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(54) Titre : PROCEDE PERMETTANT D'AUGMENTER LA STABILITE INTERNE DU PERCARBONATE DE SODIUM
(54) Title: METHOD FOR INCREASING THE INNER STABILITY OF SODIUM PERCARBONATE

(57) Abrégé/Abstract:
The invention relates to a method for increasing the inner stability of encapsulated and non-encapsulated sodium percarbonate. According to the invention, particulate, dry sodium percarbonate is treated for at least 2 minutes at a temperature of 70 to 120 °C and during the treatment, the air surrounding the particles is exchanged, in order to maintain or reduce humidity.

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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.

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(54) **Title:** METHOD FOR INCREASING THE INNER STABILITY OF SODIUM PERCARBONATE

(54) **Bezeichnung:** VERFAHREN ZUR ERHÖHUNG DER INNEREN STABILITÄT VON NATRIUMPERCARBONAT

(57) **Abstract:** The invention relates to a method for increasing the inner stability of encapsulated and non-encapsulated sodium percarbonate. According to the invention, particulate, dry sodium percarbonate is treated for at least 2 minutes at a temperature of 70 to 120 °C and during the treatment, the air surrounding the particles is exchanged, in order to maintain or reduce humidity.

(57) **Zusammenfassung:** Die Erfindung richtet sich auf ein Verfahren zur Erhöhung der inneren Stabilität von umhülltem und nicht-umhülltem Natriumpercarbonat. Erfindungsgemäß wird teilchenförmiges, trockenes Natriumpercarbonat mindestens 2 Minuten bei einer Temperatur im Bereich von 70 bis 120 °C behandelt, wobei die die Teilchen umgebende Luft während der Behandlung ausgetauscht wird, um die Feuchte konstant zu erhalten oder zu erniedrigen.

Method for increasing the inner stability of sodium percarbonate

Description

The present invention relates to a process for improving the internal stability of sodium percarbonate. The term "sodium percarbonate" is hereinafter understood to denote uncoated particulate sodium percarbonate as well as particulate sodium percarbonate coated with one or more stabilising coating layers.

Particular attention has to be paid to the question of safety when storing sodium percarbonate in bulk material containers on account of the self-decomposing properties of sodium percarbonate. In order to prevent an exothermal decomposition of sodium percarbonate into soda, water and oxygen, great efforts have been made by those involved in this specialist field to produce sodium percarbonate having the highest possible storage stability.

The term sodium percarbonate in connection with the process according to the invention includes uncoated sodium percarbonate that has been produced by a conventional process, for example by a crystallisation process or a fluidised bed-spray granulation process, as well as coated sodium percarbonate with one or more stabilising coating layers, in which the coating layers may contain one or more stabilising components such as for example alkali sulfates, sodium carbonate, sodium bicarbonate, water glass, borates and perborates, magnesium sulfate, and magnesium salts of carboxylic acids.

For the purposes of stabilising the product in the presence of detergent constituents such as zeolites, it is known to coat sodium percarbonate with one or more stabilising coating layers, although this coating has only a limited

influence on the self-decomposing properties of sodium percarbonate. Although the self-decomposing properties can be avoided to a certain extent in the production of sodium percarbonate by using stabilisers such as Mg salts and water glass, nevertheless a further improvement in the stability is desirable in order to improve the storage life of sodium percarbonate.

JP patent application publication 57-42510 discloses a process for the storage of sodium percarbonate, wherein cool air whose temperature is most equal to normal room temperature is fed to the storage container at a relative humidity of at most 70 %, and during the cooling of the sodium percarbonate particles the atmosphere in the storage container is at the same time replaced by the respective cool air. The object of this process is to stabilise sodium percarbonate that is transferred at elevated temperature from a drier to the storage container and is therefore in an atmosphere having a high relative atmospheric humidity. By passing cool air through the product stored in the silo the contents of the silo are cooled and at the same time the water content is reduced. In this way the storage life under high atmospheric humidity is raised and the tendency to agglomerate is reduced. There is nevertheless a need to improve the stability still further. This document does not given any indication however as to how the internal stability, measured for example by the so-called TAM value, can be increased still further.

EP-Patent 0 396 175 B1 relates to a process for the stabilisation of sodium perborate monohydrate granules that are stored in bulk loose in a sealed room at a temperature between 10 and 65 °C. In this case dry air is passed through the stored material during the whole duration of the storage. The dew point of the dry air should in this connection be in particular below -20 °C and the amount of dry air should be between 1 and 8 $Nm^3/(h \cdot t_{NaPb})$. This

document does not give any indication that the process could also be adapted to the storage of sodium percarbonate. Disadvantages of this process are the fact that during the overall storage time large amounts of dry air having a very low dew point have to be passed through the stored material. The document does not give any indication as to how the internal stability is improved.

The internal stability of uncoated and coated sodium percarbonate can be represented by the so-called TAM value, according to which the stability increases with decreasing TAM value. The TAM value is a microcalorimetric determination of the energy released during storage, measured by means of the TAM® Thermal Activity Monitor from Thermometric AB, Järfälla (Sweden). A good storage life is indicated by a low TAM value - the TAM value should preferably be below 10 µW/g and in particular below 8 µW/g.

The object of the present invention is accordingly to provide a process whereby the internal stability of sodium percarbonate can be improved compared to that achieved within the scope of a conventional production process comprising the reaction of hydrogen peroxide with soda and drying the particulate product. According to a further object the process should be able to be carried out in a simple manner; according to a desirable but not obligatory object, the process should be able to be carried out in apparatus that is readily available for use within the scope of the production process.

This object as well as further objects that will become apparent from the following description are solved by the process according to the invention. The present invention accordingly provides a process for improving the internal stability of sodium percarbonate, comprising a post-treatment of coated or uncoated particulate sodium percarbonate, which is characterised in that the particulate dry sodium percarbonate is treated for at least

2 minutes at a temperature in the range from 70 to 120 °C, the ambient air surrounding the particles being replaced during the treatment in order to reduce or maintain the moisture at a constant value. The subclaims are directed to preferred embodiments of the process according to the invention.

According to a preferred embodiment the thermal treatment of the particulate sodium percarbonate is carried out at a temperature in the range from 80 to 95 °C, in particular from 85 to 95 °C. The treatment time preferably ranges from 5 to 60 minutes, in particular 10 to 60 minutes. At a temperature above 95 to 120 °C the treatment time is in the lower range. The person skilled in the art will determine the optimum conditions by preliminary experiments; these depend on the nature of the production as well as on the atmospheric humidity and intensity of the air replacement.

Contrary to the generally prevailing opinion, according to which the active oxygen content of sodium percarbonate falls with increasing temperature and action time and therefore such conditions should be avoided as far as possible, it has now surprisingly been found that under the conditions according to the invention the active oxygen content remains virtually constant, but at the same time the TAM value drops considerably, whereupon the internal stability is raised and the storage life is improved. It is assumed that this stabilisation is attributable to, *inter alia*, the fact that crystal defects in the lattice are broken down.

The process according to the invention can be used on particulate sodium percarbonate that has been produced by a conventional process and/or has been coated. The convention production processes involve the stage of reacting hydrogen peroxide with soda and also a drying stage in order to separate the water present in the reaction.

By way of example reference may be made to the crystallisation process according to US-Patent 4,146,571, in which hydrogen peroxide and soda are reacted in a mother liquor containing sodium chloride. After the crystallisation, which is carried out in the presence of Mg ions in order to maintain a TAM value that is as low as possible, the sodium percarbonate is separated in a conventional device for the solid-liquid separation from the mother liquor and is then dried in a drier, for example a fluidised bed drier.

An alternative production process is the so-called fluidised bed-spray granulation process, in which an aqueous hydrogen peroxide solution and an aqueous soda solution or suspension are sprayed into a fluidised bed that contains sodium percarbonate particles whose diameter is less than that of the particles to be produced. During the spraying-in of the reactants present in the aqueous medium, water is evaporated at a fluidised bed temperature in the range from 40 to 95 °C. After completion of the spraying process the fluidised bed material is cooled. By way of example reference may be made to DE-Patent 43 29 205.

Finally, production processes are also known in which an aqueous hydrogen peroxide solution is applied to pulverulent soda; here too the reaction is followed by a drying stage.

Also in the case where sodium percarbonate is coated with an aqueous solution containing coating components, which generally take place in a fluidised bed, the water that is introduced is evaporated in the fluidised bed and in this way a coated sodium percarbonate is obtained.

The process according to the invention accordingly preferably takes place where the conventional production and coating processes end. The thermal treatment according

to the invention is therefore preferably carried out in a fluidised layer, whereby during the treatment suitably heated air is passed through the fluidised layer in order to adjust and maintain the treatment temperature. The air heated up to the treatment temperature is either atmospheric air or atmospheric air that has been directly heated by means of flue gases; an air with a low moisture content is preferred. The term "fluidised layer" is understood to include all states under which the air heated to the treatment temperature can be passed through a layer of particulate sodium percarbonate. As long as the sodium percarbonate is sufficiently granular, the treatment can also take place below the loosening point of the layer.

Provided that the treatment according to the invention immediately follows the drying stage of the production process and that this stage takes place in a fluidised bed device, the treatment according to the invention is conveniently also carried out in a fluidised bed immediately following the drying stage.

As can be seen from the examples, by means of the process according to the invention it is possible to reduce significantly the TAM value of sodium percarbonate; normally the reduction is in the range from 20 to 50 % of the initial value, and in some cases even more.

The diagram shows the course of the TAM measurement of sodium percarbonate that had been post-treated at different temperatures in a laboratory fluidised bed unit. The TAM measurement was carried out using the thermo-activator monitor from Thermometric AB, Spjutvägen 5a, S-175 61, Järfälla; measurements were made over 48 hours' storage at 40 °C in a measurement cell.

Significant advantages of the process according to the invention are that the internal stability, expressed as the TAM value, can be raised in a simple way. In the preferred

embodiment the thermal treatment is carried out in a fluidised layer, as is already available within the framework of a drying procedure as the last stage in a production or coating process.

Examples 1 to 5

Treatment according to the invention of sodium percarbonate coated with sodium sulfate. The process according to the invention was carried out in a laboratory fluidised bed drier. Suitably heated atmospheric air was used to produce the fluidised bed; in each case the atmospheric air was thermally treated for one hour. The temperatures of the fluidised bed, the active oxygen values (Oa %), the values for the weight loss (wt.%) determined by means of an IR balance, as well as the measured TAM values are shown in the Table.

Table:

No.	T (°C)	Oa (%)	Weight Loss (%) (IR Balance)	TAM Value (µW/g)
Start		13.7	1.3	10.6
1	80	13.7	1.0	9.3
2	85	13.7	0.8	8.1
3	90	13.6	1.0	7.3
4	95	13.5	1.1	6.3
5	100	13.0	1.5	4.8

Example 6

A uncoated sodium percarbonate fluidised bed granulate produced in a laboratory fluidised bed-spray granulation unit and having an Oa value of 13,5 % and a TAM value of 7,5 µW/g was treated according to the invention in a fluidised bed; after the addition of the granules to the fluidised bed drier a fluidised bed temperature of 100 °C was first of all adjusted, which then rose however for a time of 2 minutes to 120 °C. After the end of the experiment the product had an Oa content of 13,58 wt.% and a TAM value of 5.5 µW/g.

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

1. A process for increasing an internal stability of sodium percarbonate, comprising a post-treatment of coated or non-coated dry particulate sodium percarbonate, wherein the dry particulate sodium percarbonate is treated for at least 2 minutes at a temperature in the range from 80° to 100°C, wherein air surrounding the particulate is exchanged during the treatment in order to maintain a constant or reduced moisture level and a substantially constant active oxygen content is maintained.

2. A process according to claim 1, wherein the temperature is in the range from 85° to 95°C.

3. A process according to claim 1 or 2, wherein the treatment is carried out for a period ranging from 5 to 60 minutes.

4. A process according to any one of claims 1 to 3, wherein the treatment is carried out in a fluidised layer, wherein atmospheric air heated to the treatment temperature or atmospheric air directly heated by means of flue gases is passed through the fluidised layer.

5. A process according to any one of claims 1 to 4, wherein the treatment is carried out in a fluidised bed immediately following a drying stage subsequent to the production or coating of sodium percarbonate, or both.

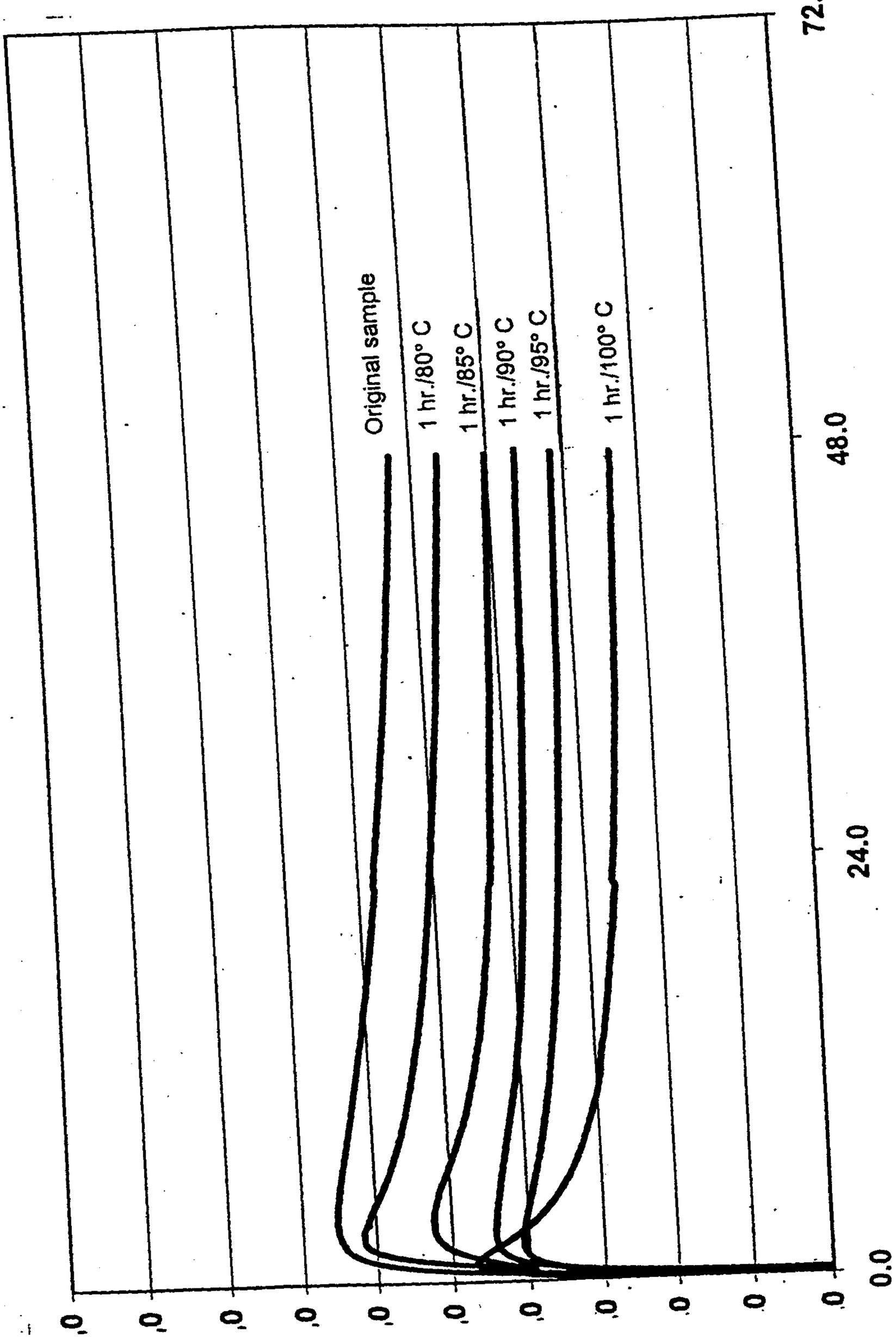
6. A process according to any one of claims 1 to 5, wherein the thermal treatment is carried out after a

coating of the sodium percarbonate with sodium sulfate as a coating component.

7. A process according to any one of claims 1 to 6, wherein said non-coated or coated sodium percarbonate is produced by fluidised bed spray granulation.

WO 02/051745

PCT/EP01/12446



Figure

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