



Office de la Propriété

Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2457844 C 2009/09/15

(11)(21) **2 457 844**

(12) **BREVET CANADIEN**
CANADIAN PATENT

(13) **C**

(86) Date de dépôt PCT/PCT Filing Date: 2002/07/04
(87) Date publication PCT/PCT Publication Date: 2003/03/06
(45) Date de délivrance/Issue Date: 2009/09/15
(85) Entrée phase nationale/National Entry: 2004/02/17
(86) N° demande PCT/PCT Application No.: EP 2002/007408
(87) N° publication PCT/PCT Publication No.: 2003/018471
(30) Priorité/Priority: 2001/08/21 (DE101 40 838.2)

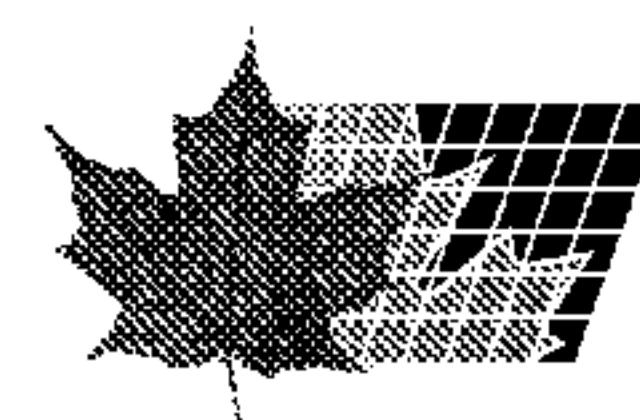
(51) Cl.Int./Int.Cl. *C01B 15/10* (2006.01)

(72) Inventeurs/Inventors:
JAKOB, HARALD, DE;
HESSBERGER, WALDEMAR, DE;
LATTICH, JUERGEN, DE;
OVERDICK, RALPH, DE
(73) Propriétaire/Owner:
EVONIK DEGUSSA GMBH, DE
(74) Agent: MARKS & CLERK

(54) Titre : PROCEDE POUR PRODUIRE DU PERCARBONATE DE SODIUM ENROBE SOUS FORME DE GRANULES
ET PRODUIT AINSI REALISE
(54) Title: METHOD FOR THE PREPARATION OF COATED GRANULAR SODIUM PERCARBONATE, AND PRODUCT
OBTAINABLE BY THE PROCESS

(57) Abrégé/Abstract:

The invention relates to a method for producing granular coated sodium percarbonate with a low TAM value. The sodium percarbonate is produced by fluid bed granulation at a temperature T_G in the range of from 45 to 75 °C and coating by spraying an aqueous solution that contains at least one coating component in a fluid bed at a temperature T_U in the range of from 35 to 100 °C. According to the invention, a) after fluid bed granulation but before coating a supplementary drying step is carried out at T_{NT} of greater than T_G , or b) fluid bed granulation is carried out in at least two steps at T_{G1} , T_{G2} , T_{Gn} , with T_{G2} or T_{Gn} being greater than T_{G1} and no supplementary drying step being required if 2/3 of the granules have been formed at T_{G1} , or c) supplementary drying is carried out not after granulation but only after coating, namely at T_{UNT} , with T_{UNT} being at least 20 °C higher than T_G .



(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum
Internationales Büro(43) Internationales Veröffentlichungsdatum
6. März 2003 (06.03.2003)

PCT

(10) Internationale Veröffentlichungsnummer
WO 03/018471 A1(51) Internationale Patentklassifikation⁷: **C01B 15/10**Drosselweg 6, 63755 Alzenau (DE). **LATTICH, Jürgen**; Neugasse 41, 61130 Nidderau (DE). **OVERDICK, Ralph**; Brückenstrasse 3, 65719 Hofheim (DE).

(21) Internationales Aktenzeichen: PCT/EP02/07408

(22) Internationales Anmelde datum:
4. Juli 2002 (04.07.2002)

(81) Bestimmungsstaaten (national): BR, CA, HU, IL, IN, JP, KR, MX, NO, PL, SI.

(25) Einreichungssprache: Deutsch

(84) Bestimmungsstaaten (regional): europäisches Patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR).

(26) Veröffentlichungssprache: Deutsch
(30) Angaben zur Priorität:
101 40 838.2 21. August 2001 (21.08.2001) DEVeröffentlicht:
— mit internationalem Recherchenbericht

(71) Anmelder: DEGUSSA AG [DE/DE]; Bennigsenplatz 1, 40474 Düsseldorf (DE).

Zur Erklärung der Zweibuchstaben-Codes und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

(72) Erfinder: **JAKOB, Harald**; Meerholzer Strasse 1, 63594 Hasselroth (DE). **HESSBERGER, Waldemar**;

(54) Title: METHOD FOR PRODUCING GRANULAR COATED SODIUM PERCARBONATE AND PRODUCT OBTAINED ACCORDING TO SAID METHOD

(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON GRANULATFÖRMIGEM UMHÜLLTEN Natriumpercarbonat UND VERFAHRENSGEMÄSS ERHÄLTLICHES PRODUKT

(57) Abstract: The invention relates to a method for producing granular coated sodium percarbonate with a low TAM value. The sodium percarbonate is produced by fluid bed granulation at a temperature T_G in the range of from 45 to 75 °C and coating by spraying an aqueous solution that contains at least one coating component in a fluid bed at a temperature T_U in the range of from 35 to 100 °C. According to the invention, a) after fluid bed granulation but before coating a supplementary drying step is carried out at T_{NT} of greater than T_G , or b) fluid bed granulation is carried out in at least two steps at T_{G1} , T_{G2} T_{Gn} , with T_{G2} or T_{Gn} being greater than T_{G1} and no supplementary drying step being required if 2/3 of the granules have been formed at T_{G1} , or c) supplementary drying is carried out not after granulation but only after coating, namely at T_{UNT} , with T_{UNT} being at least 20 °C higher than T_G .**WO 03/018471 A1**(57) Zusammenfassung: Die Erfindung betrifft ein Verfahren zur Herstellung von granulatförmigem umhüllten Natriumpercarbonat, das einen niedrigen TAM-Wert aufweist. Die Herstellung erfolgt durch Wirbelschichtsprühgranulation bei einer Temperatur T_G im Bereich von 45 bis 75 °C das Umhüllen durch Aufsprühen einer mindestens eine Hüllkomponente enthaltenden wässrigen Lösung in einer Wirbelschicht bei einer Temperatur T_U im Bereich von 35 bis 100 °C. Erfindungsgemäß wird: a) nach der Wirbelschichtsprühgranulation aber vor dem Umhüllen eine Nachtrocknung bei T_{NT} von grösser T_G durchgeführt; oder b) die Wirbelschichtgranulation wird mindestens zweistufig bei T_{G1} , T_{G2} ... T_{Gn} durchgeführt, wobei T_{G2} bzw. T_{Gn} grösser als T_{G1} und sich ein Nachtrocknen erübrigt, wenn 2/3 des Granulats bei T_{G1} gebildet worden sind; oder c) erfolgt die Nachtrocknung nicht nach der Granulation, sondern erst nach der Umhüllung, und zwar bei T_{UNT} , wobei T_{UNT} mindestens 20 °C grösser als T_G ist.

Method for the Preparation of Coated Granular Sodium Percarbonate, and Product Obtainable by the Process

Description

The invention relates to a process for the preparation of 5 coated granular sodium percarbonate having a low TAM value, and to a product obtainable by the process, which product is distinguished by a low TAM value (microcalorimetric determination of the release of energy during storage). The process according to the invention comprises (i) the 10 preparation of granular sodium percarbonate by fluidised-bed spray granulation, and (ii) coating of the granular sodium percarbonate with a coating component in a fluidised bed.

For the preparation of sodium percarbonate of the general 15 formula $2 \text{Na}_2\text{CO}_3 \cdot 3 \text{H}_2\text{O}_2$, which is used as a bleaching component in washing and cleaning agents, crystallisation processes and fluidised-bed spray granulation processes in particular are used on an industrial scale.

Although a sodium percarbonate obtained by crystallisation 20 processes can readily be stored owing to its often low TAM value *per se*, the active oxygen stability in the presence of washing agent constituents, such as, especially, zeolites, is unsatisfactory because of the porous surface. Although the stability of sodium percarbonate produced by a 25 crystallisation process to storage in the presence of washing agent constituents can be improved by coating the sodium percarbonate core with components having a stabilising action, the demands nowadays made of such a product are often no longer adequately met.

30 Fluidised-bed spray granulation processes yield substantially spherical, dense sodium percarbonate particles which have a shell-like structure, resulting from the preparation, and higher storage stability than a

product obtained by crystallisation. In order to carry out the process, an aqueous hydrogen peroxide solution and an aqueous soda solution or, optionally, soda suspension are sprayed into a fluidised bed containing sodium percarbonate particles whose diameter is smaller than that of the particles to be prepared. During the spraying in of the reactants, which are in an aqueous medium, water is evaporated off at a fluidised-bed temperature in the range from 40 to 95°C. Details regarding the implementation of the fluidised-bed spray granulation process are to be found, for example, in EP patent 0 716 640. In order further to increase the active oxygen stability in the presence of washing agent constituents, sodium percarbonate produced by fluidised-bed spray granulation can also be coated with a stabilising coating layer, for example with a sodium sulfate layer according to EP patent 0 863 842.

For reasons of safety when handling sodium percarbonate, especially increased safety during storage in a silo, there is an increased demand for sodium percarbonate having further improved storage stability, corresponding to a further reduced TAM value as compared with hitherto. Although the TAM value of sodium percarbonate can be lowered to a certain extent by coating the sodium percarbonate with an inactivating material, the effect that can be achieved thereby is in many cases still inadequate. The TAM value is a microcalorimetric determination of the release of energy during storage, determined by means of a TAM® Thermal Activity Monitor from Termometric AB, Järfälla (SE).

Various attempts have already been made to lower the TAM value of sodium percarbonate in the case of preparation by fluidised-bed spray granulation. As the inventors of the present Application have found, a sodium percarbonate prepared according to DE-OS 27 33 935, which was produced by fluidised-bed spray granulation, has a relatively low

TAM value if both a condensed phosphate and magnesium sulfate are added to the solutions for spraying. A disadvantage of that process is the large amount of those added substances that is required.

5 DE patent application 100 48 514.6, which has not yet been published, teaches a further process for the preparation of sodium percarbonate having a low TAM value, preferably of/less than 6 $\mu\text{W/g}$, by fluidised-bed spray granulation, in which process, for the purpose of lowering the TAM value,
10 there is preferably added to at least one of the solutions for spraying a magnesium compound in an amount of approximately from 100 to 1000 ppm Mg^{2+} and/or a selected chelating agent, such as an aminophosphonic acid, in an amount of from 200 to 1000 ppm. As already mentioned at the
15 beginning, a sodium percarbonate having a low TAM value must generally also be covered with a stabilising coating in order to ensure adequate storage stability of the active oxygen content in washing and cleaning agents. While the TAM value is a criterion for safety during storage in a
20 silo, the active oxygen stability is a criterion that is of importance especially for the storage of a washing agent containing sodium percarbonate.

Accordingly, the object of the present invention is to provide a process for the preparation of coated granular sodium percarbonate having a low TAM value, especially a TAM value of/less than 8 $\mu\text{W/g}$, preferably of/less than 5 $\mu\text{W/g}$. The process should be as simple as possible to implement industrially. Preferably, no process steps should be required other than those already used in the case of
25 known fluidised-bed spray granulation and coating in a fluidised bed.

These and other objects, which will become apparent from the further description, are achieved by the process according to the invention. Accordingly, there has been
30 found a process for the preparation of coated granular

sodium percarbonate, comprising (i) preparation of granular sodium percarbonate by fluidised-bed spray granulation, wherein an aqueous sodium carbonate solution or suspension and an aqueous hydrogen peroxide solution are sprayed in a 5 molar ratio of Na_2CO_3 to H_2O_2 in the range from 1:1.4 to 1:1.8 into a fluidised bed containing sodium percarbonate particles, and water is simultaneously evaporated off, and (ii) coating of the granular sodium percarbonate by the spray application, in a fluidised bed, of at least one 10 aqueous solution containing one or more coating components, with the simultaneous evaporation of water, which process is characterised in that a) the fluidised-bed spray granulation is carried out at a fluidised-bed temperature T_G in the range from 45 to 75°C, the granular sodium 15 percarbonate is dried, before it is coated, at a fluidised-bed temperature T_{NT} in the range from 60 to 100°C, T_{NT} being higher than T_G , and the coating is carried out at a fluidised-bed temperature T_U in the range from 35 to 100°C, or in that (b) the fluidised-bed spray granulation is 20 carried out in at least two steps, the fluidised-bed temperature T_{G1} being in the mentioned range for T_G and the fluidised-bed temperature T_{Gn} in the subsequent step(s) being in the range for T_{NT} , T_{GNT} being higher than T_G , and at least two thirds of the mass of the granulate having been 25 formed during the first step, and the sodium percarbonate granulate so obtained is coated, without or after being dried, at a fluidised-bed temperature in the range of T_{NT} T_U , or in that (c) the granular sodium percarbonate prepared at T_G without 30 being dried is coated and dried at a fluidised-bed temperature T_{UNT} , T_{UNT} being at least 20°C higher than T_G .

The sub-claims are directed towards preferred embodiments of the process according to the invention.

The invention relates also to coated granular sodium 35 percarbonate which has a Mg^{+2} content in the core of from

100 to 1000 ppm and which has a structure of the core and its coating obtainable by fluidised-bed spray granulation, characterised by a TAM value of less than 3 $\mu\text{W/g}$, measured after 48 hours at 40°C.

5 According to EP patent 0 716 640 referred to at the beginning, the fluidised-bed spray granulation is carried out at a fluidised-bed temperature in the range from 40 to 95°C and preferably from 50 to 70°C. That document also teaches that the sodium percarbonate fluidised-bed spray 10 granulate, which has a moisture content of from 2 to 10 wt.%, is removed from the fluidised-bed apparatus and, as required, is dried or is subjected to after-treatment for the purpose of increasing its stability. The term "drying" is to be understood as meaning that no spray 15 solution is injected into the fluidised bed during that time. There is no suggestion in that document that the drying should be carried out at a higher temperature. The coating of sodium percarbonate in a fluidised bed is such "after-treatment". There is thus no indication in that 20 document to the person skilled in the art to dry the fluidised-bed spray granulate before it is coated; rather, the person skilled in the art would place a drying step at the end of the entire process, that is to say would carry out the drying after coating of the granulate in a 25 fluidised bed. Surprisingly, it has now been found that the TAM value of coated granular sodium percarbonate can be substantially lowered if the granular sodium percarbonate obtained by fluidised-bed spray granulation is dried at a raised temperature before it is coated. By means of an 30 additional drying step following coating it is possible to achieve a further reduction in the TAM value, a very brief drying period generally being sufficient in view of the small layer thickness of the coating.

The granulation step of the process according to the 35 invention can be carried out in one or more steps. In the

case of a single-step procedure, the reactants are injected into the fluidised bed while a fluidised-bed temperature T_G in the range from 45 to 75°C, preferably from 55 to 75°C, is maintained, with the simultaneous evaporation of water.

5 Injection can be carried out by means of one or more spray nozzles. The reactants are particularly preferably injected into the fluidised-bed reactor using a 3- or 4-component nozzle, for example according to EP 0 716 640 B1 or EP 0 787 682. There are suitable for the preparation of the
10 uncoated granular sodium percarbonate conventional fluidised-bed reactors with or without grading discharge of the granulate. According to a preferred embodiment, the reactor is a flow trough which can be divided into a plurality of chambers and on the side walls of which are
15 arranged the nozzles.

According to a first embodiment of the process according to the invention, in which the fluidised-bed spray granulation is carried out with the maintenance of substantially a fluidised-bed temperature, the granulation step (i) is
20 followed by drying at a temperature T_{NT} which is higher than T_G , during which no further reactants in the form of an aqueous solution are injected. During the drying, the TAM value falls. The drying is preferably carried out at a fluidised-bed temperature T_{NT} in the range from greater
25 than 75°C to 95°C, especially 90 ± 5°C. T_{NT} is preferably from 10 to 30°C, especially from 20 to 30°C, higher than T_G .

Drying in that manner leads to a greater reduction in the TAM value than does simple drying of the coated granular sodium percarbonate. According to an alternative embodiment
30 of the process according to the invention, step (i) is carried out not at a substantially constant temperature T_G but in two or more steps with an increasing fluidised-bed temperature T_{G1} , T_{G2} ... T_{Gn} , T_{Gn} being higher than T_{G1} . The temperature difference between T_{G1} and T_{Gn} is advantageously
35 from 10 to 40°C, especially from 20 to 30°C. The

preparation of the fluidised-bed spray granulate is carried out particularly preferably in two steps at a fluidised-bed temperature T_{G1} of $70 \pm 5^\circ\text{C}$ and a fluidised-bed temperature T_{G2} ($= T_{Gn}$) of $90 \pm 5^\circ\text{C}$. The second step takes place when at

5 least half of the granulate has been formed.

Advantageously, at least $2/3$ of the mass of the granulate are produced in the course of a first step and less than $1/3$ of the mass is produced in a second or further step(s).

It has been found that the active oxygen loss is lower in

10 that embodiment than when the granulate formation takes place from the outset at a higher fluidised-bed

temperature. At the same time, the embodiment according to the invention yields granulates having a lower TAM value.

The granulate obtained by two- or multi-step fluidised-bed

15 spray granulation can, if required, also be dried at a temperature T_{NT} , T_{NT} being equal to or higher than the last temperature stage of the fluidised-bed spray granulation; accordingly, in the case of two-step fluidised-bed spray granulation, T_{NT} is equal to or higher than T_{G2} or T_{Gn} .

20 The duration of the drying in the case of single-step and, as required, also multi-step spray granulation is dependent on the desired residual moisture content and, especially, on the desired lowering of the TAM value. The drying time is usually in the range from 1 to 60 minutes, preferably in

25 the range from 15 to 45 minutes and particularly preferably 30 minutes. The optimum drying time, which is also dependent on the operating parameters of the fluidised-bed reactor, can readily be determined by means of some orienting preliminary tests.

30 Coating of the fluidised-bed spray granulate was usually carried out at a fluidised-bed temperature T_v in the range from 35 to 100°C , especially from 40 to 90°C and particularly preferably from 40 to 70°C . Coating can be carried out in one or more steps, an aqueous solution

35 containing one or more coating components in each case

being applied by spraying to the previously formed sodium percarbonate fluidised-bed granulate, with simultaneous evaporation of the water that has been introduced. The coating components are hydrate-forming inorganic salts, 5 such as magnesium sulfate, sodium sulfate, soda and sodium bicarbonate and combinations of salts; borates and chelating agents are also suitable coating components. According to a preferred embodiment, the coated granular sodium percarbonate contains up to 10 wt.% coating 10 component(s), preferably about 5 wt.%.

Where desirable in view of a further reduction in the TAM value, it is advantageous to dry the coated fluidised-bed spray granulate at a fluidised-bed temperature T_{UNT} . The temperature T_{UNT} is usually equal to or higher than T_U and 15 higher than T_G . Since the layer thickness of the coating is generally very small, it is sufficient to dry the coated material for only a few minutes, for example from 2 to 10 minutes, if the core has already been dried in accordance with the invention. If T_U is already 20 considerably higher than T_G or T_{Gn} , for example from 10 to 30°C higher, it is possible to dispense with drying.

In accordance with a further embodiment according to the invention, preparation of the granulate is immediately followed by coating thereof with a coating material, the 25 fluidised-bed temperature being T_G during preparation of the granulate and T_U during coating. In that embodiment, the coated granular sodium percarbonate is dried at a fluidised-bed temperature T_{UNT} that is at least 10°C, preferably from 20 to 30°C, higher than the temperature T_G 30 or T_{Gn} . In that embodiment, the drying time is generally from 10 to 60 minutes.

The hydrogen peroxide solution used in the preparation of the granulate, and the aqueous soda solution or suspension, can contain conventional stabilisers. In particular, the 35 soda solution or suspension contains sodium silicate and

the aqueous hydrogen peroxide solution contains a magnesium salt and, optionally, further stabilisers. The hydrogen peroxide solution particularly preferably contains a magnesium salt in such an amount that the coated sodium percarbonate contains from 100 to 1000 ppm Mg^{2+} . It has been found that it is possible by adding a magnesium salt to lower the TAM value considerably - see DE patent application 100 48 514.6.

By means of the process according to the invention it is possible to obtain coated granular sodium percarbonate having a very low TAM value. As will be seen from the Examples, it is even possible to make available coated sodium percarbonate having a TAM value below 3 $\mu W/g$. Such low TAM values were not obtainable by the prior-known processes.

The process according to the invention and the products obtained thereby are illustrated by means of the following Examples.

Examples

20 General description of the fluidised-bed spray granulation and coating as well as drying.

The fluidised-bed spray granulation (step i) was carried out according to EP 0 716 640 B1 in a laboratory fluidised-bed granulator. The reactants, that is to say the soda solution and the hydrogen peroxide solution, were sprayed by means of a three-component atomiser nozzle into a starting fluidised bed of soda cores (instead of sodium percarbonate) having a small particle diameter. Heated fluidising air (about 200°C) was drawn in by way of a fan (about 160 Nm^3/h). Spraying was continued until a mean particle diameter of 500 μm had been reached. The soda content from the starting fluidised bed in the fluidised-bed spray granulate was less than 10 %. The amount of

product in the fluidised bed was kept approximately constant at 5 kg during the test by the periodic removal of a portion. The throughput of the starting materials corresponded to 5 kg of sodium percarbonate. Soda was used 5 in the form of a 30 wt.% aqueous solution containing sodium silicate as stabiliser, and hydrogen peroxide was used in the form of a 43.5 wt.% aqueous solution. Where Mg^{2+} was used as stabiliser, it was added in the form of $MgSO_4 \cdot 7H_2O$ to the H_2O_2 solution. The molar ratio of soda to H_2O_2 was 10 set at 1:1.58.

Where the granulate was dried before being coated, the drying takes place in the fluidised-bed granulator.

Once the target particle size had been reached in the fluidised-bed spray granulation, the granulate, without or 15 after being dried, was coated with 5 % sodium sulfate in a further fluidised-bed spray reactor and dried as indicated.

The fluidised-bed temperatures, active oxygen contents O_a , TAM values (determined at 40°C and 48 h) and particulars will be found in the following Table 1. T_G stands for the 20 fluidised-bed temperature during formation of the granulate, T_U stands for the fluidised-bed temperature during coating, T_{NT} stands for the fluidised-bed temperature during drying of the granulate prior to coating, T_{Gn} stands for the fluidised-bed temperature for 25 the second granulation step, T_{UNT} stands for the fluidised-bed temperature during drying of the coated granulate.

Table 1

Example No.	Fluidised-bed temperature °C			Oa (%)	TAM (μW/g)	Remarks
	T _G ¹⁾	T _{WT} ²⁾	T _U [*]			
1	68 - 70	-	70 \Rightarrow 60	68 - 70	13.1	11.3 n.i.
2	88 - 90	-	70 \Rightarrow 60	68 - 70	12.5	6.8 n.i.
3	68 - 70	88 - 90	70 \Rightarrow 60	-	12.8	6.4 i.
4	68 - 70	88 - 90	70 \Rightarrow 60	88 - 90	12.8	4.8 i.
5	68 - 70	-	70 \Rightarrow 60	68 - 70	13.1	5.1 n.i.; Mg-stab.
6	68 - 70	-	70 \Rightarrow 60	88 - 90	13.1	3.6 i.; Mg-stab
7	68 - 70	88 - 90	70 \Rightarrow 60	-	12.8	3.6 i.; Mg-stab
8		88 - 90	70 \Rightarrow 60	88 - 90	12.8	2.9 i.; Mg-stab

1) Granulation time: about 3 h
 2) Drying time of the granulate: about 0.5 h
 3) Drying time of the coated granulate: 0.5 h
 5

12

- i. in accordance with the invention
- n.i. not in accordance with the invention
- Mg-stab. stabilised with 1000 ppm Mg^{2+}

*) Starting temperature 70°C / Temperature during coating about 60°C

Examples 1 and 2, which are not in accordance with the invention, show that although the TAM value is lowered by increasing the fluidised-bed temperature T_G , there is a simultaneous considerable fall in the active oxygen content

5 Oa. As will be seen from a comparison with Examples 3 and 4, the fall in Oa can be kept within narrower limits when the process is carried out in accordance with the invention; in addition, the TAM value is lowered further when the granulate is dried before being coated, with T_{NT} being higher than T_G - see Example 3. A further reduction 10 in the TAM value is achieved by additional drying of the coated granulate, when T_{UNT} is higher than T_U - see Example 4. The TAM value is lowered further by stabilising the core 15 of the sodium percarbonate granulate with magnesium - see Examples 5 to 8. In this case, too, there is a further lowering of the TAM value when drying is carried out at a higher temperature after formation of the granulate, that is to say before the coating, and/or after the coating - T_{NT} and T_{UNT} are higher than T_G and T_U .

20 Example 9

In this case, the granulation was carried out in two steps, with 5/6 of the granulate formation taking place at T_G and 1/6 at T_{GNT} , T_{GNT} being higher than T_G . By means of that 25 increase in temperature, a drying effect is achieved with simultaneous further washing of the granulate core, the TAM value being lowered without a great loss of active oxygen. Further drying at T_{NT} , where $T_{NT} > T_G$, led to a further 30 lowering of the TAM value. Table 2 shows the results. The products according to 9.2 and 9.3 were coated in a known manner with 5 % Na_2SO_4 , but the data in Table 2 relate to uncoated granulate without Mg stabilisation.

Example No.	Granula- tion time (min)	Fluidised-bed temperature (°C)			Oa (%)	TAM (μW/g)
		T _G	T _{GNT}	T _{NT}		
9.1	150	70	-	-	13.5	9.1
9.2	30	-	90	-	13.6	6.2
9.3	30	-	-	90	13.4	5.1

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. Process for the preparation of coated granular sodium percarbonate, comprising (i) preparation of granular sodium percarbonate by fluidised-bed spray granulation, wherein an aqueous sodium carbonate solution or suspension and an aqueous hydrogen peroxide solution are sprayed in a molar ratio of Na_2CO_3 to H_2O_2 in the range from 1:1.4 to 1:1.8 into a fluidised bed containing sodium percarbonate particles, and water is simultaneously evaporated off, and (ii) coating of the granular sodium percarbonate by spray application, in a fluidised bed, of at least one aqueous solution containing one or more coating components, with the simultaneous evaporation of water, wherein in the process:

(a) the fluidised-bed spray granulation is carried out at a fluidised-bed temperature T_G in the range from 45 to 75°C, the granular sodium percarbonate is dried at a fluidised-bed temperature T_{NT} in the range from 60 to 100°C before being coated, T_{NT} being higher than T_G , and the coating is carried out at a fluidised-bed temperature T_U in the range from 35 to 100°C;

(b) the fluidised-bed spray granulation is carried out in at least two steps, the fluidised-bed temperature T_{G1} being in the mentioned range for T_G and the fluidised-bed temperature T_{Gn} in the subsequent step(s) being in the range for T_{NT} , T_{Gn} being higher than T_G , and at least two thirds of the mass of the granulate having been formed during the first step, and the sodium percarbonate granulate so obtained is coated, without or after being dried, at a fluidised-bed temperature in the range of T_U ; or

(c) the granular sodium percarbonate prepared at T_G is coated, without being dried, at T_U and is dried at a fluidised-bed temperature T_{UNT} , T_{UNT} being at least 10°C higher than T_G .

2. Process according to claim 1, wherein the granulation is carried out at a fluidised-bed temperature T_G in the range from 55 to 75°C, and the drying is carried out at a fluidised-bed temperature T_{NT} in the range from greater than 75 to 95°C.

3. Process according to claim 1 or 2, wherein the drying is carried out with a dwell time of the granulate in the fluidised bed in the range from 15 to 45 minutes.

4. Process according to any one of claims 1 to 3, wherein the coated granular product from step (ii) is dried at a fluidised-bed temperature T_{UNT} in the range from 75 to 95°C.

5. Process according to any one of claims 1 to 4, wherein Na_2CO_3 and H_2O_2 in a molar ratio in the range from 1:1.5 to 1:1.6 are used for the preparation of the sodium percarbonate granulate.

6. Process according to any one of claims 1 to 5, wherein the fluidised-bed spray granulation and the drying of the uncoated sodium percarbonate granulate are carried out in a flow trough which is divided into a plurality of chambers, and the coating and, if necessary, the drying of the coated granular sodium percarbonate are carried out in one or more downstream chambers of the flow trough or in a separate fluidised-bed reactor arranged downstream of the flow trough.

7. Process according to any one of claims 1 to 6, wherein the dried granular sodium percarbonate is coated with one or more layers of a coating material containing sodium sulfate, the outermost coating layer containing sodium sulfate as the principal component and the total amount of coating being less than 10 wt.%, based on the coated sodium percarbonate.

8. Coated granular sodium percarbonate which has a Mg^{+2} content in the core of from 100 to 1000 ppm and which has a structure of the core and its coating obtained by fluidised-bed spray granulation, the coating comprising a hydrate-forming coating component which is sodium sulfate, soda, sodium bicarbonate, or magnesium sulfate, or any combination thereof, the coated granular sodium percarbonate having a TAM value of less than 3 $\mu W/g$, measured after 48 h at 40°C.