.8
Sodium salts of Hydroxycarboxilic acids	Glyceric acid	82.3	73.2	77.3	65.3
	Citric acid	91.5	80.3	74.6	56.2
	Tartaric acid	85.3	78.4	75.4	58.1
	Agaricic acid	83.7	74.8	72.5	59.0

These results clearly show the benefit of the sodium carboxylic acid salts in the detergent composition for improving the storage stability of sodium percarbonate. The effect is more important when the sodium carboxylic salt is coated on the percarbonate compound.

Claims

1. Powdery zeolite based detergent composition comprising a sodium percarbonate bleaching agent, a surfactant and a zeolite as detergent builder, characterized in that the composition comprises based on the weight of sodium percarbonate at least 1 weight percent of an alkali metal salt of a carboxylic acid as stabilizer for the sodium percarbonate bleaching agent, wherein the carboxylic acid is selected from the group consisting of

   (1) aliphatic monocarboxylic acids of formula $CH_3(CH_2)_nCOOH$ (I) wherein n is at least 2,
   (2) aliphatic dicarboxylic acids of formula $HOOC(CH_2)_mCOOH$ (II) wherein m is from 2 to 12 and
   (3) hydroxycarboxylic acids.

2. Powdery detergent composition according to claim 1, wherein the alkali metal carboxylic acid salt is coated on the sodium percarbonate bleaching agent.

3. Powdery detergent composition according to claim 1 wherein the alkali metal carboxylic acid salt and the sodium percarbonate bleaching agent are present in the detergent composition as separate additives.

4. Powdery detergent composition according to any one of claims 1 to 3, wherein the alkali metal salt of a carboxylic acid is sodium citrate.

5. Use of alkali metal salts of carboxylic acids as defined in claim 1 for stabilizing sodium percarbonate.

6. Sodium percarbonate bleaching agent, characterised in that the sodium percarbonate is coated with at least 1 weight percent of an alkali metal salt of a carboxylic acid as defined in claim 1.

Annex 2 (Official Communication)

1. Document D1, which belongs to the state of the art pursuant to Article 54(2) EPC, is directed to the stabilization of sodium percarbonate in zeolites based detergent compositions. Sodium percarbonate is stabilized by the use of an alkali metal salt of mono carboxylic acids of formula $CH_3(CH_2)_nCOOH$ or of an alkali metal salt of dicarboxylic acids of formula $HOOC(CH_2)_mCOOH$ (n and m are equal to or higher than 2). The alkali metal salt is either coated on the sodium percarbonate (8 wt% based on the weight of sodium percarbonate) or added to the detergent composition as a separate additive. It discloses in particular the use of sodium octanoate ($CH_3(CH_2)_6COOH$ (see example). The subject-matter of claims 1, 2, 3, 5 and 6 is therefore anticipated by D1.

   Document D2, which also belongs to the state of the art pursuant to Article 54(2) EPC, describes a powdery zeolite based detergent composition comprising a surfactant, a sodium percarbonate bleaching agent and preferably 2 to 15 % by weight, more preferably 5 to 10 % by weight based on the amount of sodium percarbonate of the sodium salt of citric acid (i.e. sodium citrate) (see claims 1 and 2, page 2, second paragraph and example). Consequently, the subject-matter of claims 1, 3 and 4 lacks novelty over D2.

   Consequently, none of the claims meets the requirements of Article 54 EPC.

2. If the applicant wishes to maintain the application, new claims should be filed which take the above objections into account. To simplify examination of this new set of claims, the applicants are invited to indicate exactly how the new claims can be derived from the documents of the application as filed (Article 123(2) EPC, Guidelines E-II, 1). In the letter of reply, the applicant should indicate how the objection set out above has been overcome. In particular, the difference between the new claims and the state of the art as well as its significance should be identified. The position of the applicant in respect of inventive step should be presented by applying the “problem-and-solution” approach.

Annex 3 (Document 1)

The present article is concerned with the stabilization of sodium percarbonate. Sodium percarbonate is a bleaching agent for detergent compositions and which contrary to perborates is environmentally friendly. Sodium percarbonate however has a poor storage stability, especially in zeolites based detergent compositions.

We have now found a new way of stabilizing sodium percarbonate. In this new method sodium percarbonate is coated with an alkali metal salt of a specific carboxylic acid, preferably a sodium salt. Alternatively, sufficient stabilization is achieved by simply adding said salt to the detergent composition containing sodium percarbonate.

The carboxylic acid used is selected from alkali metal salts of mono carboxylic acids of formula $CH_3(CH_2)_nCOOH$ or alkali metal salts of dicarboxylic acids of formula $HOOC(CH_2)_mCOOH$, wherein each of n and m is an integer, which is equal to or higher than 2. Suitable monocarboxylic acids for the alkali metal salt are octanoic acid (n = 6) or decanoic acid (n = 8). Suitable dicarboxylic acids are heptanedioic acid (m = 5) or octanedioic acid (m = 6).

Amounts of 1 to 20 % by weight, preferably 5 to 15 % by weight of alkali metal carboxylic acid salt based on the weight of sodium percarbonate are sufficient to achieve sufficient storage stability.

Example

Sodium percarbonate was coated with 8 wt.% of sodium octanoate in a fluid bed drier, wherein coating and drying are effected in one step. It was then added to a conventional powdery detergent composition in an amount of 5 % by weight based on the detergent composition. The detergent composition comprised a surfactant and 20 % by weight of zeolite. The powdery detergent was then subjected to a storage stability test at 35 °C. After 70 days, 67 % of the available peroxygen remained. This result clearly shows that the alkali metal carboxylic acid salts described above increase the storage stability of sodium percarbonate bleaching agents in zeolite based detergent compositions. The improvement in stability is believed to be due to the presence in the carboxylic acid of the unsubstituted alkyl ($CH_3(CH_2)_n$-) or unsubstituted alkylene (-$(CH_2)_m$-) groups.

Annex 4 (Document 2)

The present invention relates to a powdery detergent composition comprising a combination of zeolite and sodium citrate (i.e. the sodium salt of citric acid) as detergent builder.

Detergent builders play a central role in the course of the washing process. Their function is to neutralise the effect of water hardness and provide a better dissolution of soil. They can be selected among several types of materials such as sodium silicate, complexing agents like sodium triphosphate and ion exchangers, such as zeolites. For environmental reasons phosphates are preferably replaced by zeolites. Zeolites, however, when used as the sole builder, cannot prevent the redeposition of soil and the precipitation of calcium carbonate. In case of multiple washing cycles the washing performance significantly reduces because of the build up of inorganic incrustations on fabrics and on washing machine components. Such build up of inorganic incrustations on fabrics decreases the flexibility of fibres and consequently shorten the fabric life, in addition to greying the fabric.

It has surprisingly been found that sodium citrate efficiently reduces incrustation build up when added to a zeolite-based detergent. Sodium citrate, which acts as co-builder can be added as such directly to the washing bath, but preferably is incorporated into the detergent composition. In the latter case, sodium citrate is used in levels from about 0,5 % to about 20 %, preferably from about 1 % to about 10 % by weight, more preferably from 1 to 2 % by weight of the detergent composition.

The present detergent composition also contains surfactant and a bleaching agent. The bleaching agent is selected from peroxygenated compounds such as sodium percarbonate and sodium perborate, sodium percarbonate being however preferred, since it dissolves rapidly and can fully exhibit its bleaching effect at low temperatures. If necessary, the sodium percarbonate particles can be stabilized by coating a mixture of an aqueous boric acid solution and an aqueous alkali metal silicate solution onto the sodium percarbonate particles.

The amount of sodium percarbonate and sodium citrate are however selected so that the amount of sodium citrate is comprised between 1 and 50 % by weight, preferably 2 to 15 % by weight, more preferably 5 to 10 % by weight based on the amount of sodium percarbonate.

The detergent compositions may also contain conventional additional ingredients. Examples of those conventional ingredients are enzymes, suds suppressors, soil suspension and anti-redeposition agents and corrosion inhibitors.

Example

Sodium citrate was added to a powdery detergent composition comprising a surfactant , sodium percarbonate and a zeolite builder. The detergent composition comprised 10 % by weight of the zeolite builder and 1 % by weight of the sodium citrate co-builder. The amount of sodium citrate based on the amount of sodium percarbonate was of 10 % by weight.

The performance of the above detergent composition and of a reference composition, which contained 11 % by weight of zeolite but no sodium citrate, were measured according to the EUROPWASH standard. The test conditions were: 40 or 70 °C, 100 rpm and 100 ppm hardness.

The values obtained (average of two repeats) are reported in the table below. They demonstrate that the detergent composition of the present invention leads to less inorganic incrustation build up than those, which do not contain sodium citrate.

Builder	Co-Builder	Incrustation in %	
		40 °C	70 °C
Zeolite	absent (comparative)	1,8	3,7
Zeolite	Sodium citrate	0,7	1,4

Claims

1. Powdery zeolite based detergent composition comprising a surfactant and a bleaching agent selected from peroxygenated compounds, characterized in that it contains sodium citrate as co-builder.

2. The detergent composition according to claim 1, wherein the peroxygenated compound is sodium percarbonate.

3. A process for decreasing the build up of inorganic incrustations on fabrics and on washing machine components during multiple washing cycles with zeolite based detergents characterized by the addition during the washing cycle of sodium citrate as co-builder.