

(19) **DANMARK**

(10) **DK/EP 3519381 T3**



(12) **Oversættelse af  
europæisk patentskrift**

Patent- og  
Varemærkestyrelsen

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- (51) Int.Cl.: **C 07 C 29/76 (2006.01)** **C 07 C 31/30 (2006.01)**
- (45) Oversættelsen bekendtgjort den: **2020-10-26**
- (80) Dato for Den Europæiske Patentmyndigheds  
bekendtgørelse om meddelelse af patentet: **2020-08-26**
- (86) Europæisk ansøgning nr.: **17783947.9**
- (86) Europæisk indleveringsdag: **2017-09-29**
- (87) Den europæiske ansøgnings publiceringsdag: **2019-08-07**
- (86) International ansøgning nr.: **FR2017052675**
- (87) Internationalt publikationsnr.: **WO2018060654**
- (30) Prioritet: **2016-09-29 FR 1659382**
- (84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV  
MC MK MT NL NO PL PT RO RS SE SI SK SM TR**
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- (54) Benævnelse: **FREMGANGSMÅDE TIL FREMSTILLING AF CALCIUMDIGLYCEROXID**
- (56) Fremdragne publikationer:  
**LUKIC, IVANA ET AL: "Calcium diglyceroxide synthesized by mechanochemical treatment, its characterization and application as catalyst for fatty acid methyl esters production", FUEL, vol. 165, 23 octobre 2015 (2015-10-23), pages 159-165, XP002770448, ISSN: 0016-2361**  
**RASHMI SHARMA ET AL.: "Nanoparticule technology: formulating poorly water-soluble compounds: a review", INTERNATIONAL JOURNAL OF PHARMACEUTICAL SCIENCES AND RESEARCH, vol. 6, no. 1, 1 janvier 2015 (2015-01-01) , pages 57-71, XP002770498, ISSN: 2320-5148**





other,  $\text{CaCl}_2$  which is dissolved in anhydrous methanol. Both solutions are then mixed (temperature less than  $40^\circ\text{C}$ ) so as to carry out a precipitation reaction.

Consequently, this publication describes the manufacture of calcium diglyceroxide by means of a chemical process requiring a plurality of steps  
5 (preparation of two solutions) and a high temperature, in this case  $140^\circ\text{C}$ .

More general publications relating to nanoparticles are also known from the prior art.

By way of example, the publication by Sharma et al. "Nanoparticle technology: formulating poorly water-soluble compounds: a review", International  
10 journal of pharmaceutical sciences and research, 2015; Vol.6(1):57-71, lists different methods for obtaining nanoparticles. Indeed, it is stated that the therapeutic efficacy of a medicinal product is dependent on the bioavailability thereof and the solubility thereof in water and that these properties may be enhanced as the nanoparticle stage. In the different methods described in this  
15 document in order to reduce the size of a starting active ingredient (no chemical reaction), the Dyno Mill wet phase microbead mill is mentioned.

The document EP 2 323 964 is also known from the prior art, describing a method for producing metal glyceroxides from wet glycerol as a biodiesel production by-product and a metal hydroxide, such as calcium hydroxide. The  
20 method is carried out under stirring via for example rotary blades (Kenwood kMix food mixer). This method produces an exothermic reaction (temperature ranging from  $90$  to  $140^\circ\text{C}$ ) wherein the calcium hydroxide and water present in the glycerol react.

Consequently, this method involves the drawback of being carried out at  
25 high temperatures.

Therefore, the aim of the present invention is that of providing a simple, industrially applicable, method for manufacturing calcium diglyceroxide, particularly not requiring significant heating with an extremely short reaction time.

### 30 SUBJECT MATTER OF THE INVENTION

To this end, the present invention provides a method for manufacturing calcium diglyceroxide crystals that comprises at least the following steps:

(1) placing at least one calcium element source compound, in particular calcium oxide ( $\text{CaO}$ ), in suspension in glycerol or in a homogeneous mixture of

glycerol ( $C_3H_8O_3$ ) and an anhydrous glycerol solvent, in particular methanol ( $CH_3OH$ ), referred to as the "starting suspension", the molar ratio of (glycerol):(calcium element source compound(s)) being greater than or equal to 2, preferably from 2 to 10, and in particular from 2 to 5;

5 (2) milling said starting suspension at an ambient temperature of less than or equal to  $50^{\circ}C$ , preferably less than or equal to  $35^{\circ}C$ , in a three-dimensional liquid-phase microbead mill for a holding time of less than or equal to 15 min, preferably less than or equal to 1 minute, and ranging particularly from 5 to 25 seconds and in particular from 10 to 20 seconds;

10 (3) recovering, at the outlet of the mill, a suspension of calcium diglyceroxide crystals; and

(4) optionally, washing the obtained suspension with a glycerol solvent in order to eliminate any excess glycerol;

15 (5) optionally, said suspension of calcium diglyceroxide crystals is dried so as to obtain a powder of calcium diglyceroxide crystals.

The molar ratio of anhydrous glycerol solvent (particularly methanol): glycerol may vary from 0 to 30, more particularly from 2 to 15 and preferably from 3 to 12.

20 Among the anhydrous glycerol solvents, mention may be made of alkanols, particularly methanol, isopropanol and ethanol. The preferred solvent is methanol.

In particular, the starting suspension comprises no or merely trace levels of water, that is to say at a proportion less than or equal to 3%, preferably less than or equal to 1% and typically less than or equal to 0.3%, by mass, with respect  
25 to the total mass of the starting suspension.

According to the invention, "a proportion less than or equal to 3%" comprises the following values: 3; 2; 1; 0,5; 0,4; 0,3; 0,2; 0,1; 0 or any ranges situated between these values.

30 In the present invention, the term "calcium element source" compound denotes any compound containing calcium element and suitable for supplying during diglyceroxide synthesis the quantity of calcium element required for the formation of calcium diglyceroxide.

Among the calcium element source compounds, mention may be made of CaO or Ca(OH)<sub>2</sub>, calcium acetate or calcium methanolate, etc. or any of the combinations thereof.

The preferred calcium source compound is CaO.

5        The present invention thus makes it possible using at least two starting constituents that are distinct, generally non-nanometric and non-heat-sensitive, to obtain calcium diglyceroxide in a single step.

The present invention also relates to calcium diglyceroxide crystals obtained according to the method described above.

10       The calcium diglyceroxide crystals obtained according to the method described above may be particularly used for manufacturing a heterogeneous catalyst for biodiesel production.

For the remainder of the description, unless specified otherwise, the indication of a range of values "from X to Y" or "between X and Y", in the present  
15       invention, is understood as including the values X and Y.

#### DETAILED DESCRIPTION OF AN EMBODIMENT EXAMPLE

The invention will be better understood and further aims, features and advantages thereof will emerge more clearly on reading the following description  
20       of embodiment examples, with reference to the appended figures wherein:

- figure 1 represents a sectional view along the longitudinal axis XX of a three-dimensional liquid-phase microbead mill, according to an alternative embodiment suitable for the use of the method according to the invention;
- figure 2 represents sectional views along the axis XX and the  
25       axis AA, of alternative embodiments of three-dimensional liquid-phase microbead mills according to figure 1 wherein: (a) the agitator has discs, (b) the agitator includes fingers and (c) the milling chamber is annular;
- figure 3 is a scanning electron microscopy (SEM) photo of calcium diglyceroxide crystals obtained according to the method according to the invention  
30       using the following parameters: starting suspension comprising 980g of raw materials (glycerol + CaO) with a molar ratio of (glycerol):(CaO) equal to 5, in 1kg of anhydrous glycerol solvent (herein, methanol); a flow rate of the starting suspension in the mill of 45L/h and a bead diameter of 500 μm;

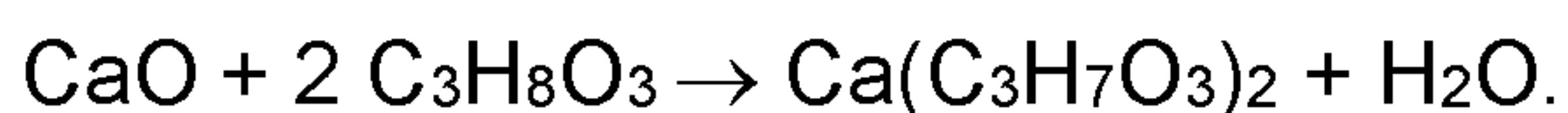
- figure 4 is an X-ray diffractometry (XRD) spectrum of calcium diglyceroxide crystals obtained under the same experimental conditions as those in figure 3;

- figure 5 are DTA/TGA curves of the calcium diglyceroxide obtained;  
5 and

- figures 6, 7 and 8 are SEM microphotographs of the calcium diglyceroxide crystals obtained using 0.5 mm and 2 mm zirconia beads and 2 mm silica beads, respectively.

- figure 9 is an X-ray diffractometry (XRD) spectrum of calcium  
10 diglyceroxide crystals obtained according to the method according to the invention using the following parameters: starting suspension comprising 1072g of raw materials (glycerol + Ca(OH)<sub>2</sub>) with a molar ratio of (glycerol):(Ca(OH)<sub>2</sub>) equal to 5, in 1kg of anhydrous glycerol solvent (herein, methanol); a flow rate of the starting suspension in the mill of 45L/h and a bead diameter of 500 µm;

15 The applicant endeavoured to develop a novel method for manufacturing calcium diglyceroxide crystals suitable for use on an industrial scale and particularly enabling, by way of example, in the case of the use of CaO as calcium source, the following synthesis:



20 In particular, the present invention relates to a method for manufacturing calcium diglyceroxide crystals that comprises at least the following steps:

(1) placing at least one mineral compound containing calcium element (CaO, Ca(OH)<sub>2</sub>, etc.), in suspension in glycerol or in a homogeneous mixture of glycerol (C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>) and an anhydrous glycerol solvent, for example  
25 methanol, referred to as the "starting suspension", the molar ratio of (anhydrous glycerol solvent):(glycerol) ranging from 0 to 30, more particularly from 2 to 15, and preferably from 3 to 12. The molar ratio of (glycerol):(calcium source compound(s)) being greater than or equal to 2, preferably from 2 to 10, and in particular from 2 to 5;

30 (2) milling said starting suspension at an ambient temperature of less than or equal to 50°C, preferably less than or equal to 35°C, in a three-dimensional liquid-phase microbead mill for a holding time of less than or equal to 15 min, preferably less than or equal to 1 minute, and ranging particularly from 5 to 25 seconds and in particular from 10 to 20 seconds;

(3) recovering, at the outlet of the mill, a suspension of calcium diglyceroxide crystals; and

(4) optionally, washing the obtained suspension with a glycerol solvent (for example methanol) in order to eliminate any excess glycerol.

5 (5) optionally, said suspension of calcium diglyceroxide crystals is dried so as to obtain a powder of calcium diglyceroxide crystals.

According to the invention, "an ambient temperature less than or equal to 50°C", comprises the following values: 50; 49; 48; 47; 46; 45; 44; 43; 42; 41; 40; 39; 38; 37; 36; 35; 34; 33; 32; 31; 30; 29; 28; 27; 26; 25; 24; 23; 22; 21; 20; 19; 10 18; 17; 16; 15; 14; 13; 12; 11; 10; etc. or any ranges situated between these values.

Likewise, according to the invention, "a holding time less than or equal to 15 min" comprises the following values: 15 min; 14 min; 13 min; 12 min; 11 min; 10 min; 9 min; 8 min; 7 min; 6 min; 5 min; 4 min; 3 min; 2 min; 1 min; 55 sec; 15 50 sec; 45 sec; 40 sec; 35 sec; 30 sec; 25 sec; 20 sec; 15 sec; 10 sec; 5 sec; etc. or any ranges situated between these values.

The applicant thus developed a method that, unexpectedly, is suitable for manufacturing calcium diglyceroxide crystals in a very short time (reaction time less than or equal to 15 minutes and in general, less than or equal to 1 minute), in 20 a single step, at ambient temperature (the method does not require a particular heating step), with a low energy consumption and furthermore an excellent yield.

As will be demonstrated in the tests hereinafter, the method according to the invention further is suitable for obtaining surprisingly calcium diglyceroxide crystals of excellent quality, that is to say of high purity.

25 The method according to the invention also offers the advantages of having a very reduced cost price (the raw materials used are indeed widely available, non-polluting and inexpensive) and of exhibiting an excellent reproducibility, which distinguishes it further from the methods described in the prior art. The method according to the invention also offers the advantages of 30 being suitable for continuous use. Indeed, these features are important for application on an industrial scale.

Furthermore, despite the extensive research conducted on calcium diglyceroxide crystal synthesis, none has suggested the abovementioned method and in particular a milling step in a three-dimensional microbead mill using a

starting suspension comprising calcium oxide (CaO) or another source of calcium and glycerol (C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>), optionally in the presence of an anhydrous glycerol solvent, such as methanol (CH<sub>3</sub>OH).

To ensure better understanding of the method according to the invention,  
5 a three-dimensional microbead mill suitable for enabling the obtaining of calcium diglyceroxide crystals, and thus within the scope of the invention, will now be described hereinafter with reference to figures 1 and 2.

As illustrated in figure 1, a three-dimensional microbead mill 1 comprises at least:

- 10 - a stationary milling chamber 2 of general cylindrical shape extending along a longitudinal axis XX, said chamber 2 being filled at least, in part, with said microbeads (not shown) and comprises: at a first end 3 at least one inlet 5 serving to introduce said starting suspension, and at a second end 4, an outlet 6 including a separating means 7 suitable for only discharging the calcium diglyceroxide  
15 suspension formed in said chamber 2; and
- an agitator 8, arranged in the stationary milling chamber 2, presented in the form of an elongated rod along the longitudinal axis XX, said agitator 8 being suitable for setting in motion the microbead/starting suspension assembly.

In particular, the inlet 5 is generally connected to a peristaltic pump (not  
20 shown). This pump makes it possible to convey the starting suspension, contained for example in a receptacle, such as a tank, inside the milling chamber 2 via the inlet 5. The pump makes it possible furthermore, during the operation of the three-dimensional mill, to convey this starting suspension according to a certain rate that is adjustable, hereinafter referred to as "flow rate". This flow rate further forms a  
25 flow in the milling chamber 2 suitable for carrying the starting suspension from the inlet 5 to the outlet 6.

The outlet 6 of the milling chamber 2 comprises in particular the system 7 for separating the microbeads from the final suspension comprising mostly the calcium diglyceroxide crystals, methanol and optionally the remaining unreacted  
30 raw materials. This separation means 7 may be a sieve wherein the orifices exhibit a size less than that of the microbeads or a separating slot wherein the width is also suitable for retaining the microbeads inside the chamber 2.

The internal wall 9 of the milling chamber 2 comprises according to a first embodiment a smooth internal surface. However, according to an alternative

embodiment described hereinafter, fingers 11 may be provided on this internal surface 9.

As mentioned above, inside the milling chamber 2 is arranged the agitator 8 which, in addition to the flow rate, also enables the setting in motion of the starting suspension.

In particular, the agitator 8 is suitable for rotating about the axis X via a rotary shaft (14, figure 2) to impart inside the milling chamber 2 a swirling motion to the starting suspension and thus carry out intense mixing between this starting suspension and the microbeads present in the chamber 2 along the internal wall 9 of this chamber 2.

In particular, the mill via the rotary shaft 14 has a rotational speed greater than or equal to 100 revolutions per minute, advantageously of 1000 revolutions per minute, preferably greater than or equal to 2000 revolutions per minute and typically greater than or equal to 2500 revolutions per minute.

According to the invention, "a rotational speed greater than or equal to 100 revolutions per minute" comprises the following values: 100; 150; 200; 250; 300; 350; 400; 450; 500; 550; 600; 650; 700; 750; 800; 850; 900; 950; 1000; 1100; 1200; 1300; 1400; 1500; 1600; 1700; 1800; 1900; 2000; 2100; 2200; 2300; 2400; 2500; 2600; 2700; 2800; 2900; 3000; 3100; 3200; 3300; 3400; 3500; 3600; 3700; 3800; 3900; 4000; 4500; 5000; 5500; 6000; etc., or any ranges included between these values.

In general, the mill has a rotational speed ranging from 1000 rpm to 5000 rpm, in particular from 1500 rpm to 4500 rpm, preferably from 2000 rpm to 4000 rpm and typically from 2800 to 3200 rpm.

In order to improve this mixing, the agitator 8, like the internal wall 9 of the chamber 2, may have various possible configurations represented for example in figure 2.

According to a first configuration illustrated in figure 2a, the agitator 8 comprises along the elongated rod thereof discs 10, arranged perpendicularly thereto. The number thereof may vary from 2 to 8, preferably from 2 to 5. These discs 10 make it possible on one hand, to improve the milling of the starting suspension by mixing the microbeads further and, on the other, to accelerate the reaction time.

According to a second configuration illustrated in figure 2b, the agitator 8 may also comprise along the rod thereof one or a plurality of discs 10 arranged perpendicular and that are further suitable for engaging with fingers 11, arranged perpendicular, with respect to the internal wall 9 of the chamber 2. A finger is presented particularly in the form of a ring which extends perpendicularly from the wall 9. For this configuration, the discs 10 and the fingers 11 are arranged in staggered rows, that is to say the discs 10 and the fingers 11 are arranged in alternation in the chamber 2. Furthermore, the thickness of the rod 8 is increased with respect to the previous configuration (figure 2a) such that the periphery of the discs 10 is near the internal wall 9 and that of the fingers 11 is close to the periphery of the rod of the agitator 8. Thus, in this configuration, the volume of the chamber is reduced with respect to the preceding configuration, consequently enabling, superior mixing between the starting suspension, the microbeads and the internal wall 9 of the chamber 2.

The volume of the chamber 2 may further be reduced as illustrated in figure 2c. In this configuration, the agitator 8 has an external diameter slightly less than the internal diameter of the chamber 2, thus forming an annular chamber 12 of small volume arranged between the external wall of the agitator 8 and the internal wall 9 of the chamber 2. The microbeads (not shown) are arranged in this annular chamber 12. During the operation of this configuration, the starting suspension is introduced via the inlet 5 with a certain flow rate, that will then pass through the annular chamber 12 to the outlet 6 while being mixed by the microbeads.

In general, the mill suitable for carrying out the method according to the invention comprises a milling chamber having a diameter of 75 mm to 300 mm for a length of 80 mm to 900 mm and an agitator having a size ranging from 65 mm to 260 mm. Thus, the volume of the milling chamber varies from 0.35 L to 600 L, preferably from 0.35 L to 400 L, and typically from 0.35 L to 62 L.

According to the invention, "a milling chamber volume ranging from 0.35 L to 600 L" comprises the following values: 0.35; 0.5; 0,8; 1; 2; 3; 4; 5; 6; 7; 8; 9; 10; 15; 20; 25; 30; 35; 40; 45; 50; 55; 60; 65; 70; 80; 85; 90; 100; 110; 120; 130; 140; 150; 160; 170; 180; 190; 200; 210; 220; 230; 240; 250; 260; 270; 280; 290; 300; 350; 400; 450; 500; 550; 600 etc., or any ranges included between these values.

The geometry of the milling chamber and the agitator may be adjusted by a person skilled in the art according to the quantity of calcium diglyceroxide crystals sought, as well as the reaction time sought. For example, it is also possible that the milling chamber 2 comprises an accelerator in order to improve the milling of the starting suspension.

Furthermore, the microbeads housed in the milling chamber 2 and suitable for the method according to the invention are substantially of spherical shape and have a mean diameter less than or equal to 5 mm, generally ranging from 0.05 mm to 4 mm, preferably from 0.2 to 3 mm, in particular from 0.3 to 2 mm, and typically of the order of 0.5 to 1 mm. Preferably, the diameter of the microbeads is less than or equal to 1 mm and is typically of the order of 0.05 mm to 1 mm.

They are preferentially chosen among the microbeads having a high hardness and a relatively good abrasion resistance.

In particular, the microbeads have a Vickers hardness measured as per the EN ISO 6507-1 standard greater than or equal to 900 HV1, preferably ranging from 900 HV1 to 1600 HV1, typically ranging from 1000 to 1400 HV1 and particularly ranging from 1100 to 1300 HV1.

According to the invention, "a Vickers hardness greater than or equal to 900 HV1" comprises the following values: 900; 910; 920; 930; 940; 950; 960; 970; 980; 990; 1000; 1010; 1020; 1030; 1040; 1050; 1060; 1070; 1080; 1090; 1000; 1110; 1120; 1130; 1140; 1150; 1160; 1170; 1180; 1190; 1200; 1300; 1400; 1500; 1600; 1700; etc., or any ranges included between these values.

Advantageously, they have a high true density. In general, the microbeads according to the invention have a true density greater than or equal to 2 g/cm<sup>3</sup>, in particular ranging from 2 to 15 g/cm<sup>3</sup>, preferably from 3 to 12 g/cm<sup>3</sup>, and typically from 4 to 10 g/cm<sup>3</sup>.

Thus, the microbeads according to the invention may be ceramic microbeads, (zirconium oxide ZrO<sub>2</sub>, zirconium silicate ZrSiO<sub>4</sub>); steel microbeads, tungsten carbide microbeads, glass microbeads or any of the combinations thereof.

Preferably, the microbeads are made of ceramics as they do not generate pollution due to the wear thereof.

In particular, the microbeads are made of zirconium oxide.

Optionally, the zirconium oxide microbeads may be stabilised by another oxide, such as cerium oxide, yttrium oxide and/or silicon.

By way of examples, the following compositions, summarised in table 1 hereinafter, are suitable for forming the microbeads according to the invention:

| Microbead composition                                                                                                                                                                                                                                     | Hardness<br>HV1 | True<br>density<br>(g/cm <sup>3</sup> ) | Manufacturer                                                    |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------|-----------------------------------------|-----------------------------------------------------------------|
| Zirconium oxide microbeads stabilised with cerium oxide <ul style="list-style-type: none"><li>- 80% ZrO<sub>2</sub></li><li>- 20% CeO</li></ul>                                                                                                           | 1180            | ≥ 6.10                                  | Saint-Gobain (Zirmil®Y Ceramic Beads) or EIP (Procerox® ZO Cer) |
| Zirconium oxide microbeads stabilised with yttrium <ul style="list-style-type: none"><li>- 95% ZrO<sub>2</sub></li><li>- &lt;5% Al<sub>2</sub>O<sub>3</sub></li><li>- Remainder: Y<sub>2</sub>O<sub>3</sub></li></ul>                                     | 1250            | ≥ 5.95                                  | EIP (Procerox® ZO (Y))                                          |
| Zirconium oxide microbeads stabilised with yttrium and silicon: <ul style="list-style-type: none"><li>- 78% ZrO<sub>2</sub>,</li><li>- 12% SiO<sub>2</sub>,</li><li>- 5% Al<sub>2</sub>O<sub>3</sub> et</li><li>- 4% Y<sub>2</sub>O<sub>3</sub></li></ul> | > 700           | >4.80                                   | Saint-Gobain (ER120 Ceramic Beads)                              |
| Zirconium silicate ZrSiO <sub>4</sub> microbeads                                                                                                                                                                                                          | ≥ 800           | > 6.5                                   | Saint-Gobain (Rimax Ceramic Beads)                              |
| Glass microbeads                                                                                                                                                                                                                                          | 500             | > 3.76                                  | -                                                               |
| Steel microbeads                                                                                                                                                                                                                                          | 700             | > 7.7                                   | -                                                               |

5

Table 1

Generally, the microbeads suitable for the method according to the invention are not made of glass or exclusively of glass.

In particular, the microbeads represent, in volume, with respect to the total volume of the stationary chamber 2 from 50% to 85%, preferably from 55% to 70%.

10

According to the invention, "a volume from 50 to 85 %" comprises the following values: 50; 55; 60; 65; 70; 75; 80; 85; etc., or any ranges included between these values.

By way of example, the three-dimensional liquid-phase microbead mill  
5 suitable for carrying out the method according to the invention may correspond to mills marketed by the companies WAB, Dyno-Mill range: Multi Lab, ECM and KD, NETZCH or Alpine Hosokawa, for example, Agitated Media Mill AHM.

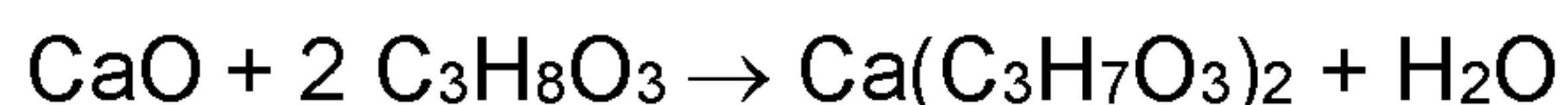
The manufacturing method according to the invention will now be described more explicitly hereinafter.

10 As mentioned above, the manufacture of the calcium diglyceroxide crystals according to the invention comprises firstly (1) placing a Ca element source compound, for example calcium oxide (CaO), or a mineral compound containing calcium element (Ca(OH)<sub>2</sub>, etc.) in suspension in glycerol (C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>), optionally in a homogeneous mixture with an anhydrous glycerol solvent such as  
15 methanol (CH<sub>3</sub>OH), referred to as the "starting suspension".

The starting suspension is conventionally prepared by mixing the raw material (CaO + C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>) optionally with the anhydrous solvent (methanol) in a suitable apparatus, such as a receptacle or a tank, equipped with a stirring system (such as a magnetic stirrer, stirring blades, etc.). The apparatus and the stirring  
20 system may be adapted by a person skilled in the art according to the quantity of calcium diglyceroxide crystals to be manufactured.

Preferably, the calcium element source compound and glycerol are mixed in stoichiometric proportions.

In particular, calcium oxide and glycerol are mixed, preferably, in  
25 stoichiometric proportions in the starting suspension to produce the reaction:



This is equivalent, in mass proportions to 56 kg of CaO for 184 kg of glycerol, or 23.3% CaO and 76.6% glycerol. Thus, the starting suspension is generally free from water or the latter is only present at trace levels in the  
30 suspension.

It is obviously possible to deviate substantially from the stoichiometric proportion, for example, by mixing from 18 to 28%, by mass of CaO, with respectively from 72 to 82% by mass of glycerol, with respect to the total weight of

CaO + glycerol, if for example a calcium diglyceroxide composition containing an excess either of glycerol, or of calcium oxide, is sought.

The presence of methanol, not required for the reaction (optional), promotes the setting in motion of the microbeads of the mill for superior milling of the starting suspension and therefore superior calcium diglyceroxide crystal synthesis.

In general, the calcium element source compound of the starting suspension is found in powder form. This powder has a particle size less than or equal to 100  $\mu\text{m}$ , preferably less than or equal to 50  $\mu\text{m}$ , in particular less than or equal to 30  $\mu\text{m}$ , such as 20  $\mu\text{m}$  or 10  $\mu\text{m}$ . Thus, it is not necessary for the calcium source element to be on the nanometric scale.

The calcium oxide suitable for the present invention has preferably a particle size less than or equal to 200  $\mu\text{m}$  and preferably less than or equal to 100  $\mu\text{m}$ , and in particular the particle size ranges from 0.01  $\mu\text{m}$  to 20  $\mu\text{m}$ . The calcium oxide having the CAS number: 1305-78-8 and marketed for example by Sigma Aldrich of purity greater than or equal to 99% is suitable for carrying out the method according to the invention.

The glycerol suitable for the present invention is found in liquid form. The glycerol having the CAS number: 56-81-5 and marketed for example by Mondroguiste.com of purity greater than or equal to 99.5% is suitable for carrying out the method according to the invention.

Preferably, the calcium oxide and the glycerol have a high purity, generally greater than or equal to 90%, in particular greater than or equal to 95% and typically greater than or equal to 99%, or even greater than or equal to 99.9%.

Once the starting suspension has been prepared, it is conveyed to the three-dimensional microbead mill 1 generally by means of the adjustable flow rate peristaltic pump via the inlet 5. The peristaltic pump makes it possible to continue mixing the starting suspension prior to entering the chamber 2. Furthermore, as mentioned above, this pump makes it possible to introduce the starting suspension into the chamber 2 with a controlled flow rate.

Generally, the starting suspension is introduced at a flow rate greater than or equal to 10 L/h.

According to the invention, "a flow rate greater than or equal to 10 L/h" comprises the following values: 10 L/h; 15 L/h; 20 L/h; 25 L/h; 30 L/h; 35 L/h; 40 L/h; 45 L/h; 55 L/h; 60 L/h; 65 L/h; 70 L/h; 80 L/h; 85 L/h; 90 L/h; 95 L/h; 100 L/h; 110 L/h; 120 L/h; 130 L/h; 140 L/h; 150 L/h; 50 L/h; 55 L/h; 60 L/h; 65 L/h; 70 L/h; 75 L/h; 80 L/h; 85 L/h; 90 L/h; 95 L/h; 100 L/h; 105 L/h; 110 L/h; 115 L/h; 120 L/h; 125 L/h; 130 L/h; 135 L/h; 140 L/h; 145 L/h; 150 L/h; 155 L/h; 160 L/h; 165 L/h; 170 L/h; 175 L/h; 180 L/h; 200 L/h; 300 L/h; 400 L/h; 500 L/h; 600 L/h; 700 L/h; 800 L/h; 900 L/h; 1 m<sup>3</sup>/h; 2 m<sup>3</sup>/h; 3 m<sup>3</sup>/h; 4 m<sup>3</sup>/h; 5 m<sup>3</sup>/h; 6 m<sup>3</sup>/h; 7 m<sup>3</sup>/h; 8 m<sup>3</sup>/h; 9 m<sup>3</sup>/h; 10 m<sup>3</sup>/h; 11 m<sup>3</sup>/h; 12 m<sup>3</sup>/h; 13 m<sup>3</sup>/h; 14 m<sup>3</sup>/h; 15 m<sup>3</sup>/h; etc., or any ranges included between these values.

In particular, the starting suspension is introduced at a flow rate ranging from 10 to 130 L/h, preferably ranging from 20 to 100 L/h and typically ranging from 30 to 90 L/h.

Obviously, the flow rates may vary according to the size of the three-dimensional microbead mill used to carry out the method. For example, for a three-dimensional microbead mill having a stationary chamber 2 of 0.5L of volume, the flow rate may be of the order of 40 to 150 L/h, such as about 45 L/h; whereas for larger-sized mills having in particular a stationary chamber 2 of 60L, the flow rate may be of the order of 2 to 15 m<sup>3</sup>/h, such as about 4 m<sup>3</sup>/h.

Once the starting suspension has been introduced into the chamber 2, the milling step (2) commences.

Under the effect of the flow created by the flow rate, the starting suspension passes through the stationary chamber 2 from the inlet 5 to the outlet 6, while being set in motion by the agitator 8 which enables intense mixing of this suspension with the microbeads and, if applicable, with the discs 10, fingers 11, etc., along the internal wall 9 of the chamber 2.

The rotational speed of the agitator may for example vary from 4 to 20 Pi rad/s, preferably from 4 to 8 Pi rad/s.

The holding time of the starting suspension is less than or equal to 15 min, preferably less than or equal to 5 minutes, in particular less than or equal to 1 minute, and ranges particularly in the mill from 5 to 25 seconds and in particular from 5 to 20 seconds, such as from 1 to 15 seconds. It is indeed inherent to the bulk volume of the beads and to the flow rate.

For example, if the total bulk volume of the beads is  $270 \text{ cm}^3$  (beads of bulk density of  $3.7 \text{ g/cm}^3$ ) and the suspension feed rate is  $45 \text{ L/h}$ , or  $12.45 \text{ cm}^3/\text{s}$ , then the holding time of the suspension in the chamber 2 is estimated at about 22 seconds. Consequently, the holding time may be advantageously adjusted, for example by controlling the bulk density of the microbeads, as well as the flow rate.

The term "bulk volume" denotes the volume of the microbeads including the interstitial air between the beads. The bulk density is the ratio between the mass of the microbeads and the bulk volume.

Furthermore, by adjusting the size of the microbeads and the flow rate, more or less fine crystals may be obtained. For example, finer milling may be obtained if the flow rate of the starting suspension is slowed down.

The milling step may be carried out in continuous mode or discontinuous mode in one or a plurality of passages (pendular or recirculating mode).

When carried out in discontinuous mode, the number of passages of the so-called starting suspension may be from 1 to 10, preferentially from 1 to 5 (that is to say, after a first passage, the suspension is recovered at the outlet 6 and reinjected once again, by means of the pump, into the chamber 2 via the inlet 5 to enable a second passage). In particular, the number of passages of the starting suspension is 1.

Indeed, the applicant observed that a single passage in the microbead mill, despite a very short holding time, made it possible to obtain at the outlet 6 a suspension comprising very predominantly calcium diglyceroxide crystals (particularly when the starting materials are in stoichiometric proportions), of very satisfactory purity and size.

Thus, this milling step will be carried out preferably in continuous mode.

Advantageously, this milling step is carried out at an ambient temperature less than or equal to  $50^\circ\text{C}$ , that is to say most frequently at an ambient temperature ranging from  $15^\circ\text{C}$  to  $45^\circ\text{C}$ , in particular from  $18^\circ\text{C}$  to  $35^\circ\text{C}$  and in general is of the order of  $20^\circ\text{C}$  to  $25^\circ\text{C}$ . Indeed, the method according to the invention requires no particular heating in order to manufacture the calcium diglyceroxide crystals, contrary to the teaching disclosed in the prior art. Thus, the starting reagents/starting suspension are/is introduced into the mill at ambient temperature (generally around  $20\text{-}25^\circ\text{C}$ ). However, depending on the starting reagents used, an exothermic reaction may take place during this milling step and

the temperature may rise slightly (generally the temperature at the mill outlet is less than or equal to 50°C).

Once the milling step has been carried out, (3) the calcium diglyceroxide suspension is recovered at the outlet 7 of the mill 1 and is optionally (4) washed of the traces of excess glycerol using methanol, and optionally (5) dried so as to obtain a calcium diglyceroxide powder.

According to an alternative embodiment, the calcium diglyceroxide suspension may be air-dried. Indeed, it has emerged that the carbonation reaction is very slow between calcium diglyceroxide and the CO<sub>2</sub> in the air.

According to a further alternative embodiment, the calcium diglyceroxide suspension may be dried at a temperature of 50 to 100°C for 1 to 4 hours.

The final product is generally stored until the use thereof in the form of paste or mixed with a solvent. It may also be recovered in solid form and stored in a tight receptacle.

As demonstrated in the tests hereinafter, homogeneous calcium diglyceroxide crystals are obtained, of overall parallelepiped shape.

The calcium diglyceroxide crystals obtained using the method according to the invention generally has the following population distributions according to the grain size distribution measured with a liquid process laser granulometer:

$0.5\mu\text{m} \leq D_{x50} \leq 50\mu\text{m}$ , preferably  $1\mu\text{m} \leq D_{x50} \leq 10\mu\text{m}$  and  
 $1\mu\text{m} \leq D_{x90} \leq 75\mu\text{m}$ , preferably  $5\mu\text{m} \leq D_{x90} \leq 40\mu\text{m}$ .

Furthermore, as mentioned above, the characteristics of the calcium diglyceroxide crystals (size, thickness, etc.) may be adjusted, according to the needs of the envisaged use, by varying some parameters, such as the flow rate, the microbead diameter of the anhydrous glycerol solvent content in the starting suspension.

The present invention may relate to the use of the calcium diglyceroxide crystals obtained according to the abovementioned method.

The calcium diglyceroxide may be used a heterogeneous catalyst for biodiesel production as mentioned in the publication "Direct synthesis of calcium glyceroxide from hydrated lime and glycerol and its evaluation in the transesterification reaction" published in the journal "Fuel 138 (2014) – 126 to 133".

In particular, the calcium diglyceroxide may be used as a heterogeneous catalyst for biodiesel production by reacting methanol with plant oils.

Further applications of catalysis may be envisaged, particularly those requiring a base catalyst such as Bronsted.

5

#### EXAMPLES

The description of the tests hereinafter is given merely by way of illustrative and non-limiting example.

10

##### A° Characterisation

##### ✓ SEM

Scanning electron microscopy (SEM) was carried out on a Zeiss EVO MA 15 apparatus, with secondary and backscattered electrons (chemical contrast) with a primary beam of 5 to 20 kV.

15

To carry out the SEM tests, the calcium diglyceroxide crystal suspensions were previously air-dried at 50°C so as to obtain a powder.

##### ✓ XRD

The X-ray diffractometry (XRD) spectra were collected with a D8 ADVANCE Series II diffractometer marketed by Bruker using CuK $\alpha$ 1 radiation (0.15406 nm) according to the Bragg-Brentano configuration.

20

The detector used is a LynxEye 1D detector from Bruker. The aperture of the detector is 3° (150 bands).

25

The XRD measurements were made between 10° and 120° (at the scale 2 $\theta$ ) with a step of 0.008° (1 s/step).

To carry out the XRD tests, the calcium diglyceroxide crystal suspensions were likewise previously air-dried at 50°C, so as to obtain a powder. Four consecutive scans were carried out in order to confirm the progression over time of the powder studied.

30

##### ✓ LIQUID-PROCESS GRANULOMETRY

The liquid-process granulometry measurements were made with a Mastersizer 3000E model laser granulometer from Malvern.

For this measurement, 5cm<sup>3</sup> of the calcium diglyceroxide crystal suspension samples were previously dispersed in a receptacle having a diameter of 40 mm using a 28khz/40khz ultrasound generator equipped with a 20mm diameter sonotrode.

- 5 This measurement gives the distribution in volume (as %) of the particles of the sample for each grain size class in  $\mu\text{m}$  (which is equivalent to the longest calcium diglyceroxide crystal length).

✓ DTA/TGA

- 10 The differential thermal (DTA) and thermogravimetric (TGA) analyses were carried out with a Linseis STA PT1000 model combined DTA/TGA apparatus.

The analyses were performed in air, with a temperature gradient of 10°C/min, ranging from 20°C to 900°C.

- 15 To carry out the tests, the calcium diglyceroxide crystal suspensions were previously air-dried at 50°C, so as to obtain a powder.

B° Test sample preparation procedure

✓ Apparatus

The tests were performed in a Dyno Mill MultiLab three-dimensional microbead mill from Willy A. Bachofen AG containing 1 kg of microbeads.

- 20 The microbeads are made of zirconium oxide and have a diameter of 0.5, 1.0 or 2.0 mm. The characteristics of the microbeads used for the tests are summarised in table 2 hereinafter:

| Beads                      | 500 $\mu\text{m}$                                                           | 1.0mm                                                                       | 2.00mm                                                                      |
|----------------------------|-----------------------------------------------------------------------------|-----------------------------------------------------------------------------|-----------------------------------------------------------------------------|
| Composition<br>(% by mass) | 93%<br>ZrO <sub>2</sub><br>5% Y <sub>2</sub> O <sub>3</sub><br>2%<br>others | 93%<br>ZrO <sub>2</sub><br>5% Y <sub>2</sub> O <sub>3</sub><br>2%<br>others | 93%<br>ZrO <sub>2</sub><br>5% Y <sub>2</sub> O <sub>3</sub><br>2%<br>others |
| Specific density           | 6g/cm <sup>3</sup>                                                          | 6g/cm <sup>3</sup>                                                          | 6g/cm <sup>3</sup>                                                          |
| Bulk density               | 3.7 kg/L                                                                    | 3.7 kg/L                                                                    | 3.7 kg/L                                                                    |
| Vickers hardness           | 1250<br>HV1                                                                 | 1250<br>HV1                                                                 | 1250<br>HV1                                                                 |

Table 2

The 500  $\mu\text{m}$  microbeads are particularly marketed under the trade name Zirmil® Y Ceramic Beads by Saint-Gobain.

The milling chamber of the mill has a capacity of 309 mL and is filled, in volume, with respect to the total volume thereof and according to the tests, to 80%  
5 with the microbeads described above.

In operation, the microbeads are placed under stirring by an agitator at a rotational speed of 2890 rpm (where 1 rpm=1/60 Hz). The agitator further includes two 64mm diameter polyurethane mixing discs.

10

✓ Raw materials

For the tests, the starting raw materials are: calcium oxide (CaO) having a purity  $\geq 99\%$  marketed by Sigma Aldrich, and glycerol of purity  $\geq 99.5\%$   
15 marketed by Mon-droguiste.com.

✓ General operating procedure for tests:

To carry out each test hereinafter, the following steps are carried out:

- a starting suspension is prepared in a beaker using calcium oxide and glycerol, in stoichiometric proportions, in an anhydrous glycerol solvent  
20 (methanol), then the starting suspension is placed under stirring using a magnetic stirrer;

- it is then conveyed, via an adjustable flow rate peristaltic pump to the Dyno Mill MultiLab mill described above: the flow rate in the mill may be up to 60L/h. In this test, it was set to 45L/h corresponding to a holding time of 8s;

25 - the starting suspension is then milled in the mill containing microbeads 0.5 mm; 1mm or 2mm in diameter for a given time (which is dependent on the flow rate of the starting suspension) at ambient temperature (20-25°C), thus make it possible, at the mill outlet, to obtain a calcium diglyceroxide crystal suspension;

- finally, the calcium diglyceroxide crystal suspension is recovered.

30 C° Characterisation of the calcium diglyceroxide crystals obtained  
(figures 3, 4 and 5)

As can be seen in figure 3, according to the method according to the invention, after merely one passage in the microbead mill and thus a holding time of 8 seconds, the calcium diglyceroxide crystals are obtained (instead of much

longer times, of up to several hours, according to the methods according to the prior art).

The following parameters were used: starting suspension comprising 980g of raw materials (glycerol + CaO with a molar ratio of (glycerol): CaO equal to 5, in 1kg of anhydrous glycerol solvent (herein, methanol); a flow rate of the starting suspension in the mill of 45L/h and a bead diameter of 500  $\mu\text{m}$ ;

With reference to figure 4, it is observed that the lines of the four XRD spectra, scanned successively, are fully conforming with respect to those of the reference spectrum of calcium diglyceroxide, known to those skilled in the art (CDDC deposition ref #828033), both for the angular positions thereof and for the relative intensities thereof, that is to say:

- The presence of the three primary peaks is observed (crystallographic planes [200], [111] and [131]), at respectively 8.281°/ 10.177° and 21.179°,
- All the other significant peaks are present at the envisaged angles, such as 20.436°/ 24.466°/ 25.071°/ 26.671°/ 27.973°/ 34.446°/ 36.505°/ 36.894°/ 39.130°/ 40.850; with substantially the envisaged intensities,

These XRD spectra also demonstrate that the sample analysed has an excellent purity. Indeed, no contamination is recorded:

- the primary peaks of CaO (as per JCPDS 037-1481), which are at 30.204°/ 37.347° and 53.856° do not appear therein;
- the primary peaks of Ca(OH)<sub>2</sub> (as per JCPDS 044-1481), which are at 18.008° / 28.672° /34.102° likewise do not appear therein;
- and the primary peak of CaCO<sub>3</sub> (as per JCPDS 005-0586) which is at 29.4° is not significantly present.

Finally, the TGA/DTA spectra presented in figure 5 are conforming with respect to the behaviour of calcium diglyceroxide crystals. This behaviour was particularly described by L. Leon-Reina et al. in the publication entitled "Structural and surface study of calcium glyceroxide, an active phase for biodiesel production under heterogeneous catalysis" dated 2013 and published in the Journal of Catalysis 300. The two characteristic outcomes are thus observed:

- A loss of mass of about 55% between 180°C and 500°C, which may correspond to the breakdown of calcium diglyceroxide to calcium carbonate, which would induce a theoretical loss of mass of 55%.

- A loss of mass of about 19% between 700°C and 850°C, which may correspond to the decarbonation of calcium carbonate to calcium oxide, which would be marked by a theoretical loss of mass of 19.8%.

5 In conclusion, the method according to the invention makes it possible to immediately obtain very pure calcium diglyceroxide crystals.

#### D° Influence of bead diameter and type

The purpose of this example is to determine whether the size and composition of the beads used when carrying out the method have an influence on  
10 the quality of the calcium diglyceroxide crystals obtained.

Similarly to the tests in the previous example, the calcium diglyceroxide crystals were synthesised according to the general procedure mentioned above and using in particular the following parameters:

- A starting suspension containing 980g of raw materials (CaO +  
15 glycerol) with a molar ratio of (glycerol):(CaO) equal to 5, per 1kg of anhydrous glycerol solvent (methanol);
- A flow rate of 45L/h;
- Milling beads of 500µm or 2mm in diameter, that may be predominantly made up of SiO<sub>2</sub> (Silibeads ® type S) or predominantly made up of  
20 ZrO<sub>2</sub> (Zirmil® Y Ceramic Beads);
- And only carrying out a single passage in the mill;

The results of these tests are illustrated in figures 6 to 8.

According to the SEM images, it is observed that the conversion of calcium oxide and glycerol into calcium diglyceroxide is very close to 100%,  
25 regardless of the size or composition of the beads used.

Likewise, it was observed that, regardless of the type of beads or the diameter thereof, the size of the calcium diglyceroxide crystals is substantially constant. In particular, the following grain size distribution is obtained (table 3):

| Tests                             | Dx(10) (µm) | Dx(50) (µm) | Dx(90) (µm) |
|-----------------------------------|-------------|-------------|-------------|
| 1) ZrO <sub>2</sub> beads – 500µm | 0.96        | 2.4         | 8.69        |
| 2) SiO <sub>2</sub> beads – 500µm | 1.08        | 2.85        | 9.10        |
| 3) ZrO <sub>2</sub> beads – 2mm   | 1.12        | 3.13        | 8.69        |
| <i>Mean</i>                       | <i>1.05</i> | <i>2.79</i> | <i>8.83</i> |

|                           |             |             |             |
|---------------------------|-------------|-------------|-------------|
| <i>Standard deviation</i> | <i>0.08</i> | <i>0.37</i> | <i>0.24</i> |
|---------------------------|-------------|-------------|-------------|

*Table 3*

Thus, the method, according to the invention, makes it possible to obtain homogeneous calcium diglyceroxide crystals of small sizes (Dx(50) preferably between 1 and 10  $\mu\text{m}$  and particularly between 1 and 5 $\mu\text{m}$ ).

5        E/ Grain size distribution of calcium diglyceroxide crystals according to number of passages.

For this example, different numbers of passages in the three-dimensional mill were tested (1 and 45 passages), in order to check the impact thereof on the grain size distribution of the calcium diglyceroxide crystals obtained.

10       Thus, the calcium diglyceroxide crystals tested were synthesised according to the general procedure mentioned above and using the following parameters:

- A starting suspension containing 306g of raw materials (CaO + glycerol) with a molar ratio of (glycerol):(CaO) equal to 2, per 1kg of anhydrous
- 15       glycerol solvent (methanol);
- A flow rate of 45L/h;
- 500 $\mu\text{m}$  milling beads predominantly made up of ZrO<sub>2</sub> (Zirmil® Y Ceramic Beads);
- And carrying out a single or 45 passages in the mill;

20       The grain size distribution is as follows (Table 4):

| <b>Tests</b> | Dx(10) ( $\mu\text{m}$ ) | Dx(50) ( $\mu\text{m}$ ) | Dx(90) ( $\mu\text{m}$ ) |
|--------------|--------------------------|--------------------------|--------------------------|
| 1 passage    | 1.08                     | 3.23                     | 9.99                     |
| 45 passages  | 0.41                     | 0.82                     | 6.43                     |

*Table 4*

It is observed that a greater number of passages makes it possible to obtain smaller sized crystals.

25       Thus, the method according to the invention makes it possible to obtain calcium diglyceroxide crystals, the size whereof may be adapted readily by modifying the number of passages in the mill.

F° Characterisation of the calcium diglyceroxide crystals obtained using another calcium source

For this example, another mineral source containing calcium element, that is to say  $\text{Ca}(\text{OH})_2$ , was used to synthesise the calcium diglyceroxide crystals.

5 The general procedure mentioned above was applied using the following parameters:

- A starting suspension containing 1072g of raw materials ( $\text{Ca}(\text{OH})_2$  + glycerol) with a molar ratio of (glycerol):( $\text{Ca}(\text{OH})_2$ ) equal to 5, per 1kg of anhydrous glycerol solvent (methanol);

- 10
- A flow rate of 45L/h;
  - 500 $\mu\text{m}$  milling beads predominantly made up of  $\text{ZrO}_2$  (Zirmil® Y Ceramic Beads);
  - And carrying out a single passage in the mill.

15 With reference to figure 9, it is observed that the lines of the four XRD spectra, scanned successively, are fully conforming with respect to those of the reference spectrum of calcium diglyceroxide, known to those skilled in the art (CDDC deposition ref #828033), both for the angular positions thereof and for the relative intensities thereof, that is to say:

- The presence of the three primary peaks is observed

20 (crystallographic planes [200], [111] and [131]), at respectively 8.281° / 10.177° and 21.179°,

- All the other significant peaks are present at the envisaged angles, such as 20.436° / 24.466° / 25.071° / 26.671° / 27.973° / 34.446° / 36.505° / 36.894° / 39.130° / 40.850; with substantially the envisaged intensities,

25 These XRD spectra also show the residual presence of unconverted matter. Indeed:

- the primary peaks of  $\text{Ca}(\text{OH})_2$  (as per JCPDS 044-1481), which are at 18.008° / 28.672° / 34.102° are present;

- and the primary peak of  $\text{CaCO}_3$  (as per JCPDS 005-0586) which is

30 at 29.4° is also observed

Thus, it was demonstrated that calcium diglyceroxide crystals may be synthesised using  $\text{Ca}(\text{OH})_2$  by way of calcium element source raw material. Particularly, under the conditions of the general procedure mentioned, that is to say with a single passage in the mill for a flow rate of 45L/h, it was observed that

the calcium diglyceroxide crystals obtained with  $\text{Ca}(\text{OH})_2$  are slightly less pure than those obtained under similar conditions with  $\text{CaO}$  (example C). However, a conversion approaching 100% for  $\text{Ca}(\text{OH})_2$  can be envisaged, particularly by increasing the holding time in the mill.

5                    G° Conclusion

Thus, it was demonstrated that for all the tests, a powder insoluble in the anhydrous glycerol solvent is obtained. After testing by XRD analysis, it emerged that this powder corresponded to calcium diglyceroxide crystals (all the XRD spectra produced by the applicant show a conversion of the starting compounds  
10 into calcium diglyceroxide, the spectra indeed indicate the lines corresponding to calcium diglyceroxide, with merely a few residual traces of initial compounds).

The DTA/TGA curves were found to be fully in line with the elements of the prior art well-known to those skilled in the art, with particularly a total loss of mass after  $850^\circ\text{C}$  of 75%, that may correspond to the breakdown of calcium  
15 diglyceroxide into calcium oxide (74.8%).

The images obtained by scanning electron microscopy show calcium diglyceroxide crystals. It is likewise found that the powder obtained essentially consists of well-formed crystals, the grain size distribution  $D_x(50)$  whereof is generally less than  $10\mu\text{m}$ .

20                    Obviously according to the milling parameters, for example by adjusting the microbead sizes, it is possible to obtain crystals that are larger in size, ( $D_x(50)$  up to  $50\mu\text{m}$ ) or smaller ( $D_x(50) < 1\mu\text{m}$ ).

Furthermore, the laboratory mill makes it possible to produce  $54\text{kg/h}$  of calcium diglyceroxide. This figure could be multiplied by 10 with the addition of an  
25 acceleration accessory. Likewise, there exist industrial versions of the mill using for example up to  $100\text{ kg}$  of beads. With this type of mill, it would consequently be possible to manufacture several tonnes of calcium diglyceroxide per hour.

**Patentkrav**

1. Fremgangsmåde til fremstilling af calciumdiglyceroxidkrystaller der omfatter mindst følgende trin:

- 5           (1) at anbringe mindst en calciumelementkildeforbindelse, især calcium-oxid ( $\text{CaO}$ ), i suspension i glycerol eller i en homogen blanding af glycerol ( $\text{C}_3\text{H}_8\text{O}_3$ ) og et vandfrit glycerolopløsningsmiddel, især methanol ( $\text{CH}_3\text{OH}$ ), kaldet "udgangssuspension", hvor molforholdet mellem (glycerol) : (calciumelementkildeforbindelsen eller -forbindelserne) er større  
10           end eller lig med 2, fortrinsvis er fra 2 til 10 og især fra 2 til 5;  
            (2) at formale udgangssuspensionen ved en omgivelsestemperatur på mindre end eller lig med  $50^\circ\text{C}$ , fortrinsvis mindre end eller lig med  $35^\circ\text{C}$ , i en tredimensional mikrokuglemølle i væskefasen i løbet af en opholdstid på mindre end eller lig med 15 minutter, fortrinsvis mindre end eller lig  
15           med 1 minut, og især fra 5 til 25 sekunder og især fra 10 til 20 sekunder;  
            (3) at opsamle en suspension af calciumdiglyceroxidkrystaller ved møllens udløb og  
            (4) eventuelt at vaske den opnåede suspension med et glycerolopløsningsmiddel for at eliminere eventuelt overskydende glycerol,  
20           (5) eventuelt at tørre suspensionen af calciumdiglyceroxidkrystaller for at opnå et pulver af calciumdiglyceroxidkrystaller.

2. Fremgangsmåden ifølge krav 1, hvor molforholdet mellem (vandfrit glycerolopløsningsmiddel) : (glycerol) går fra 0 til 30, mere specifikt fra 2 til 15 og for-  
25           trinsvis fra 3 til 12.

3. Fremgangsmåde ifølge krav 1 eller 2, hvor glycerol og calciumelementkildeforbindelsen eller -forbindelserne blandes i støkiometriske forhold, eventuelt i nærvær af vandfrit glycerolopløsningsmiddel.

30

4. Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 3, hvor calciumelementkildeforbindelsen er calciumoxid  $\text{CaO}$ ,  $\text{Ca}(\text{OH})_2$ , calciumacetat eller calciummethanolat eller en hvilken som helst af kombinationerne deraf.

**5.** Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 4, hvor det vandfrie glycerolopløsningsmiddel er methanol ( $\text{CH}_3\text{OH}$ ), isopropanol og ethanol, og er fortrinsvis methanol.

5

**6.** Fremgangsmåde ifølge et af de foregående krav, hvor mikrokuglerne er sfæriske og har en gennemsnitlig diameter, der går fra 0,05 mm til 4 mm, fortrinsvis fra 0,2 til 3 mm, især fra 0,3 til 2 mm, og er typisk af størrelsesordenen 0,5 til 1 mm.

10

**7.** Fremgangsmåde ifølge et af de foregående krav, hvor mikrokuglerne har en Vickers-hårdhed, der er målt ifølge EN ISO 6507-1-standarden, som er større end eller lig med 900 HV1, fortrinsvis går fra 900 HV1 til 1600 HV1, typisk går fra 1000 til 1400 HV1 .

15

**8.** Fremgangsmåde ifølge et af de foregående krav, hvor mikrokuglerne har en absolut densitet, der går fra 2 til  $15 \text{ g/cm}^3$ .

**9.** Fremgangsmåde ifølge et af de foregående krav, hvor formalingen udføres ved en omgivelsestemperatur, der går fra  $15^\circ\text{C}$  til  $45^\circ\text{C}$ , især fra  $18^\circ\text{C}$  til  $35^\circ\text{C}$ , og generelt er af størrelsesordenen  $20^\circ\text{C}$  til  $25^\circ\text{C}$ .

**10.** Fremgangsmåde ifølge et af de foregående krav, hvor den tredimensionale mikrokuglemølle omfatter mindst:

- 25        - et stationært formalingskammer med generel cylindrisk form der strækker sig langs en længdeakse XX, hvilket kammer er fyldt mindst delvist med mikrokuglerne og omfatter: ved den første ende, mindst et indløb der tjener til at indføre udgangssuspensionen, og ved en anden ende, et udløb der indbefatter et separationsmiddel, som er i stand til kun at ud-
- 30        tømme calciumdiglyceroxidsuspensionen, der er dannet i kammeret; og
- en omrører der er anbragt i det stationære formalingskammer, og foreligger i form af en langstrakt stang langs længdeaksen XX, hvilken omrører er i stand til at sætte mikrokugle/udgangssuspensionen i bevægelse.

**11.** Fremgangsmåden ifølge krav 10, hvor mikrokuglerne, efter volumen, i forhold til det samlede volumen af det stationære kammer udgør fra 50 % til 85 %, fortrinsvis fra 55 % til 70 %.

5

**12.** Fremgangsmåde ifølge et af de foregående krav, hvor møllen fungerer kontinuerligt.

**13.** Fremgangsmåde ifølge et af kravene 10 til 12, hvor omrørerens omdrejningshastighed er større end eller lig med 100 omdrejninger pr. minut.

10

**14.** Fremgangsmåde ifølge et af de foregående krav, hvor udgangssuspensionen har en opholdstid i den tredimensionale mikrokuglemølle i væskefasen, der er mindre end eller lig med 1 minut.

15

**15.** Fremgangsmåde ifølge et af de foregående krav, hvor mikrokuglerne vælges blandt: keramiske mikrokugler, stålmikrokugler, wolframcarbidsmikrokugler, glasmikrokugler eller en hvilken som helst af kombinationerne deraf.

20

1

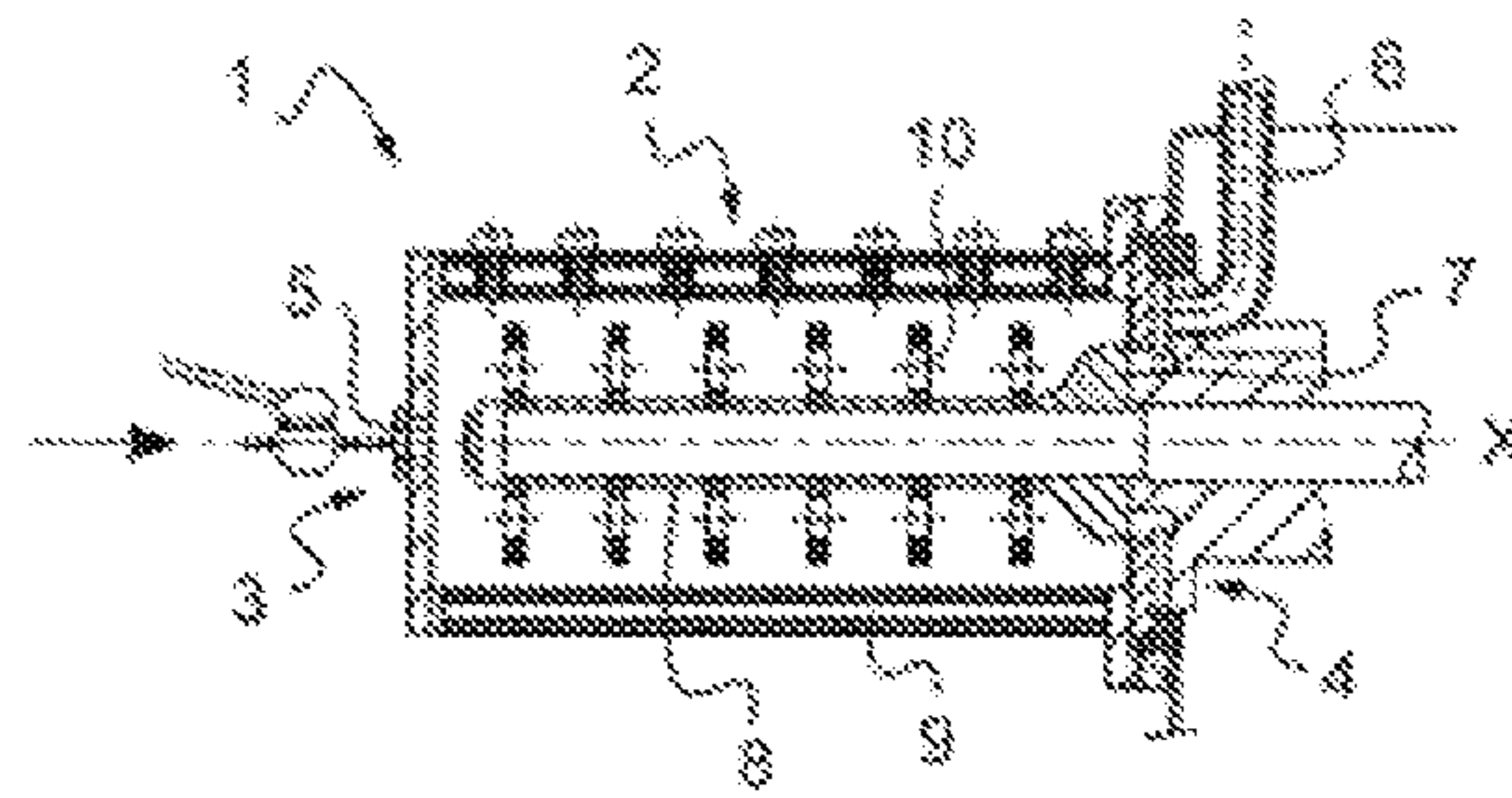


Figure 1

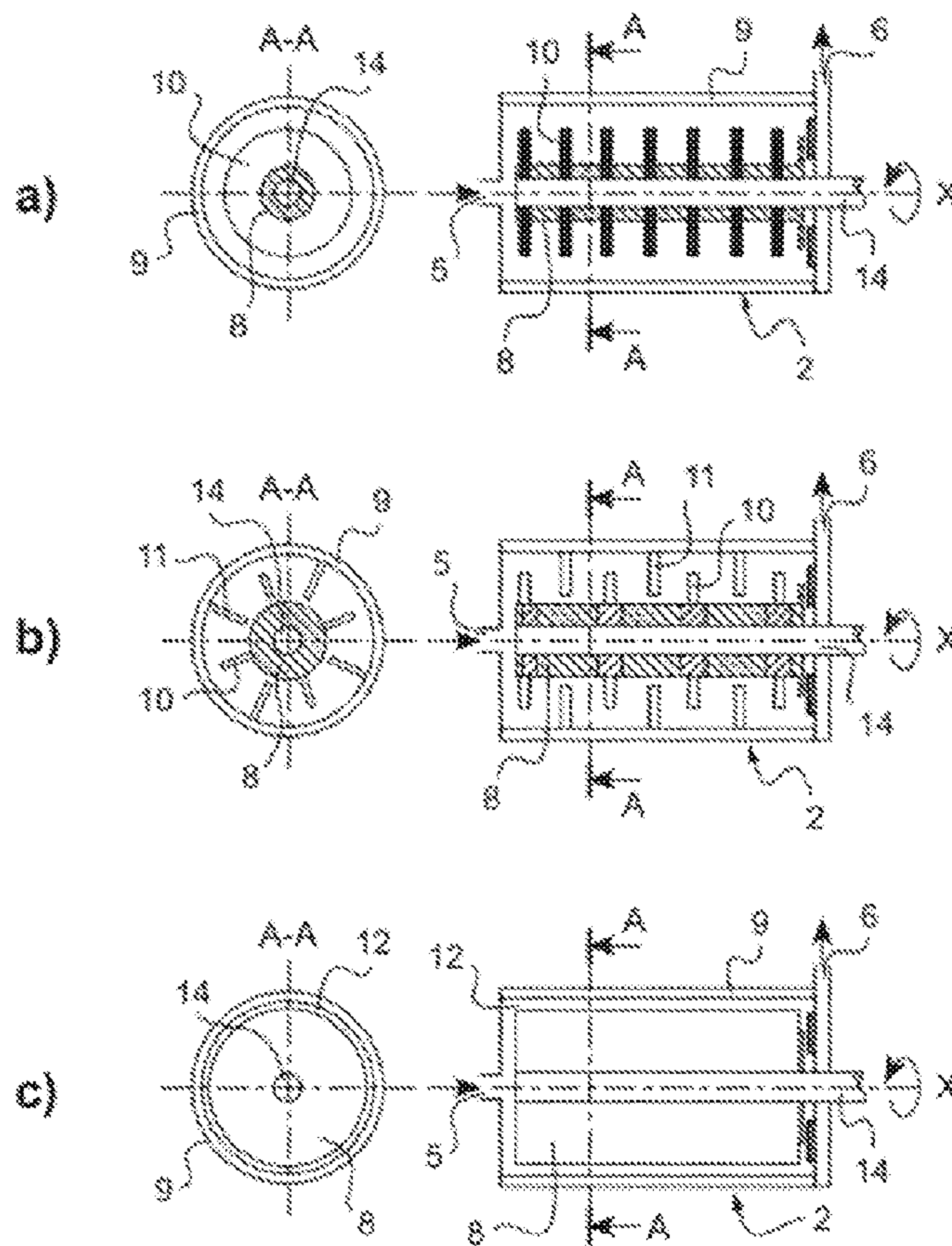


Figure 2

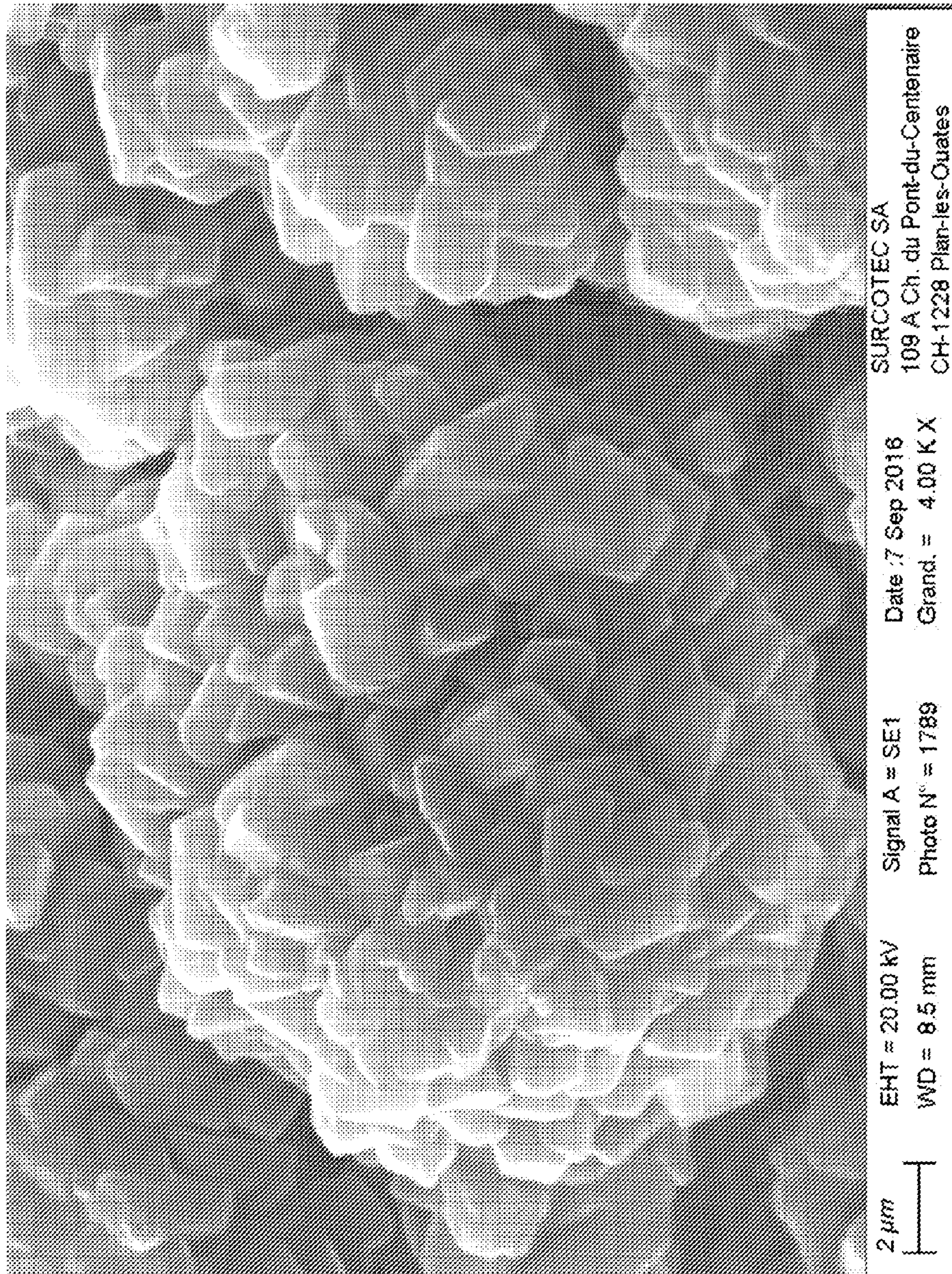


Figure 3 : Cliché MEB de cristaux de diglycéroxyde de calcium

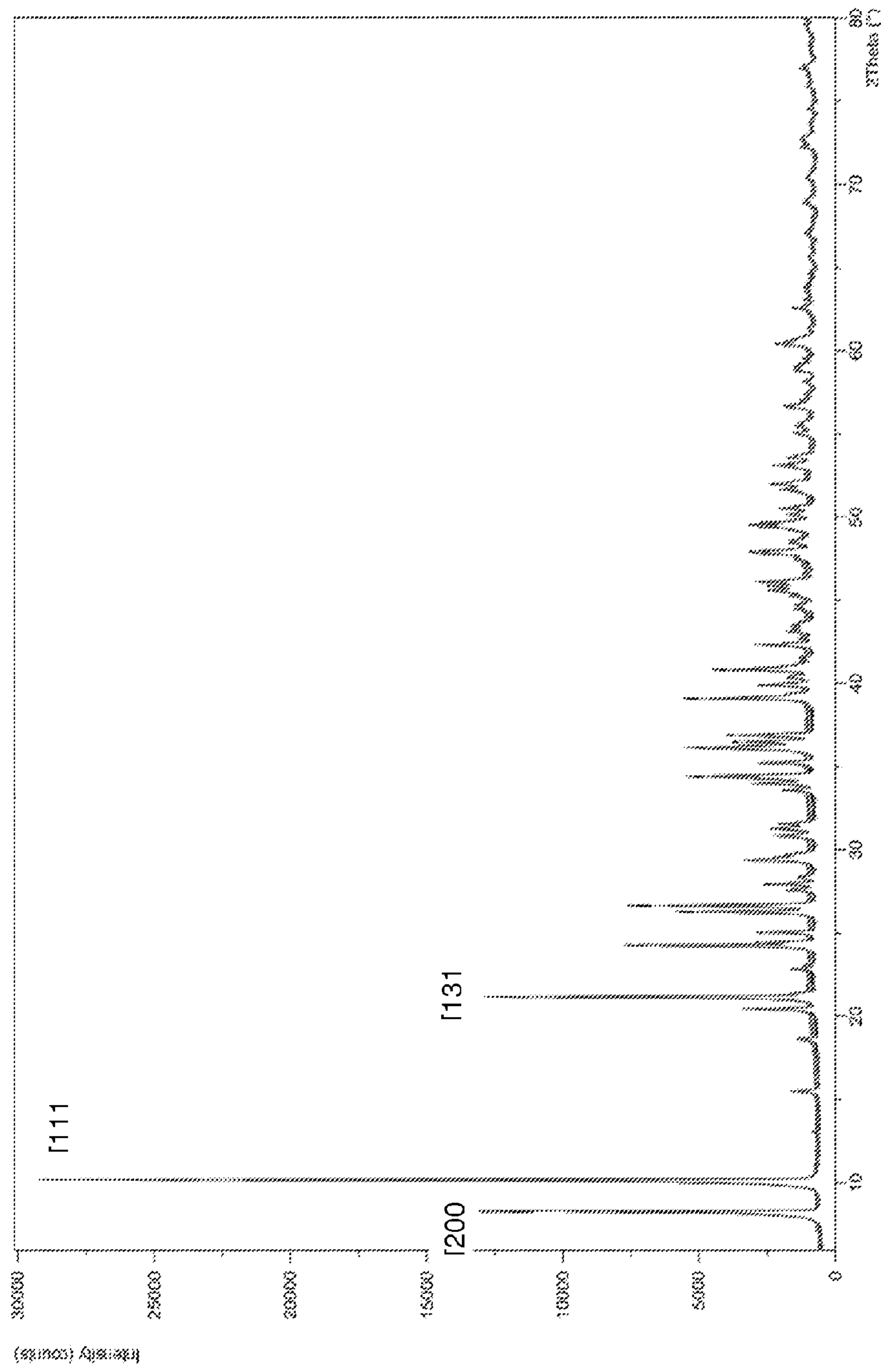


Figure 4 : Spectre DRX des cristaux de diglycéroxyde de calcium

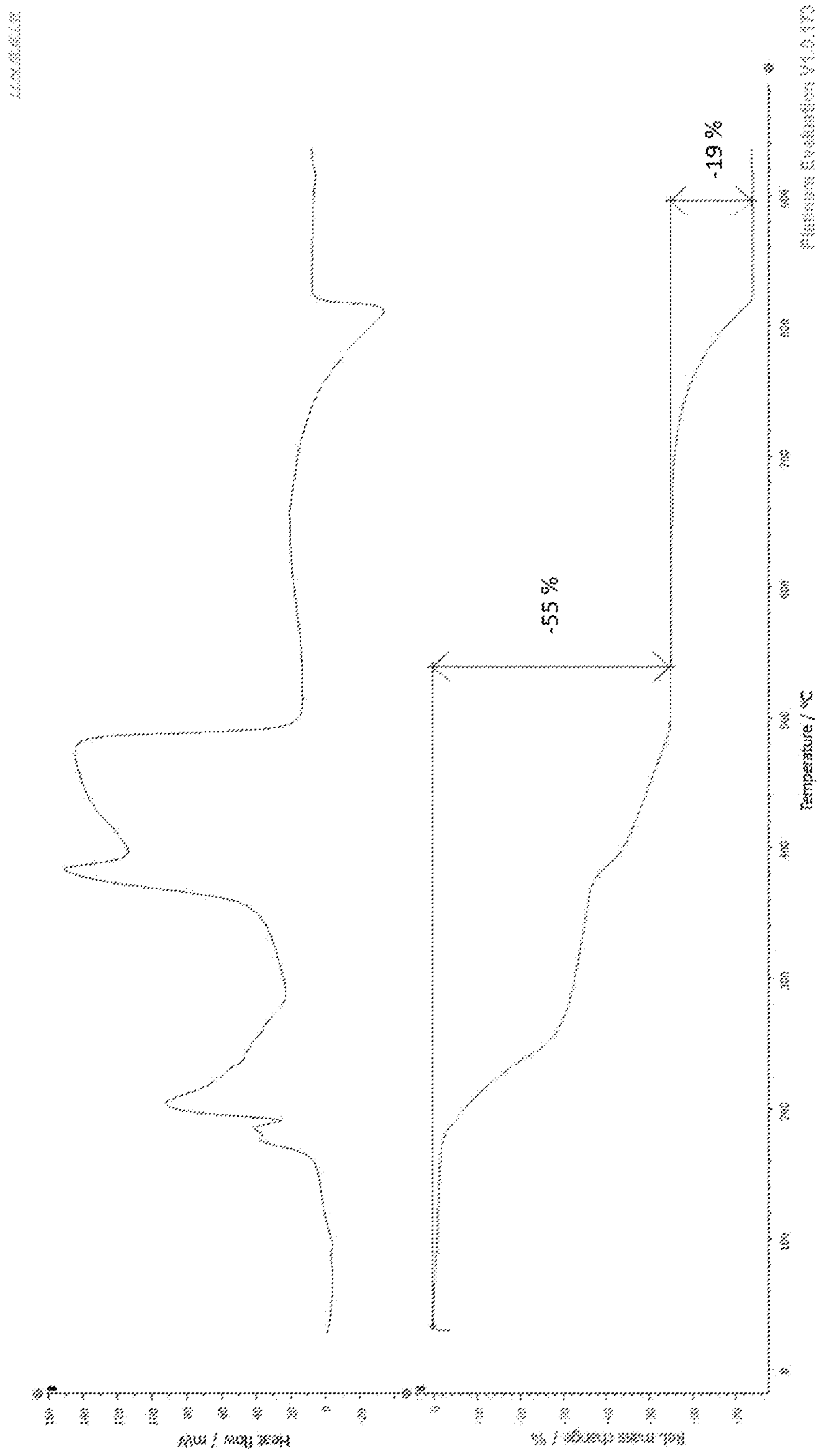


Figure 5 : Courbes ATD/ATG du diglycéroxyde de calcium

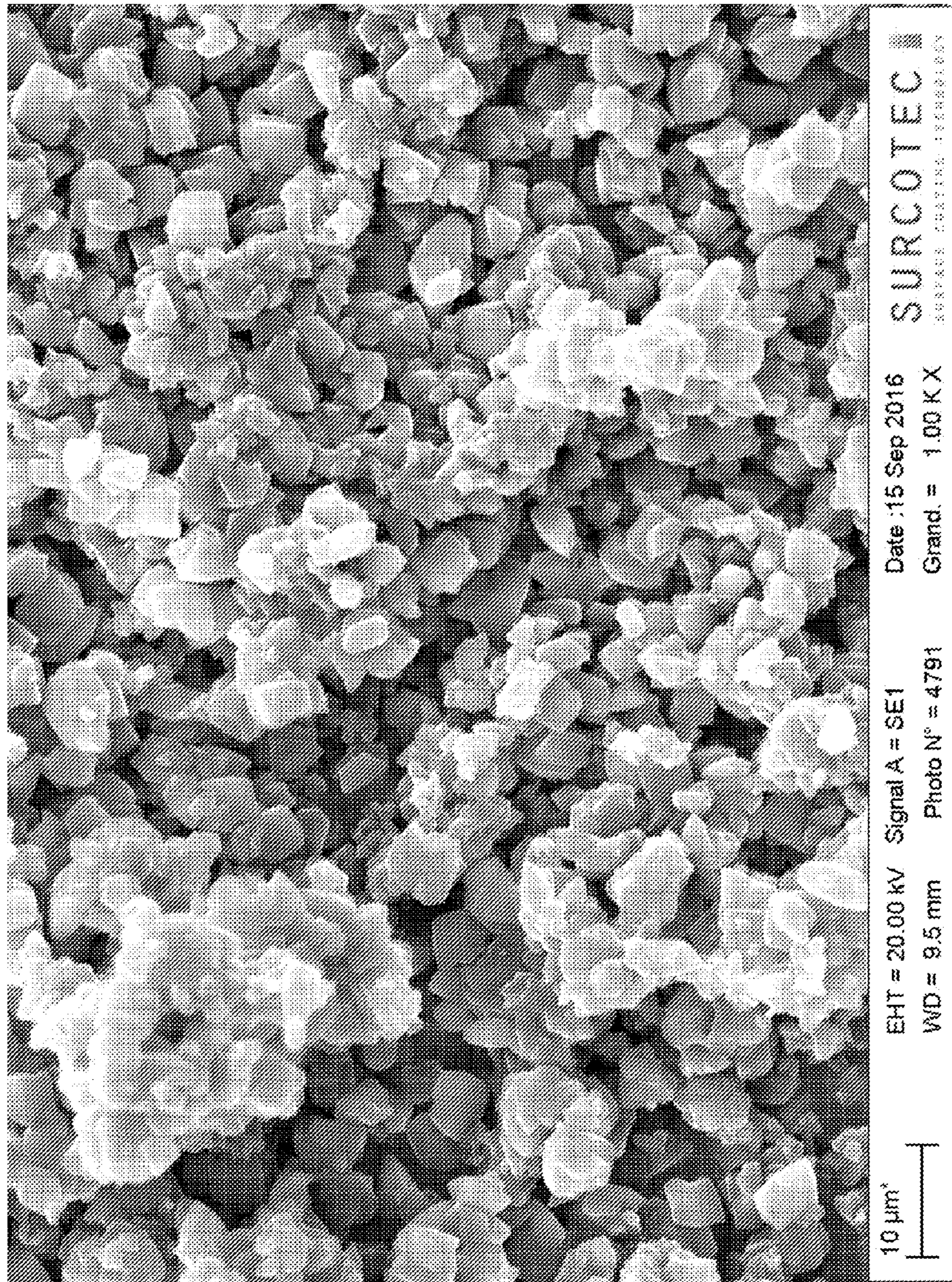


Figure 6 : Cliché MEB des cristaux de diglycéroxyde de calcium faits avec les billes Zirmill 0.5 mm

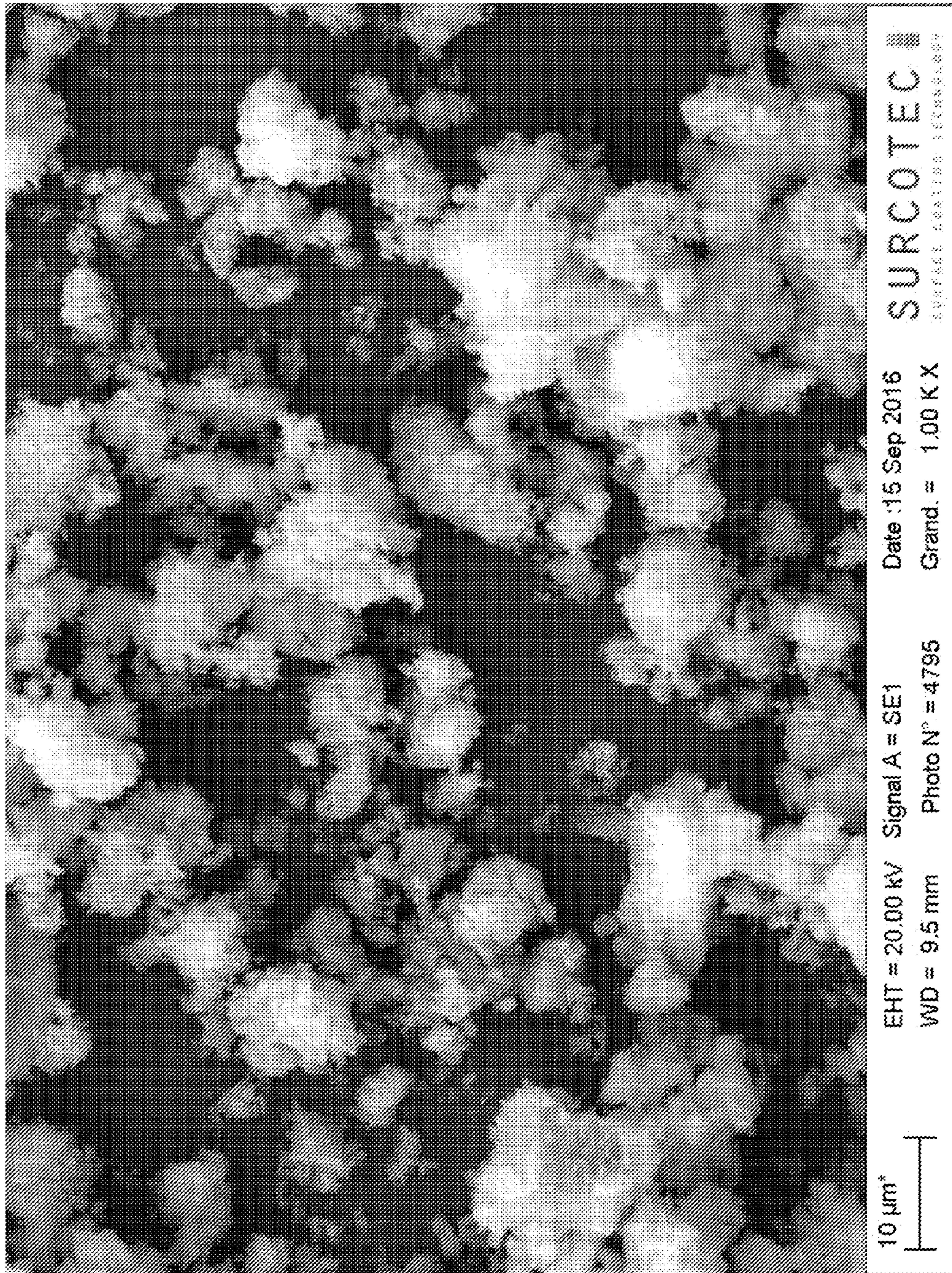


Figure 7 : Cliché MEB des cristaux de diglycéroxyde de calcium faits avec les billes Zirmill 2mm

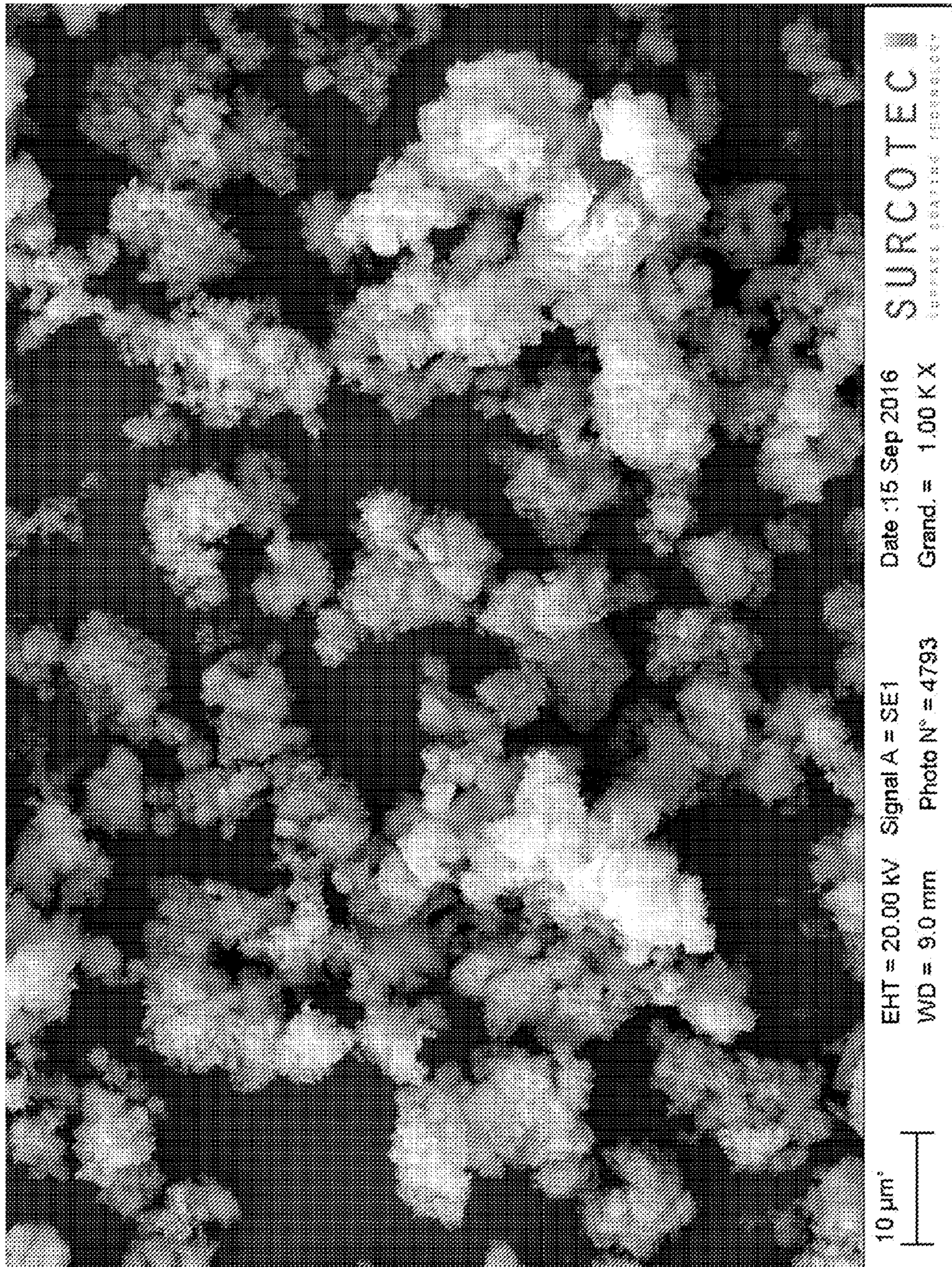


Figure 8 : Cliché MEB des cristaux de diglycéroxyde de calcium fait avec les billes Silibeads 2mm (échantillon 241.1)

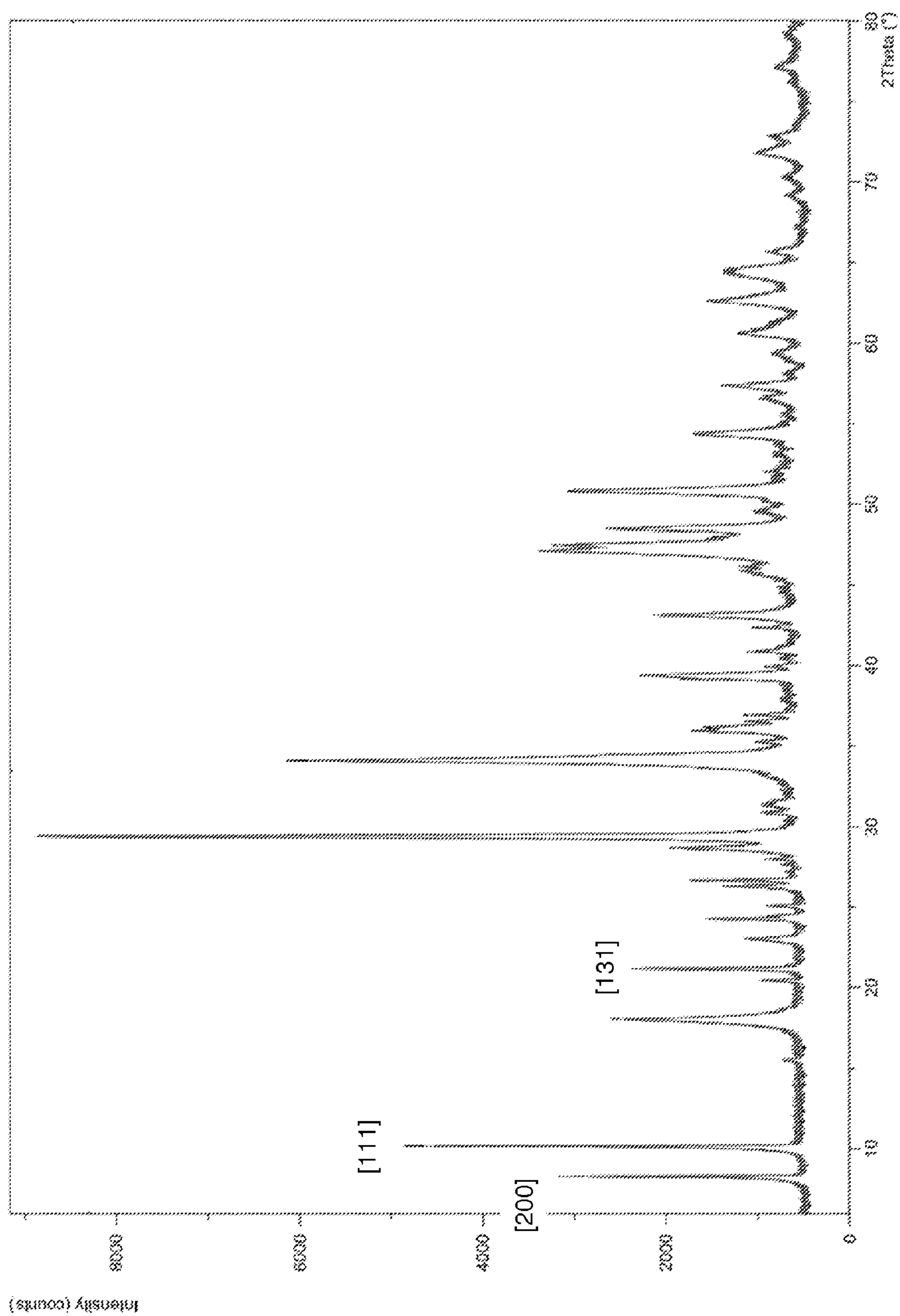


Figure 9 : Cliché MEB des cristaux de diglycéroxyde de calcium faits avec  $\text{Ca(OH)}_2$