

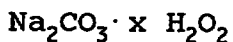
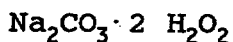
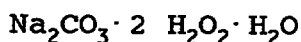
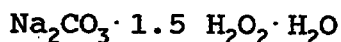
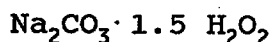
# Process for the preparation of sodium percarbonate

## Description

The present invention relates to a process for the preparation of sodium percarbonate (also referred to below as "PCS" for short) having active oxygen contents of at least 10% by weight, in particular from >14.5 to 15.2% by weight, and to the PCS itself and to bleach and detergent compositions containing the novel PCS product.

Sodium percarbonate is used as a bleaching ingredient in pulverulent detergents, bleaches and cleaning agents. It is distinguished by good water solubility and a rapid release of the hydrogen peroxide and is environmentally friendly since its decomposition products do not pollute the environment.

For sodium percarbonate, the literature gives the empirical formula  $\text{Na}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}_2$  with a theoretical active oxygen content of 15.28% by weight. However, it should be borne in mind here that sodium percarbonate prepared industrially from hydrogen peroxide and sodium carbonate is generally not such a well-defined, homogeneous compound but, on the one hand, is a mixture of various hydrated compounds of the formulae



and, on the other hand, additionally contains a certain proportion of unoxidized sodium carbonate and further additives emerging from the preparation, such as, for example, sodium sulphate or sodium chloride, depending on the preparation process. The product properties are decisively influenced both by the preparation condi-

tions and by the respective additives, not only with respect to the stability but also with regard to, for example, the active oxygen content, the solubility and the bulk density or the particle size of the sodium percarbonate. Thus, the achievable active oxygen content in industrial sodium percarbonate is from 13.4 to 14.5% by weight only in favourable cases but, owing to additives used in the preparation (sulphate, sodium chloride) and stabilizing measures, is often far lower. Furthermore, the essentially good solubility of the sodium percarbonate is often reduced, for example by the presence of other salts, such as sodium carbonate, sodium sulphate and sodium chloride, from the preparation. Moreover, the achievable bulk density or particle size of the sodium percarbonate in the preparation processes of the prior art is generally only slightly variable and is mostly limited from the outset to narrow ranges of values by the type of process or the sodium carbonate used.

However, there is an increasing desire for sodium percarbonates having a high active oxygen content and different bulk densities or particle sizes, depending in each case on the various requirements of the detergent producers, for example for applications in light powder detergents having a low bulk density or in compact detergents having a high bulk density of the ingredients of the detergent, bleach and cleaning agent. In particular, it is also necessary to tailor the bulk densities of the individual ingredients of such compositions to one another in order substantially to rule out separation which would inevitably occur if the ingredients had different bulk densities.

The prior art discloses three technologies for the preparation of sodium percarbonate: crystallization processes, spray processes and dry processes.

As a rule, sodium percarbonate is prepared by the crystallization process. Here, a solution or suspension of sodium carbonate is reacted with hydrogen peroxide at from 10 to 20°C and crystallized in the presence of stabilizers, such as, for example, of waterglass, inorganic or organic phosphonic acids, etc. However, owing to the good solubility of the sodium percarbonate, it is necessary to salt out the sodium percarbonate from the reaction mixture to increase the yield, for which purpose preferably sodium chloride in a concentration of about 240 g/l is introduced into the reaction mixture in the prior art. However, the crystallization is difficult to control so that, in order to obtain an advantageous yield of crystals, it is advisable to add so-called crystallization improvers, such as polyphosphates or polyacrylates. The crystallized sodium percarbonate is then removed by centrifuging and is dried by customary methods, for example in a fluidized bed. The PCS obtained by crystallization processes is, however, not yet optimum for many applications, and in particular its properties are often impaired by the sodium chloride content arising from the preparation.

In the spray processes for the preparation of sodium percarbonate, it is not necessary to filter or to centrifuge in order to remove the sodium percarbonate from the mother liquor. Rather, in these spray processes an aqueous solution (or optionally also a low-concentration suspension) of sodium carbonate and hydrogen peroxide is dried in a spray dryer. However, spray-dried products have as a rule a very low bulk density of only about 0.35 kg/l and therefore cannot yet be used as such for present day detergent formulations which increasingly contain granular ingredients having higher bulk densities. In addition, a great deal of water must be removed during spraying

of solutions, which, however, requires additional energy.

In modifications of the spray process, for example, solutions of sodium carbonate and hydrogen peroxide are sprayed continuously onto a bed fluidized with hot air and comprising initially introduced sodium percarbonate. The spraying and drying stage may be carried out alternatively in one stage or two stages. In a further modification of the spray process, solutions of sodium carbonate and hydrogen peroxide are sprayed through separate nozzles into a reaction chamber, a hot mixture of air and carbon dioxide simultaneously being passed through the reaction chamber. However, this process gives a fairly porous sodium percarbonate which does not meet the requirements for detergent compositions of today's standards with respect to bulk density and abrasion resistance.

In the so-called drying processes, sodium percarbonate is prepared by reacting anhydrous  $\text{Na}_2\text{CO}_3$  with a concentrated hydrogen peroxide solution comprising from 50 to 80% by weight and evaporating off the small amounts of liberated water during the reaction itself. In this process, an essentially (substantially) dry reaction mixture is present during the entire reaction. The process can be carried out, for example, in mixers, in fluidized-bed reactors or in tubular reactors having injection apparatuses for  $\text{H}_2\text{O}_2$ . Apart from the long reaction times, this process has the disadvantage that there is no purification of the sodium carbonate [sic] thus prepared, so that additional measures must be taken during the reaction itself in order to stabilize the product, for example the addition of specific stabilizers. A particular disadvantage is that hydrogen peroxide has to be used in a large excess in order to obtain a PCS having a sufficient active oxygen content. In addition, this

process is not very variable with respect to the properties of the sodium percarbonate granules, for example with respect to bulk density and particle size, since the shape of the sodium percarbonate granules corresponds essentially (i.e. apart from slight rounding due to the reaction) to the shape of the granules of the sodium carbonate used. Particularly in the preparation of sodium percarbonate granules having a high bulk density for compact detergents, it is therefore necessary to use heavy sodium carbonate, in which, however, only a small surface area is available for the reaction with hydrogen peroxide. The reaction is therefore incomplete, so that only relatively low active oxygen contents and only inhomogeneous products having a relatively high, non-uniformly distributed sodium carbonate fraction are obtained, the alkalinity of which impairs the stability of the product.

It is the object of the present invention to overcome the disadvantages of the prior art with regard to the preparation of sodium percarbonate and to provide a process for the dry preparation (dry process) of sodium percarbonate having beneficial properties, which process can be carried out efficiently and with high flexibility. The dry process proposed according to the invention should in particular make it possible to provide, with as efficient an active oxygen yield as possible, a high-quality sodium percarbonate having variable, but in particular high, active oxygen contents and having variable granule parameters in accordance with the use envisaged in each case.

The object is achieved by the process, according to the invention and stated in the claims, for the preparation of sodium percarbonate and by the novel sodium percarbonate stated in the claims and having unexpectedly beneficial properties, and the stated solid bleach and detergent compositions.

The process according to the invention for the dry preparation of sodium percarbonate having an active oxygen content of at least 10% by weight is distinguished by the fact that solid sodium carbonate monohydrate is reacted with a quasi-stoichiometric amount, based on the active oxygen content desired in the sodium percarbonate, of, in particular, a 50 to 70% strength by weight aqueous hydrogen peroxide solution at reaction temperatures up to not more than 80°C in a mixing apparatus to give a pasty or doughy material comprising moist sodium percarbonate and a sodium percarbonate having an active oxygen content of from 10 to 15.2% by weight, preferably from >14.5 to 15.2% by weight, and having desired particle parameters, such as bulk density and mean particle diameter, is subsequently obtained by drying and/or granulation.

The process according to the invention can be carried out per se in any mixer which permits sufficiently rapid and hence thorough mixing of solid (in particular of sodium carbonate monohydrate and of resulting PCS) and hydrogen peroxide used. For example, the following mixers are suitable: stirrer-equipped vessels having stirrer types suitable for flowable media, for example having propeller stirrers, disc stirrers, paddle stirrers, bar-type stirrers or grid stirrers; intensive mixers, for example high-speed rotor-stator stirrers and turbo mixers, which may additionally be equipped with a knife head for breaking up large agglomerates, are very effective. Rapid or thorough mixing is understood as any mixing intensity which corresponds to a stirrer speed of, initially, at least about 100 rpm, in particular about 100 to 150 rpm. Preferred mixers are equipped with kneading tools, by means of which the pasty to doughy material forming during the reaction can be particularly readily and homogeneously processed. The reaction can be carried out both batchwise and continuously. The solid

sodium carbonate monohydrate is fed into the mixer expediently by means of a metering screw if the reaction is to be operated continuously. In the batchwise reaction, the sodium carbonate monohydrate is initially introduced into the mixer. In both process variants, i.e. in the continuous and batchwise procedure, the aqueous hydrogen peroxide solution is metered into the mixer in the required amount preferably via a nozzle, in particular a binary nozzle, in the continuous procedure the rate of addition being tailored to the addition of sodium carbonate monohydrate, the residence time of the reaction mixture in the mixer and the amount of the resulting PCS which is continuously removed by unit time.

For controlling the temperature of the exothermic reaction between sodium carbonate monohydrate and hydrogen peroxide, the mixer used can be equipped with cooling means. This is particularly expedient for absorbing the heat of reaction to protect the active oxygen content in the hydrogen peroxide and the resulting sodium percarbonate. As a rule, the cooling capacity of tap water is sufficient for the cooling, which can expediently be effected by means of a simple cooling jacket, so that usually no further energy need be supplied for cooling. In the course of the reaction, the reaction temperature can be easily increased to 80°C without the product properties, in particular the active oxygen content, suffering as a result. Controlling the temperature during the reaction presents no problems, and the reaction can therefore also be carried out at above 20°C without impairing the product, with the result that a rapid procedure, i.e. relatively rapid mixing of sodium carbonate monohydrate and hydrogen peroxide, is permitted. Temperatures higher than 80°C should however be avoided, since otherwise the active oxygen yield is impaired by premature decomposition of hydrogen

peroxide. The reaction temperatures during the exothermic reaction are expediently kept in the range from room temperature to not more than 80°C, preferably in the range from above 20°C to not more than 80°C.

5           An important feature of the process according to the invention consists in the fact that sodium carbonate monohydrate, i.e. a specific form of sodium carbonate having essentially a defined content of water of hydration, is used as a starting material. The  
10   sodium carbonate monohydrate is expediently obtained by conditioning sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), i.e. by reacting the anhydrous form of sodium carbonate with up to about 1.5 times the molar amount of water. For this purpose, preferably preheated sodium carbonate (e.g. water bath  
15   temperatures up to about 100°C) is reacted with the calculated amount of boiling water in a mixer over a sufficient period of time and the conversion to sodium carbonate monohydrate is then checked analytically in a manner known per se, for example by DSC analysis and  
20   titration of the total alkalinity. The conditioning of sodium carbonate to give the monohydrate for the process according to the invention is independent of the type of sodium carbonate to be conditioned. For example, both superlight sodium carbonate having bulk  
25   densities of less than 0.50 kg/l, for example 0.20 kg/l to 0.48 kg/l, light calcined sodium carbonate having a bulk density of, for example, 0.50 to 0.55 kg/l and heavy calcined sodium carbonate having a bulk density of 1.0 to 1.1 kg/l may be conditioned. The process  
30   according to the invention takes place particularly advantageously with the use of sodium carbonate monohydrate which is obtained by conditioning light forms of sodium carbonate, for example in particular light sodium carbonate having bulk densities of about  
35   0.50 to 0.55 kg/l or alternatively superlight sodium carbonate having a bulk density of less than 0.50 kg/l. These light forms of sodium carbonate can, after

conditioning to give sodium carbonate monohydrate, be processed to a particularly homogeneous sodium percarbonate with substantially complete reaction with hydrogen peroxide. Use of sodium carbonate monohydrate obtained from light forms of sodium carbonate permits a rapid and complete reaction with  $H_2O_2$ , which is complete within a few minutes to not more than about 1.5 h, but in particular within as little as 1 h, depending on the amount to be reacted. As shown in the exemplary embodiments, it is possible to react, for example, kg amounts with conventional water cooling in periods of minutes; thus, for example, 2 kg of light sodium carbonate monohydrate can be completely converted in less than about 15 minutes with water cooling.

However, even with the use of heavy calcined sodium carbonate for conditioning to the monohydrate, short reaction times are possible in the subsequent reaction with hydrogen peroxide and substantially homogeneous PCS particles are obtainable, provided that, if required, the conditioning time is prolonged for adequate penetration of the sodium carbonate particles with the water provided for the hydration or optionally alternatively or additionally a slight excess of water is provided for the hydration; as in the case of conditioning of light sodium carbonate, monitoring of the sodium carbonate monohydrate characteristics is effected by DSC analysis or titration of the total alkalinity.

The ratio of sodium carbonate monohydrate to the active oxygen content of the hydrogen peroxide is controlled in the process according to the invention in a manner such that the molar ratios correspond to the active oxygen content to be achieved in the PCS, optionally only a small excess of hydrogen peroxide of the order of magnitude of up to about 5% being required. Since the process according to the invention ensures an essentially complete active oxygen yield,

the use of a quasi-stoichiometric amount of  $\text{H}_2\text{O}_2$  is thus sufficient (based on sodium percarbonate having the theoretical empirical formula  $\text{Na}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}_2$ ; theoretical active oxygen = 15.28% by weight) and expensive  $\text{H}_2\text{O}_2$  excesses can be avoided. In the case of molar ratios of  $\text{H}_2\text{O}_2$  to sodium carbonate monohydrate of about 1.0, sodium percarbonates having active oxygen contents of about 10% by weight are obtained. In a preferred embodiment of the invention, the molar ratio of  $\text{H}_2\text{O}_2$  to sodium carbonate is set at about 1.5 to 1.52, so that an active oxygen content in the sodium percarbonate of at least 14% by weight, in particular from >14.5 to 15.2% by weight, is achieved. In the process according to the invention, the concentration of the aqueous hydrogen peroxide used is 50 to 70% by weight, concentrations of 55 to 65% by weight, however, being preferred. The hydrogen peroxide is stabilized as a rule in a manner known per se; all active oxygen stabilizers known in the prior art are suitable, for example, inter alia, Turpinal SL.

The drying and granulation of the reaction product of sodium carbonate monohydrate and  $\text{H}_2\text{O}_2$  can be carried out by customary methods and, depending on the process and the apparatus used, can be controlled in such a way that a sodium percarbonate having any desired particle size (= mean particle diameter) from about 150 to about 1300  $\mu\text{m}$  is obtained. In a preferred embodiment of the invention, in particular sodium percarbonates having particle sizes of 350 to 1300  $\mu\text{m}$  are prepared. The process according to the invention thus permits the preparation of sodium percarbonates having particle size ranges for light detergents or compact detergents with particle sizes from about 550 to 600  $\mu\text{m}$ , in particular from 640 to 1100  $\mu\text{m}$ , preferably with particle sizes from about 800 to 1000  $\mu\text{m}$ . The granulation conditions to be maintained in each case for this purpose are not critical per se

and correspond to the customary conditions of the granulation apparatus used in each case. Sodium percarbonates having a bulk density of 0.2 kg/l to 1.1 kg/l, preferably 0.5 to 1.1 kg/l, can thus be prepared by the process according to the invention. Further particularly preferred particle sizes and bulk densities are described further below in conjunction with the PCS products according to the invention.

The drying and granulation step can be carried out, for example, in a turbo dryer (granulating dryer) and also in other short-retention-time drying apparatuses or granulation apparatuses customary per se under the conditions customary in each case. Thus, the drying can also be carried out in fluidized-bed dryers or recirculation dryers. In all process variants of the invention, the granulation can be effected in a manner customary per se, for example as dry granulation in a compacting process or as moist granulation (pelleting) in granulating mixers, such as, for example, ploughshare mixers or V-type blenders. A combined embodiment of the granulation and drying step comprises a procedure in a turbo dryer, which in principle is a turbo mixer equipped with a heating apparatus. The procedure in the turbo dryer is advisable in particular for continuous procedures in which the reaction slurry or the reaction paste is dried and simultaneously granulated immediately after the reaction. Alternatively, the granulation can be carried out after the mixing of the starting materials, also in an extrusion process. In the granulation/drying step, granulation assistants (such as, for example, silicates) and stabilizers (such as organic phosphonic acids or phosphonates) can, if desired, be added but as a rule are not absolutely essential in the case of PCS prepared according to the invention.

In a particularly preferred embodiment of the invention, the process is distinguished by the fact

that the sodium percarbonate obtained after drying -  
for example drying in a recirculation dryer in this  
variant of the invention - is subjected to compacting  
with subsequent dry granulation. This process for the  
5 preparation of a sodium percarbonate product is  
distinguished by the fact that, in a first step  
(= reaction step), a sodium percarbonate is prepared  
and dried by the reaction process described above and,  
in a second step (= compaction/dry granulation step),  
10 the sodium percarbonate obtained after drying in the  
first step is compacted to give shells, if desired with  
the addition of up to 1% by weight of a lubricant,  
preferably of alkali metal and/or alkaline earth metal  
stearate, and the shells are then converted by a dry  
15 granulation method, by crushing and sieving, into  
sodium percarbonate granules having the desired  
particle parameters, such as bulk density and mean  
particle diameter.

According to this variant of the process  
20 according to the invention, substantially dry primary  
particles are subjected to a compression process  
(compacting) and are compacted by the action of the  
pressure applied for this purpose. The desired  
agglomeration of the primary particles used is thus  
25 achieved. Since the agglomeration occurs as a result  
of pressing or exerting a pressure, the intensification  
process under pressure is also referred to as  
compacting or compressive or pressure agglomeration or,  
in the case of the preparation of granules, also as  
30 compressive or pressure granulation. The compressive  
agglomeration process for the preparation of  
agglomerates or granules should therefore be dis-  
tinguished from the so-called agglomeration processes  
(pelletizing processes) in which the adhesion between the  
35 particles is imparted exclusively by adhesive bonding  
with liquid (e.g. water) and/or binders, without  
substantial action of pressure.

The temperature range in which the compacting can be carried out corresponds to the temperature range in which there is good thermal stability of the active-oxygen-containing compounds used and the process can be carried out without problems from safety points of view. For example, in an expedient embodiment of the invention, the compacting of the sodium percarbonate particles is carried out at ambient temperature. In this temperature range, the process can be carried out without problems with regard to the active oxygen content of the primary sodium percarbonate particles to be compressed; losses of active oxygen which impair the product are not observed in the case of PCS prepared according to the invention, in contrast to conventional PCS crystallization processes of the prior art.

Although the magnitude of the pressure to be applied can be freely chosen within wide limits and can therefore be adapted to specific desires or requirements with respect to the product, the pressure is governed by, inter alia, two specifications towards lower values. On the one hand, the minimum pressure to be applied should be sufficient to impart sufficient mechanical strength and bulk density to the agglomerate of the primary particles. Minimum pressure to be applied for achieving the desired properties depends on the type of presses used and on the adhesive properties of the product, and can be readily determined by a person skilled in the art, with respect to the desired processing and product properties, in a few preliminary experiments. The upper limit of the pressure to be applied is restricted by the maximum pressure technically achievable or permissible in each case for the apparatuses used for the compacting and by the adhesive properties of the product. In an exemplary embodiment of the invention using a roll press, for example, the amorphous primary particles of sodium percarbonate are compacted by compression at pressures

of at least 50 bar to not more than 150 bar.  
Compaction is preferably carried out at pressures of 80 to 120 bar.

5 Compared with the fine primary particle beds  
of PCS, the agglomerates obtained according to the  
invention are shaped products which, after comminution  
by crushing and sieving, have less tendency to dust  
formation, adhesion, caking and separation, can be  
readily metered and transported and have good  
10 flowability and a defined bulk density. Product  
properties such as granule shape and size and bulk  
density of the PCS may be adapted to the requirements  
for different intended uses or other market  
requirements by the process according to the invention.  
15 The desired product properties play a decisive role in  
determining the compacting process which is most  
expedient in each case.

All compressive agglomeration apparatuses  
customary per se can be used for the compacting.  
20 Although it is possible here for the primary particles  
to be agglomerated by compression also in moist form,  
optionally with the addition of small amounts of  
liquid, binder, lubricant, further assistants and/or  
other desired or expedient additives, preferably the  
25 advantages of the invention are fully displayed with  
the use of those compacting processes in which  
exclusively dry primary particle material is  
compressed, since in this process the stability of the  
product (in particular the active oxygen stability)  
30 cannot be adversely affected by liquid (in particular  
water) present or fed in and drying after the  
compacting is unnecessary. A further advantage arises  
from the fact that although on the one hand binder,  
lubricant and/or further assistants can, if desired, be  
35 added in the dry compressive agglomeration process, on  
the other hand, however, they are not absolutely  
essential for the procedure; undesired changes in the

properties of the compressed percarbonate, which may be caused by these additives and assistants, may thus be avoided. On the other hand, it is quite possible to mix other desired additives modifying the agglomerates in an expedient manner, for example advantageously up to about 1% by weight of sodium stearate or magnesium stearate, with the microcrystalline percarbonate particles to be compressed, in a homogeneous manner prior to the compressive agglomeration.

Suitable compacting apparatuses are, for example, roll presses, such as calenders, structured rolls or shaping rolls (briquetting rolls). These apparatuses can be operated with or optionally also without positive feeding means for the primary particle material to be compressed. Depending on the compacting apparatus used, the primary particles are compressed under pressure to give defined shapes, for example to give dense, smooth or structured sheets, i.e. to give so-called shells. The shells are then comminuted to granules of the desired size.

In particularly expedient embodiments of the compacting process, roll presses are used; structured rolls are preferred. The structured rolls are corrugated or continuously profiled rolls for producing smooth or profiled sheets (shells), strips or compacts. In the case of the structured rolls, slightly or more strongly profiled rolls may be used, the latter in open or closed form. Thus, more or less smooth, slightly or more strongly structured (e.g. waffle-like) shells, corrugated sheets or, in the case of rolls profiled uniformly over the total roll width and in closed form, also rods.

Since the products obtained by compacting do not yet have the desired product form, in particular shells, corrugated sheets or rods, they are comminuted to granules of the desired particle size and bulk density by methods known per se. For the comminution,

for example, cake or shell crushers are suitable for coarse granulation or granulating screens for fine granulation.

5       The sodium percarbonate granules prepared by the process according to the invention can, if desired, also be provided with coatings in a manner known per se. Suitable coating materials are, for example, the materials described in the prior art, such as, for example, borates, salts such as  $\text{Na}_2\text{CO}_3$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$  and  
10       mixtures thereof, organic coating agents, e.g. lactic acid and derivatives thereof. If an additional coating of the sodium percarbonate granules prepared according to the invention is desired, the granulation step can be followed by the coating process in an  
15       expedient manner known per se.

      The invention also relates to novel sodium percarbonates which are distinguished by beneficial properties which have not been achievable to date by the processes of the prior art. The sodium  
20       percarbonate (PCS) according to the invention is distinguished by an active oxygen content of >14.5 to 15.2% by weight, calculated without any added granulation assistants or coating materials.

      In one variant, this novel PCS is  
25       distinguished by a dissolution rate of at least 95% after 1 min and at least 99% after 2 min (in each case standard conditions: 2 g, 15°C). In another variant, the novel PCS is distinguished by an exothermic DSC peak above about 155°C, preferably greater than or  
30       equal to 159°C, in particular in the range from 159 to 162°C. In a further variant, the novel PCS is distinguished by the fact that it has a stability loss of less than 6.2%, preferably of 3.4 to 5.1%, measured under standard conditions (105°C, 2 h).

35       The novel PCS products have a number of further advantageous properties. Thus, the sodium percarbonate has in particular a mean particle diameter

of 550 to 1100  $\mu\text{m}$ , preferably of 640 to 1000  $\mu\text{m}$ . The bulk density of the sodium percarbonate is preferably 0.85 to 1.1 kg/l. Further, the sodium percarbonate has an advantageous abrasion value of less than 5% (measured under standard conditions).

In a variant of the invention, the sodium percarbonate is distinguished by the fact that it contains up to 1% by weight of a lubricant from the group consisting of the alkali metal or alkaline earth metal stearates introduced during the granulation and that it has a bulk density of 0.93 to 1.1 kg/l. This sodium percarbonate has an abrasion value of less than 8% (measured under standard conditions).

The novel sodium percarbonates can be prepared by the process according to the invention and described above, in particular by the process variant comprising compacting and dry granulation. If the sodium percarbonate is prepared by the advantageous process variant comprising compacting and dry granulation, the compacting can alternatively be effected with or without the addition of lubricants.

If the sodium percarbonate is prepared by the advantageous process variant comprising compacting and dry granulation without the addition of lubricants during the compacting/dry granulation, it is distinguished in one variant by a stability loss of less than 6.2%, measured under standard conditions (105°C, 2 h). In a further variant, the sodium percarbonate obtainable without the addition of lubricants during the compacting/dry granulation has a mean particle diameter of 550 to 1100  $\mu\text{m}$ , preferably of 640 to 1000  $\mu\text{m}$ . In a further variant, the sodium percarbonate which is obtainable by the process without the addition of lubricants during compacting/dry granulation has a bulk density of 0.85 to 1.1 kg/l. This sodium percarbonate is furthermore distinguished

by an abrasion value of less than 5% (standard conditions).

5 In another variant of the invention, the preparation of the sodium percarbonate is carried out by the process variant comprising compacting and dry granulation with the addition of lubricants during the compacting. The sodium percarbonate obtainable hereby is distinguished in one variant of the invention by the fact that it is obtainable with the addition of up to 10 1% by weight of a lubricant during the compacting/dry granulation, preferably with the addition of alkali metal and/or alkaline earth metal stearate, and that it has an active oxygen content of more than 14.5% by weight, preferably of more than 14.8% by weight, and a stability loss of not more than 12.0 (measured under standard conditions: 105°C, 2 h). In another variant of the invention, the sodium percarbonate obtainable with the addition of up to 1% by weight of a lubricant during the compacting/dry granulation, preferably with the addition of alkali metal or alkaline earth metal stearate, is distinguished by the fact that it has an active oxygen content of more than 14.5% by weight to 15% by weight, preferably of more than 14.8% by weight to 15.0% by weight, and a mean particle diameter of 800 to 1000  $\mu\text{m}$ . In another variant of the invention, the sodium percarbonate which is obtainable with the addition of up to 1% by weight of a lubricant during the compacting/dry granulation, preferably with the addition of alkali metal or alkaline earth metal stearate, has an active oxygen content of more than 14.5% by weight to 15% by weight, preferably of more than 14.8% by weight to 15.0% by weight, and a bulk density of 0.95 to 1.1 kg/l. This sodium percarbonate has an advantageous abrasion value of not more than 8% (measured under standard conditions).

The novel PCS products according to the invention are outstandingly suitable for use in solid

bleach and detergent compositions. The invention therefore also relates to solid bleach or detergent compositions containing 0.5 to 40% by weight, preferably 5 to 25% by weight, of the sodium percarbonate according to the invention and 99.5 to 60% by weight, preferably 95 to 75% by weight, of formulation substances and assistants customary in bleach or detergent compositions and from the group consisting of surfactants, builders, bleach activators, peracid bleach precursors, enzymes, enzyme stabilizers, antiredeposition agents and/or compatibilizers, complexing and chelating agents, lather regulators and additives, such as optical brighteners, opacifiers, corrosion inhibitors, antielectrostatic agents, dyes and bactericides. Owing to the outstanding stability of the sodium percarbonate according to the invention to detergent ingredients, it is advantageously suitable for bleach and detergent compositions which contain the sodium percarbonate in the presence of builders from the group consisting of the zeolites. The particle sizes and bulk densities of the sodium percarbonate according to the invention permit the use in compact detergent compositions in an advantageous manner.

In the compositions according to the invention, it is possible to use a wide range of zeolite builders, which are sometimes alternatively also referred to as aluminosilicate builders. Suitable zeolites usually have a substantial calcium or alkaline earth metal ion exchange capacity (elimination of water hardness). The ion exchange capacity is expressed here in calcium carbonate equivalents and is at least 150 mg of  $\text{CaCO}_3$  per g and, for preferred zeolites, the ion exchange capacity is 200 to 250 mg of  $\text{CaCO}_3$  equivalents per g. The zeolites are usually described by the general empirical formula  $\text{M}_z[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$ , in which M represents an alkali metal, preferably sodium; z and y are integers of at least 6 with a molar ratio

of y:z of 1:1 to 2:1 and x is an integer of at least 5 and preferably from 10 to about 280. Many zeolites are hydrated and contain up to about 30% by weight of water, of which about 10 to 25% by weight are bound in the zeolite. The zeolites may be amorphous but the majority of the preferred zeolites have a crystalline structure. Although certain aluminosilicates occur naturally, most aluminosilicates are synthetic. Suitable crystalline zeolites having a well known structure and formula are, for example, zeolite A, zeolite X, zeolite B, zeolite P, zeolite Y, zeolite HS and zeolite MAP. The amount of the zeolite in the bleach and detergent compositions according to the invention is at least 5% by weight and in many cases at least 10% by weight, based on the total composition. Usually, the amount of zeolite is not greater than about 60% by weight and often not greater than 50% by weight; in particular, the amount of zeolite in the composition is not more than 40% by weight, based on the total composition.

Although in a preferred embodiment of the invention the sodium percarbonates according to the invention are described for those bleach and detergent compositions which contain one or more zeolites as builders, the bleach and detergent compositions can, in a general embodiment of the invention, similarly contain the sodium percarbonate according to the invention also with amorphous zeolites or with sheet silicates in the above-mentioned weight ranges.

Suitable sheet silicates, in particular of a crystalline nature, often correspond in general to the formula  $\text{Na}_2\text{Si}_x\text{O}_{2x+1} \cdot y\text{H}_2\text{O}$  or to the corresponding compounds in which a sodium ion is replaced by a hydrogen ion. Here, X is in particular in the range from 1.9 to 4 and y is in particular in the range from 0 to 20. The sheet silicates may be used both as a mixture with

zeolite builders and without zeolite builders in the bleach and detergent compositions.

In another more general embodiment of the invention the bleach and detergent compositions which contain the sodium percarbonate according to the invention may also contain non-zeolite builders instead of zeolite builders. Such detergent builders may be, for example, the above-mentioned sheet silicates, or alkali metal phosphates, in particular tripolyphosphates, as well as tetrapyrophosphates and hexametaphosphates, which are present in particular in the form of the sodium salt, alkali metal carbonate and preferably sodium carbonate, alkali metal silicates and alkali metal borates and preferably sodium borates. A further group of builders which may be contained in the bleach and detergent compositions are organic chelate builders, such as, for example, aminopolycarboxylates and aminopolymethylenephosphonates or hydroxyphosphonates, including nitrilotriacetate or trimethylenephosphonate, ethylenediaminetetraacetate or tetramethylenephosphonate, diethylenetriaminepenta-methylenephosphonate or cyclohexane-1,2-diaminetetramethylenephosphonate, which are usually present completely or partially in the form of the sodium salt. Chelating carboxylate builders comprise monomeric and oligomeric carboxylates, including glycolic acid derivatives and ether derivatives, for example salts and derivatives of succinic acid, tartaric acid, citrates, carboxy derivatives of succinates, and polyaspartates. Further examples are ethane- and propanetetra-carboxylates and various sulphosuccinates. The stated chelate builders may be present in relatively small amounts in the bleach and detergent compositions, for example for enhancing the builder properties and the peracid-stabilizing effect; amounts of 1 to 10% by weight are suitable for this purpose, but it is also possible to use larger amounts of up to

40% by weight, preferably in the range from 5 to 20% by weight.

Furthermore, the bleach and detergent compositions according to the invention generally also contain one or more surfactants, which may be present in amounts of 2 to 40% by weight and in particular in amounts of 5 to 25% by weight. Suitable surfactants are customary surfactants from the group consisting of the anionic, cationic, nonionic, zwitterionic, amphoteric and ampholytic surfactants, as well as natural or synthetic soaps. Examples of surfactants are, for example as anionic surfactants, the carboxylic acid soaps, alkylarylsulphonates, olefin sulphonates, linear alkylsulphonates, hydroxyalkylsulphonates, long-chain alcohol sulphates, sulphated glycerides, sulphated ethers, sulfosuccinates, phosphate esters, sucrose esters and anionic fluorine surfactants; examples of cationic surfactants include quaternary ammonium or quaternary pyridinium salts, which contain at least one hydrophobic alkyl or arylalkyl group; nonionic surfactants are, for example, condensates of long-chain alcohols with either polyethylene oxides or with phenol, or condensates of long-chain carboxylic acids or amines or amides with polyethylene oxide, or corresponding compounds in which the long-chain unit is condensed with an aliphatic polyol, for example, sorbitol, or condensation products of ethylene oxides or propylene oxides or fatty acid alkanolamides and fatty acid amine oxides; amphoteric/zwitterionic surfactants are, for example, sulphonium and phosphonium surfactants which, if desired, are substituted by a further solubilizing anionic group. The above list is to be understood as being by way of example and not as definitive.

Further optional components of the bleach and detergent compositions are, for example as already stated: antiredeposition agents, bleach activators,

optical brighteners, enzymes, softeners, fragrances, dyes and optionally also process assistants. The optional components, with the exception of the process assistants, which form a separate component, are usually contained in amounts of up to not more than 20% by weight, based on the composition; usually 10% by weight is sufficient. The process assistants, as a separate component, may, if desired, form from 0 to 40% by weight of the composition. Antiredeposition agents are usually, for example, methyl, carboxymethyl or hydroxyethyl derivatives of cellulose or polyvinylpyrrolidone, or polycarboxylic acid polymers, such as, for example, copolymers of maleic anhydride with methacrylic acid or ethylene [sic] or methyl vinyl ether. Customary bleach activators are, for example, O-acyl or N-acyl compounds which form peracid by reaction with the sodium percarbonate, in particular TAED, SNOBS and its isononyl analogue, TAGU and sugar esters. Optical brighteners are, for example, suitably substituted aminostilbenes and in particular triazineaminostilbene. The enzymes may be selected from the group consisting of amylases, neutral or alkaline proteases, lipases, esterases and cellulases, which are each commercially available. Softeners are, for example, water-insoluble tertiary amines, sometimes in combination with long-chain quaternary ammonium salts and/or high molecular weight polyethylene oxides. The process assistants are usually sodium sulphate and/or magnesium sulphate. In concentrated or ultra-concentrated compositions, however, the process assistants form only a relatively small proportion of up to not more than 5% by weight; in traditional compositions, however, the proportion may readily be 20 to 40% by weight.

The bleach and detergent compositions according to the invention can be prepared in any customary manner, for example by dry blending of the

particulate sodium percarbonate with the desired ingredients, which may also be preprocessed as a premix or preformulation in the customary manner.

The process according to the invention and the sodium percarbonate prepared according to the invention are distinguished by the following advantages:

The invention provides a simple and economically feasible process for the batchwise or continuous preparation of essentially homogeneous PCS particles or granules having variable active oxygen contents of 10 to 15.2% by weight, in particular high active oxygen contents of >14.5 to 15.2% by weight. The process according to the invention is energy-saving since, on the one hand, no refrigeration energy is required during the reaction and instead the temperature can be controlled by normal water cooling alone, and, on the other hand, only a small amount of water has to be evaporated for drying the product. In contrast to the so-called wet processes (crystallization processes), according to the invention chloride-free PCS products are formed, with the result that the risk of corrosion in the plant is reduced. In contrast to the wet process, no wastewater which has to be disposed of is formed in the process according to the invention; in contrast, the wet process gives rise to alkaline wastewater which contains hydrogen peroxide and chloride and furthermore must also be neutralized prior to disposal and in which optionally the hydrogen peroxide fraction must also be decomposed. In contrast to the so-called dry processes, which permit only active oxygen contents of about 10% by weight in the PCS, a variable active oxygen content of 10 to 15.2% by weight and in particular >14.5 to 15.2% by weight can be obtained by the process according to the invention. In the dry process according to the invention with the use of a defined sodium carbonate monohydrate, the active oxygen

content in the PCS product is therefore readily controllable and adaptable to the respective market requirements or different products. The dry process according to the invention guarantees quasi-loss-free hydrogen peroxide use and hence an essentially complete active oxygen yield; expensive  $H_2O_2$  excesses can therefore be avoided and the reaction of sodium carbonate monohydrate with  $H_2O_2$  can be carried out quasi-stoichiometrically. The PCS prepared by the process according to the invention is furthermore distinguished by high homogeneity and purity. The PCS particles obtainable according to the invention therefore have beneficial stability properties. The process is very flexible since, in contrast to the dry processes of the prior art (where tubular reactors are used), it can be carried out in mixing and dryer apparatuses which are conventional per se. The flexibility of the process according to the invention is also evident from the fact that it can be carried out in a readily controllable manner not only by the batchwise procedure but also by the continuous procedure.

The Examples which follow serve for further illustration of the invention, without however restricting it in its scope. % data in tables and text mean as a rule % by weight data.

### Examples

#### Example 1:

Conditioning of sodium carbonate to give sodium carbonate monohydrate

For the preparation of sodium carbonate monohydrate, light sodium carbonate was conditioned in a Lödige laboratory mixer with jacket heating (water bath,  $99^\circ C$ ). For this purpose, 2000 g of sodium carbonate were introduced into the mixer and preheated at low speed (about 20 rpm) for 15 minutes.

Thereafter, the speed of the mixer was increased to about 120 rpm and boiling water in an amount of 520 g was then added rapidly. After a residence time of about 35 minutes, the product was removed from the mixer. Checking of the conversion to sodium carbonate monohydrate was carried out by DSC analysis and titration of the total alkalinity.

6 batches of sodium carbonate monohydrate were prepared (also see Example 3). The general process conditions and the average analytical results of the sodium carbonate monohydrate products are shown in Tables Ia and Ib below.

**Table Ia:** Conditioning of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) to give sodium carbonate monohydrate ( $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ) in a Lödige mixer

|    |                                                         |                                                       |
|----|---------------------------------------------------------|-------------------------------------------------------|
| 5  | $\text{Na}_2\text{CO}_3$ (light sodium carbonate)       | 2000 g (79.37% by weight)                             |
|    | $\text{H}_2\text{O}$ (boiling)                          | 520 g (20.63% by weight)                              |
|    | Molar ratio $\text{Na}_2\text{CO}_3:\text{H}_2\text{O}$ | 1:1.53                                                |
|    | Preheating time of sodium carbonate (mixer)             | 15 minutes                                            |
| 10 | Procedure                                               | Lödige laboratory mixer (120 rpm) with jacket heating |
|    | Addition time for $\text{H}_2\text{O}$                  | On average 34 seconds (25 to 45 seconds)              |
|    | Temperature of jacket heating                           | 99°C                                                  |
|    | Reaction time                                           | On average 38 minutes (35 to 45 minutes)              |

15 **Table Ib:** Analysis and properties of sodium carbonate monohydrate (obtained by conditioning of sodium carbonate)

|    |                                                                   |                                                                         |
|----|-------------------------------------------------------------------|-------------------------------------------------------------------------|
|    | DSC endothermic peak                                              | On average 99°C (94 to 102°C)<br>On average -403 J/g (-390 to -420 J/g) |
|    | $\text{H}_2\text{O}$ (total alkalinity)                           | On average 13.95% (13.45 to 14.23)                                      |
| 20 | $\text{Na}_2\text{CO}_3$ (total alkalinity)                       | On average 86.05% (86.55 to 85.77%)                                     |
|    | $\text{Na}_2\text{CO}_3:\text{H}_2\text{O}$ ratio (from analysis) | On average 1:0.95 (1:0.92 to 1:0.98)                                    |

**Example 2:****Preparation of sodium percarbonate**

The sodium carbonate monohydrate prepared in each case according to Example 1 was subsequently reacted with hydrogen peroxide to give sodium percarbonate. For this purpose, a weighed amount (about 2000 g) of sodium carbonate monohydrate was introduced in each case into a mixer having kneading tools (Lödige mixer). 1.5 mol of aqueous hydrogen peroxide (60% strength by weight) were weighed out per 1 mol of sodium carbonate monohydrate weighed in and stabilized by adding Turpinal SL (60% strength by weight) (amount: 5.75% by weight of TSL (100% strength), based on  $H_2O_2$  (100% strength)). The hydrogen peroxide solution stabilized in this manner was sprayed into the Lödige mixer via a binary nozzle. The spraying time was about 13 min at a mixer speed of about 120 rpm. To control the temperature during the reaction, the mixer was cooled with tap water via the jacket. After the reaction, the product was removed from the mixer and was dried at 80°C in a recirculation dryer. The drying was terminated as soon as the water content or active oxygen content in the end product reached the desired value (< about 0.2% by weight; water determination according to Sartorius). After the resulting sodium percarbonate product had been cooled, the quality control was carried out by the customary analyses for PCS.

Altogether, 6 batches of sodium carbonate monohydrate from Example 1 were reacted as described above. The general process conditions of the reaction experiments and the average analytical results of the sodium percarbonate obtained are summarized in Tables IIa and IIb below.

**Example 3:**

Further experiments for conditioning and PCS preparation

Further experiments for the preparation of PCS from sodium carbonate monohydrate were carried out analogously to Examples 1 and 2. The individual process conditions and the properties of the starting materials and products are shown in Table III below.

**Table IIa:** Reaction of sodium carbonate monohydrate with hydrogen peroxide to give sodium percarbonate

|                                                           |                                                                                                                       |
|-----------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------|
| Procedure                                                 | Lödige laboratory mixer (about 100 rpm) with jacket cooling                                                           |
| Starting materials                                        | $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (conditioning)<br>$\text{H}_2\text{O}_2$ (w = 0.6)<br>TSL (w = 0.6) |
| Molar ratio $\text{Na}_2\text{CO}_3:\text{H}_2\text{O}_2$ | 1:1.5                                                                                                                 |
| Amount of Turpinal                                        | 5.75% of 100% strength TSL, based on 100% strength $\text{H}_2\text{O}_2$                                             |
| Temperature                                               | Room temperature/water cooling                                                                                        |
| Addition time of $\text{H}_2\text{O}_2$ (binary nozzle)   | On average 13 minutes (12 to 14 minutes)                                                                              |
| Active oxygen content of moist product                    | On average 11.43% (10.90 to 11.68%)                                                                                   |
| Drying<br>- Temperature<br>- Drying time                  | Recirculation dryer<br>80°C<br>150 to 180 min                                                                         |

**Table IIb:** Analysis and properties of sodium per-carbonate prepared according to the invention

|                                                                                                |                                                                           |
|------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------|
| Active oxygen content                                                                          | On average 15.02% (14.98 to 15.06%) = 31.91% of $\text{H}_2\text{O}_2$    |
| 5 $\text{H}_2\text{O}$ (Sartorius)                                                             | On average 0.15% (0.07 to 0.33%)                                          |
| $\text{Na}_2\text{CO}_3$ (total alkalinity)                                                    | On average 66.01%                                                         |
| NaCl                                                                                           | On average 0.1% (0.08%/0.09%)                                             |
| Turpinal SL                                                                                    | On average 1.69% (0.501% P)                                               |
| 10 Sum $\text{H}_2\text{O}/\text{H}_2\text{O}_2/\text{Na}_2\text{CO}_3/\text{TSL}/\text{NaCl}$ | 99.86%                                                                    |
| $\text{Na}_2\text{CO}_3:\text{H}_2\text{O}_2$ ratio                                            | 1:1.51                                                                    |
| DSC exothermic peak                                                                            | On average 161°C (159 to 162°C)<br>On average +133 J/g (+130 to +140 J/g) |
| Stability loss 2 h/105°C                                                                       | On average 4.6% (3.4 to 5.1%)                                             |

**Table III:** Further experiments for conditioning and PCS preparation

Conditioning:

|                                                                   | Experiment 3.1                    | Experiment 3.2                    |
|-------------------------------------------------------------------|-----------------------------------|-----------------------------------|
| 5 $\text{Na}_2\text{CO}_3$ (Rheinberg light)                      | 2000 g (79.37%)                   | 2000 g (79.37%)                   |
| $\text{H}_2\text{O}$ (boiling)                                    | 520 g (20.63%)                    | 520 g (20.63%)                    |
| $\text{Na}_2\text{CO}_3:\text{H}_2\text{O}_2$ ratio               | 1:1.53                            | 1:1.53                            |
| Procedure                                                         | Lödige laboratory mixer (120 rpm) | Lödige laboratory mixer (120 rpm) |
| 10 Addition time for $\text{H}_2\text{O}$                         | 45 seconds                        | 40 seconds                        |
| Temperature                                                       | 99°C                              | 99°C                              |
| Time                                                              | 45 minutes                        | 40 minutes                        |
| $\text{H}_2\text{O}$ (total alkalinity)                           | 14%                               | 13.45%                            |
| 15 $\text{Na}_2\text{CO}_3$ (total alkalinity)                    | 86%                               | 86.55%                            |
| $\text{H}_2\text{O}$ (Sartorius)                                  | 13.52%                            | 13.48%                            |
| $\text{Na}_2\text{CO}_3:\text{H}_2\text{O}$ ratio (from analysis) | 1:0.96                            | 1:0.92                            |

## Reaction with hydrogen peroxide:

|                                                       | Experiment 3.1                                           | Experiment 3.2                                           |
|-------------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|
| Procedure                                             | Lödige laboratory mixer (about 100 rpm)                  | Lödige laboratory mixer (about 100 rpm)                  |
| Starting materials                                    | 1940 g of $\text{H}_2\text{O}_2$ (w=0.6)/TSL (w=0.6)     | 2035 g of $\text{H}_2\text{O}_2$ (w=0.6)/TSL (w=0.6)     |
| 5 $\text{Na}_2\text{CO}_3:\text{H}_2\text{O}_2$ ratio | 1:1.5 (1.338 g of $\text{H}_2\text{O}_2$ /76.9 g of TSL) | 1:1.5 (1.412 g of $\text{H}_2\text{O}_2$ /81.2 g of TSL) |
| Temperature                                           | Room temperature/<br>water cooling                       | Room temperature/<br>water cooling                       |
| Time                                                  | 13 minutes                                               | 12 minutes                                               |
| Drying                                                | Recirculation dryer<br>80°C, 150 min                     | Recirculation dryer<br>80°C, 160 min                     |
| Product yield                                         | 2089 g                                                   | 2271 g                                                   |
| 10 Active oxygen content of moist product             | 10.90%                                                   | 11.62%                                                   |
| 15 Active oxygen content of end product               | 15.00% 14.95%<br>15.04%                                  | 15.06% 15.04%                                            |
| $\text{H}_2\text{O}$ (Sartorius)                      | 0.17%                                                    | 0.22% 0.43%                                              |
| Stability loss 2 h/105°C                              | 5.1%                                                     | 4.9%                                                     |

## Conditioning:

|                                                                         | Experiment 3.3                    | Experiment 3.4                    |
|-------------------------------------------------------------------------|-----------------------------------|-----------------------------------|
| Na <sub>2</sub> CO <sub>3</sub> (Rheinberg light)                       | 2000 g (79.37%)                   | 2000 g (79.37%)                   |
| H <sub>2</sub> O (boiling)                                              | 520 g (20.63%)                    | 520 g (20.63%)                    |
| Na <sub>2</sub> CO <sub>3</sub> :H <sub>2</sub> O ratio                 | 1:1.53                            | 1:1.53                            |
| Procedure                                                               | Lödige laboratory mixer (120 rpm) | Lödige laboratory mixer (120 rpm) |
| Addition time for H <sub>2</sub> O                                      | 30 seconds                        | 35 seconds                        |
| Temperature                                                             | 99°C                              | 99°C                              |
| Time                                                                    | 40 minutes                        | 35 minutes                        |
| H <sub>2</sub> O (total alkalinity)                                     | 13.9%                             | 14.15%                            |
| Na <sub>2</sub> CO <sub>3</sub> (total alkalinity)                      | 86.1%                             | 85.85%                            |
| H <sub>2</sub> O (Sartorius)                                            | 13.83%                            | 13.98%                            |
| Na <sub>2</sub> CO <sub>3</sub> :H <sub>2</sub> O ratio (from analysis) | 1:0.95                            | 1:0.97                            |

## Reaction with hydrogen peroxide:

|                                                       | Experiment 3.3                                          | Experiment 3.4                                          |
|-------------------------------------------------------|---------------------------------------------------------|---------------------------------------------------------|
| Procedure                                             | Lödige laboratory mixer (about 100 rpm)                 | Lödige laboratory mixer (about 100 rpm)                 |
| Starting materials                                    | 2000 g of $\text{H}_2\text{O}_2$ (w=0.6)/TSL (w=0.6)    | 2132 g of $\text{H}_2\text{O}_2$ (w=0.6)/TSL (w=0.6)    |
| 5 $\text{Na}_2\text{CO}_3:\text{H}_2\text{O}_2$ ratio | 1:1.5 (1381 g of $\text{H}_2\text{O}_2$ /79.4 g of TSL) | 1:1.5 (1468 g of $\text{H}_2\text{O}_2$ /84.4 g of TSL) |
| Temperature                                           | Room temperature/<br>water cooling                      | Room temperature/<br>water cooling                      |
| Time                                                  | 12 minutes                                              | 14 minutes                                              |
| Drying                                                | Recirculation dryer<br>80°C, 165 min                    | Recirculation dryer<br>80°C, 170 min                    |
| Product yield                                         | 2193 g                                                  | 2448 g                                                  |
| 10 Active oxygen content of moist product             | 11.68%                                                  | 11.42%                                                  |
| 15 Active oxygen content of end product               | 15.08% 15.04%                                           | 15.00% 14.96%                                           |
| $\text{H}_2\text{O}$ (Sartorius)                      | 0.06% 0.07%                                             | 0.16% 0.17%                                             |
| Stability loss 2 h/105°C                              | 5.1%                                                    | 4.7%                                                    |

## Conditioning:

|                                                                         | Experiment 3.5                    | Experiment 3.6                    |
|-------------------------------------------------------------------------|-----------------------------------|-----------------------------------|
| Na <sub>2</sub> CO <sub>3</sub> (Rheinberg light)                       | 2000 g (79.37%)                   | 2000 g (79.37%)                   |
| H <sub>2</sub> O (boiling)                                              | 520 g (20.63%)                    | 520 g (20.63%)                    |
| Na <sub>2</sub> CO <sub>3</sub> :H <sub>2</sub> O ratio                 | 1:1.53                            | 1:1.53                            |
| Procedure                                                               | Lödige laboratory mixer (120 rpm) | Lödige laboratory mixer (120 rpm) |
| Addition time for H <sub>2</sub> O                                      | 25 seconds                        | 30 seconds                        |
| Temperature                                                             | 99°C                              | 99°C                              |
| Time                                                                    | 35 minutes                        | 35 minutes                        |
| H <sub>2</sub> O (total alkalinity)                                     | 14.23%                            | 13.96%                            |
| Na <sub>2</sub> CO <sub>3</sub> (total alkalinity)                      | 85.77%                            | 86.04%                            |
| H <sub>2</sub> O (Sartorius)                                            | 14.10%                            | 13.96%                            |
| Na <sub>2</sub> CO <sub>3</sub> :H <sub>2</sub> O ratio (from analysis) | 1:0.98                            | 1:0.96                            |

## Reaction with hydrogen peroxide:

|                                                       | Experiment 3.5                                          | Experiment 3.6                                          |
|-------------------------------------------------------|---------------------------------------------------------|---------------------------------------------------------|
| Procedure                                             | Lödige laboratory mixer (about 100 rpm)                 | Lödige laboratory mixer (about 100 rpm)                 |
| Starting materials                                    | 2073 g of $\text{H}_2\text{O}_2$ (w=0.6)/TLS (w=0.6)    | 2066 g of $\text{H}_2\text{O}_2$ (w=0.6)/TSL (w=0.6)    |
| 5 $\text{Na}_2\text{CO}_3:\text{H}_2\text{O}_2$ ratio | 1:1.5 (1426 g of $\text{H}_2\text{O}_2$ /81.9 g of TSL) | 1:1.5 (1425 g of $\text{H}_2\text{O}_2$ /82.0 g of TSL) |
| Temperature                                           | Room temperature/<br>water cooling                      | Room temperature/<br>water cooling                      |
| Time                                                  | 13 minutes                                              | 12 minutes                                              |
| Drying                                                | Recirculation dryer<br>80°C, 175 min                    | Recirculation dryer<br>80°C, 180 min                    |
| Product yield                                         | 2368 g                                                  | 2252 g                                                  |
| 10 Active oxygen content of moist product             | 11.39%                                                  | 11.58%                                                  |
| 15 Active oxygen content of end product               | 15.04% 15.00%                                           | 14.96% 15.00%                                           |
| $\text{H}_2\text{O}$ (Sartorius)                      | 0.08% 0.14%                                             | 0.08% 0.06%                                             |
| Stability loss 2 h/105°C                              | 4.2%                                                    | 3.4%                                                    |

**Example 4:****Compacting and dry granulating**

5           The microcrystalline sodium percarbonates prepared in Example 2 or 3 were subjected to compacting and subsequent dry granulation. The compacting was carried out on a compacting machine of the type WP-50 N/75 having a dry granulating unit from Alexander-Werke, this machine being suitable for the continuous compacting of dry, pulverulent or finely crystalline products with subsequent comminution (granulation) of the compressed product. The granulation of the shells obtained by compacting could be controlled by incorporating various screen inserts. Screen inserts having mesh sizes of 2.00, 1.25 and 1.00 mm were available for this purpose.

10           In addition to the sodium percarbonates prepared in Example 2 or 3, a sodium percarbonate obtained by crystallization processes of the prior art was also compacted and dry-granulated for comparison (the average particle size of this PCS was  $d = 500 \mu\text{m}$ ). If desired, 1.0% by weight of sodium stearate powder was added to the sodium percarbonate used, for the compacting. As a result of this, the detachment of the shells from the roll surface could, if required, be improved. The shells then lifted off by themselves, without the aid of the built-in scraper. The granulometry was not influenced by the addition of the sodium stearate.

20           In order to find advantageous process conditions, the pressure of the rolls was first increased stepwise from 25 to 120 bar with constant product feed in preliminary experiments. The shells produced at high pressure could be readily granulated over a 1.25 mm screen insert. The granules then consisted of approximately cuboid particles which had satisfactory strength. Below 50 bar, only brittle shells formed, which easily disintegrated into powder

during granulation. An increase in the product feed led to thicker shells, which however increasingly flaked off from the roll with increasing pressure. Roll pressures of 50 to 100 bar therefore proved to be advantageous process conditions.

The coarse-particled sodium percarbonate granules having a mean particle diameter of 650  $\mu\text{m}$  (or 873  $\mu\text{m}$  in the case of the addition of sodium stearate) and prepared in the above compacting and granulation via a screen insert having a mesh size of 1.25 mm were investigated with respect to their properties. The granular products had low abrasion (<5 or <8% according to ISO 5.937), a low dry stability loss (6% at 105°C, 2 h) and a high dissolution rate (99% after 1 min, 15°C). The bulk density of sodium percarbonate prepared according to the invention was 0.87 g/ml or 0.93 g/ml with the addition of sodium stearate. According to the results of the microcalorimetric measurements (LKB) and the zeolite test, the PCS granules prepared according to the invention had a beneficial shelf life in a detergent base. In the microcalorimetric measurement, values of 49  $\mu\text{W/g}$  or 57  $\mu\text{W/g}$  (with the addition of sodium stearate) were obtained for sodium percarbonate prepared according to the invention and, in the zeolite test, the residual oxygen content was about 50%, or 56% in the case of the addition of sodium stearate (measured in each case relative to PBS-1 as standard). The detailed analytical results of customary sodium percarbonate (obtained by crystallization processes, or the compacted form thereof) and the sodium percarbonate products prepared according to the invention, without and with the addition of stearate, are listed in Table IV below as an overview.

**Table IV:** Properties of sodium percarbonates prepared according to the invention and Comparative Experiments

|       |                                                                                             |
|-------|---------------------------------------------------------------------------------------------|
| 4.1 = | PCS according to the invention after compacting                                             |
| 4.2 = | PCS according to the invention after compacting with the addition of sodium stearate        |
| C1 =  | Comparative Experiment: properties of commercial PCS, prepared by crystallization processes |
| C2 =  | Comparative Experiment: PCS as in C1 but after additional compacting                        |

|    |                                       | 4.1 <sup>*)</sup> | 4.2 <sup>*)</sup> | C1 <sup>*)</sup> | C2 <sup>*)</sup> |
|----|---------------------------------------|-------------------|-------------------|------------------|------------------|
|    | AVOX [%]                              | 15.04             | 14.83             | 14.32            | 14.36            |
|    | NaCl [%]                              | 0.1               | 0.1               | 2.7              | 2.9              |
|    | H <sub>2</sub> O [%]                  | 0.29              | 0.38              | 0.34             | 0.40             |
| 5  | Bulk density [kg/l]                   | 0.870             | 0.933             | 1.005            | 0.915            |
|    | Particle analysis [%]                 |                   |                   |                  |                  |
|    | >1.400 mm                             | 1.6               | 7                 | 1.2              | 5.0              |
| 10 | >1.000 mm                             | 19.6              | 34                | 9.8              | 32.0             |
|    | >0.850 mm                             | 13.1              | 13                | 5.5              | 14.8             |
|    | >0.600 mm                             | 16.6              | 14                | 13.5             | 13.4             |
|    | >0.425 mm                             | 12.8              | 9                 | 20.1             | 9.2              |
|    | >0.250 mm                             | 14.8              | 8                 | 27.1             | 8.4              |
| 15 | >0.150 mm                             | 10.4              | 7                 | 12.4             | 4.8              |
|    | <0.150 mm                             | 10.8              | 8                 | 10.4             | 12.4             |
|    | Mean particle diameter [μm]           | 648.8             | 827.9             | 511.4            | 787.5            |
|    | Abrasion [%]                          | 4.6               | 7.8               | 7.6              | 12.8             |
| 20 | Stability loss [%]<br>(105°C, 2 h)    | 6.1               | 12.0              | 9.2              | 16.4             |
|    | Dissolution rate<br>(2 g, 15°C) 1 min | 99                | 96                | 82.8             | 79.0             |
| 25 | [%] 2 min                             | 100               | 99                | 94.1             | 93.3             |
|    | 3 min                                 | 100               | 100               | 97.9             | 96.7             |
|    | LKB <sup>**) [μW/g]</sup>             | 49.6              | 57.1              | 54.7             | 87.3             |
|    | Zeolite test [%]                      | 50.3              | 55.8              | 41.1             | 38.7             |

<sup>\*)</sup> All original samples; no fractions removed by sieving;

<sup>\*\*) Measurement of LKB value in zeolite-containing detergent base; mixing ratio: 20% by weight of percarbonate and 80% by weight of detergent base.</sup>

Legend

|    |                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
|----|----------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|    | PCS                  | = Sodium percarbonate                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |
|    | AVOX                 | = Active oxygen (content)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
| 5  | Turpinal SL<br>(TSL) | = Aqueous 60% strength by weight<br>solution of 1-hydroxyethane-1,1-<br>diphosphonic acid (HEDP);<br>stabilizer for peroxides                                                                                                                                                                                                                                                                                                                                                                                      |
| 10 | Waterglass           | = 36% strength by weight solution of<br>sodium silicate in water (8% by<br>weight of $\text{Na}_2\text{O}$ ; 25.5% by weight of<br>$\text{SiO}_2$ )                                                                                                                                                                                                                                                                                                                                                                |
|    | IFB                  | = Integrated fluidized bed                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
|    | h                    | = hour                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
|    | min                  | = minute                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
| 15 | mmWC                 | = mm water column                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |
|    | P, dP                | = Pressure, pressure difference                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
|    | rpm                  | = revolutions per minute                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
|    | DSC                  | = Differential scanning calorimetry.<br>DSC includes all processes with<br>energy consumption or release,<br>i.e. endothermic and exothermic<br>phase transformations.                                                                                                                                                                                                                                                                                                                                             |
| 20 |                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
|    | LKB measurements     | = Heat flow measurements<br>In these heat flow measurements,<br>the heat flows occurring under<br>isothermal measuring conditions<br>provide information about the<br>stability of the product<br>containing active oxygen; in par-<br>ticular, it is also possible to<br>determine the stability of the<br>product in the presence of<br>detergent components if the heat<br>flow measurements are carried out<br>on samples in which the product<br>containing active oxygen is<br>present as a mixture with the |
| 25 |                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
| 30 |                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
| 35 |                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |

detergent components. The heat flow measurements were carried out in an LKB 2277 Bio Activity Monitor at 40°C over a period of 20 h. The lower the measured heat flow, the higher the stability of the product containing active oxygen in the detergent base, or the more stable the respective PCS particles.

Avox loss,  
Avox stability,  
stability loss

= To determine the chemical stability of the sodium percarbonate prepared, the active oxygen loss (Avox stability) was determined. For this purpose, the product was heated to 105°C for 2 h and the loss of active oxygen due to decomposition was determined. The determination of the active oxygen was carried out by customary titrimetric methods.

H<sub>2</sub>O (Sartorius)

= Sample weight in each case 7.5 g; test temperature 60°C; end of test: <5 mg/90 seconds.

Zeolite test

= 10 g of product and 10 g of zeolite A (molecular sieve 2 to 3  $\mu$ m, Aldrich) are mixed; store for 48 h in an open Petri dish at 32°C and 80% relative humidity; zeolite index = residual active oxygen content of the sample after storage divided by residual active oxygen content of the standard PBS-1 after storage. (PBS-1 = sodium perborate monohydrate)

**Abrasion test**

= The determination of the abrasion was carried out according to ISO 5934; i.e. the amount of fine fractions  $< 150 \mu\text{m}$  which was produced on fluidization of the sample in a vertical tube by means of compressed air was determined gravimetrically. The proportion of fine fraction produced relative to the total amount gave the percentage for the abrasion.

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## Patent Claims

1. Process for the preparation of sodium percarbonate (PCS), characterized in that solid sodium carbonate monohydrate is reacted with a quasi-stoichiometric amount, based on the active oxygen content desired in the sodium percarbonate, of a 50 to 70% strength by weight aqueous hydrogen peroxide solution at reaction temperatures of up to not more than 80°C in a mixing apparatus to give a pasty or doughy material comprising moist sodium percarbonate and a sodium percarbonate having an active oxygen content of 10 to 15.2% by weight, preferably >14.5 to 15.2% by weight, and having desired particle parameters, such as bulk density and mean particle diameter, is subsequently obtained by drying and/or granulation.

2. Process according to Claim 1, characterized in that the reaction temperatures during the exothermic reaction are kept in the range from room temperature to not more than 80°C, preferably in the range from above 20°C to not more than 80°C.

3. Process according to Claim 1, characterized in that a quasi-stoichiometric amount, based on sodium percarbonate having the theoretical empirical formula  $\text{Na}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}_2$ , preferably 1.49 to 1.52 mol ( $\text{H}_2\text{O}_2$ ), of the aqueous hydrogen peroxide solution is used.

4. Process according to Claim 1, characterized in that 55 to 65% strength by weight aqueous hydrogen peroxide solution is used.

5. Process according to Claim 1, characterized in that the aqueous hydrogen peroxide solution is metered via a nozzle, preferably a binary nozzle, into the mixer containing initially introduced solid sodium carbonate monohydrate.

6. Process according to Claim 1, characterized in that a solid sodium carbonate monohydrate obtained





by conditioning from light sodium carbonate having a bulk density of 0.50 to 0.55 kg/l is used.

7. Process according to Claim 1, characterized in that a solid sodium carbonate monohydrate obtained by conditioning from superlight sodium carbonate having a bulk density of less than 0.50 kg/l is used.

8. Process according to Claim 1, characterized in that the reaction of sodium carbonate monohydrate with the aqueous hydrogen peroxide solution is carried out as rapidly as possible in an intensive mixer.

9. Process according to Claim 8, characterized in that sodium percarbonate granules having a bulk density of 0.2 to 1.1 kg/l, preferably of 0.5 to 1.1 kg/l, are prepared.

10. Process for the preparation of sodium percarbonate granules, characterized in that, in a first step (= reaction step), a sodium percarbonate is prepared and dried by a process of Claims 1 to 9, and, in a second step (= compacting/dry granulation step), the sodium percarbonate obtained after drying in the first step is compacted to give shells, if desired with the addition of up to 1% by weight of a lubricant, preferably of alkali metal and/or alkaline earth metal stearate, and the shells are then obtained by a dry granulation method, by crushing and sieving into sodium percarbonate granules having desired particle parameters, such as bulk density and mean particle diameter.

11. Process according to Claim 10, characterized in that the compacting is carried out at a pressure of at least 50 bar to not more than 150 bar, preferably at a pressure of 80 to 120 bar.

12. Process according to Claim 8 or 10, characterized in that sodium percarbonate granules having a mean particle diameter of 350 to 1300  $\mu\text{m}$ , preferably of 550 to 1100  $\mu\text{m}$ , are prepared.

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13. Process according to Claims 10 and 12, characterized in that sodium percarbonate granules having a mean particle diameter of more than 600  $\mu\text{m}$ , preferably of 640 to 1000  $\mu\text{m}$ , are prepared.

14. Process according to Claim 10, characterized in that sodium percarbonate granules having a bulk density of 0.85 to 1.1 kg/l, preferably 0.93 to 1.1 kg/l, are prepared.

15. Process according to any of Claims 10 to 14, characterized in that compacting is effected with the addition of up to 1% by weight of sodium stearate and/or magnesium stearate.

16. Sodium percarbonate (PCS), characterized in that it has an active oxygen content of >14.5 to 15.2% by weight, calculated without any granulating assistants added during the preparation and/or granulation, and that it has a dissolution rate of at least 95% after 1 minute and at least 99% after 2 minutes (in each case standard conditions: 2 g, 15°C).

17. Sodium percarbonate (PCS), characterized in that it has an active oxygen content of >14.5 to 15.2% by weight, calculated without any granulating assistants added during the preparation and/or granulation, and that it has an exothermic DSC peak above about 155°C, in particular in the range from 159 to 162°C.

18. Sodium percarbonate (PCS), characterized in that it has an active oxygen content of >14.5 to 15.2% by weight, calculated without any granulating assistants added during the preparation and/or granulation, and that it has a stability loss of less than 6.2%, preferably of 3.4 to 5.1%, measured under standard conditions (105°C, 2 h).

19. Sodium percarbonate according to any of Claims 16 to 18, characterized in that it has a mean particle diameter of 550 to 1100  $\mu\text{m}$ , preferably of 640 to 1000  $\mu\text{m}$ .

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20. Sodium percarbonate according to any of Claims 16 to 18, characterized in that it has a bulk density of 0.85 to 1.1 kg/l.

21. Sodium percarbonate according to either of Claims 19 and 20, characterized in that it has an abrasion value of less than 5% (measured under standard conditions).

22. Sodium percarbonate according to either of Claims 16 and 17, characterized in that it contains up to 1% by weight of a lubricant introduced during the granulation and from the group consisting of the alkali metal or alkaline earth metal stearates and that it has a bulk density of 0.93 to 1.1 kg/l.

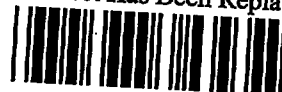
23. Sodium percarbonate according to Claim 22, characterized in that it has an abrasion value of less than 8% (measured under standard conditions).

24. Sodium percarbonate according to any of Claims 16 to 23, characterized in that it is obtainable by a process of Claims 1 to 15, preferably by a process of Claims 10 to 15.

25. Sodium percarbonate according to any of Claims 16 to 18, characterized in that it is obtainable by a process of Claims 10 to 15 without the addition of lubricants during the compacting/dry granulation and has a stability loss of less than 6.2%, measured under standard conditions (105°C, 2 h).

26. Sodium percarbonate according to any of Claims 16 to 18, characterized in that it is obtainable by a process of Claims 10 to 15 without the addition of lubricants during the compacting/dry granulation and has a mean particle diameter of 550 to 1100  $\mu\text{m}$ , preferably of 640 to 1000  $\mu\text{m}$ .

27. Sodium percarbonate according to any of Claims 16 to 18, characterized in that it is obtainable by a process of Claims 10 to 15 without the addition of lubricants during the compacting/dry granulation and has a bulk density of 0.85 to 1.1 kg/l.





28. Sodium percarbonate according to either of Claims 26 and 28, characterized in that it has an abrasion value of less than 5% (standard conditions).

29. Sodium percarbonate according to either of Claims 16 and 17, characterized in that it is obtainable by a process of Claims 10 to 15 with the addition of up to 1% by weight of a lubricant during the compacting/dry granulation, preferably with the addition of alkali metal and/or alkaline earth metal stearate, and that it has an active oxygen content of more than 14.5% by weight, preferably of more than 14.8% by weight, and a stability loss of not more than 12.0 (measured under standard conditions: 105°C, 2 h).

30. Sodium percarbonate according to either of Claims 16 and 17, characterized in that it is obtainable by a process of Claims 10 to 15 with the addition of up to 1% by weight of a lubricant during the compacting/dry granulation, preferably with the addition of alkali metal or alkaline earth metal stearate, and that it has an active oxygen content of more than 14.5% by weight to 15% by weight, preferably of more than 14.8% by weight to 15.0% by weight, and a mean particle diameter of 800 to 1000  $\mu\text{m}$ .

31. Sodium percarbonate according to either of Claims 16 and 17, characterized in that it is obtainable by a process of Claims 10 to 15 with the addition of up to 1% by weight of a lubricant during the compacting/dry granulation, preferably with the addition of alkali metal or alkaline earth metal stearate, and that it has an active oxygen content of more than 14.5% by weight to 15% by weight, preferably of more than 14.8% by weight to 15.0% by weight, and a bulk density of 0.93 to 1.1 kg/l.

32. Sodium percarbonate according to either of Claims 30 and 31, characterized in that it has an abrasion value of not more than 8% (measured under standard conditions).

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33. Solid bleach or detergent compositions, containing 0.5 to 40% by weight, preferably 5 to 25% by weight, of the sodium percarbonate according to any of Claims 16 to 32 and 99.5 to 60% by weight, preferably 95 to 75% by weight, of formulation substances and assistants customary in bleach or detergent compositions, from the group consisting of surfactants, builders, bleach activators, peracid bleach precursors, enzymes, enzyme stabilizers, antiredeposition agents and/or compatibilizers, complexing and chelating agents, lather regulators and additives such as optical brighteners, opacifiers, corrosion inhibitors, antielectrostatic agents, dyes and bactericides.

34. Bleach and detergent composition according to Claim 33, characterized in that it contains a sodium percarbonate according to any of Claims 16 to 27 in the presence of builders from the group consisting of the zeolites.

35. Bleach and detergent composition according to Claim 33 or 34, characterized in that it is a compact detergent composition.

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