

PULVERULENT COMPOSITIONS OF A COMPLEX BETWEEN AN ACID AND A HIGH-TEN METAL OF SULFUR ORGANIC COMPOUNDS AND THEIR PREPARATION METHOD

5 The present invention relates to pulverulent compositions of an acid-metal complex with a high content of organic compounds sulfur compounds, and the process for their preparation.

 Methionine, an essential amino acid, and 2-hydroxy-4-methylthio-butanoic acid (HMTBA), a methionine analogue, are widely used in man as a dietary supplement or drug,
10 and animal nutrition. Their metal salts, for example calcium, magnesium or zinc, in solid form, are advantageous because they make it possible to fill in deficiencies in elements or trace elements. The most known HMTBA salt is the dicalcium salt, comprising two moles of HMTBA equivalent per mol of calcium corresponding to the formula $(\text{HMTBA})_2\text{Ca}$.

 Many examples describe the manufacture of methionine or methionine analogue salts,
15 especially HMTBA.

 In the case of HMTBA, if the concentrated acid product is found in liquid form, at a high concentration often higher than 87% of HMTBA, the salts are in solid form and are less concentrated in HMTBA due to the cations used for salt formation.

 The powder forms have for the most part a composition corresponding to the
20 stoichiometry of the dicalcium salt $(\text{HMTBA})_2\text{Ca}$.

 Thus, US Pat. No. 4,335,257 describes the preparation of a salt of formula $(\text{HMTBA})_2\text{Ca}$ which makes it possible to obtain a composition in solid form which brings no more than 85% HMTBA in its composition by mass.

 US Pat. No. 3,272,860, EP 0 049 057, US Pat. No. 6,287,627 and FR 2,964,968 thus
25 describe the production of salts of formula $(\text{HMTBA})_2\text{Ca}$ obtained from HMTBA which are all in stoichiometric proportions and therefore at HMTBAs from 80% to 87%.

 Few documents of the prior art relate the obtaining of compositions containing an HMTBA content higher than the stoichiometric proportion of the formation of the dicalcium salt $(\text{HMTBA})_2\text{Ca}$.

 Romoser et al. (Poult. Sci. 1976, 55 (3), pp. 1099-1103) obtain an MHA-rich
30 composition in the acid form (HMTBA) by spraying said acid form on a solid support (vermiculite). In this case, however, the HMTBA content is only 50%.

Likewise, EP 140865 describes the production of calcium salts of HMTBA consisting of more than two and less than ten moles of equivalent of HMTBA per mole of calcium. These salts are obtained by reacting Γ HMTBA with a calcium source selected from calcium oxide (CaO), calcium hydroxide (Ca(OH)₂), calcium carbonate (CaCO₃) and a salt of calcium HMTBA, e.g. salt (HMTBA)₂Ca. The HMTBA is generally in highly concentrated aqueous solution, to which the source of calcium is mixed, then the reaction medium thus obtained is dried at a temperature of the order of 70.degree.

The product obtained is 94% HMTBA equivalent. However, the reaction medium of HMTBA with the source of calcium is very viscous and sticky: it is therefore very difficult to homogenize in mixers or reactors equipped with conventional stirring systems and, at the end of the reaction, it is necessary to carry out drying in-situ in order to drain the reactor. It also requires a shaping step after drying by grinding and then sieving. Finally, this method, necessarily by batch, does not allow continuous process adaptation.

Recycling of the calcium salt of HMTBA, for example salt (HMTBA)₂Ca, to the calcium source before adding Γ HMTBA, makes it possible to improve the consistency of the reaction medium and facilitates the implementation of the process. However, as described in US Pat. No. 4,335,257, this improvement requires at least 20% by weight of said salt and up to 80% of said salt. As a result of this requirement, this process reduces productivity and increases the over-dimensioning of installations.

It is therefore an object of the present invention to provide complexes between an acid and a solid powdered metal having a content of organic sulfur compounds, in particular HMTBA, of greater than 87%.

Another object of the invention is to provide, complexes between an acid and a metal, in the form of stable powders, easily manipulated and adapted to the application to which said complexes are intended.

Another object of the invention is to provide a process for the preparation of complexes between an acid and a metal, in batch, without difficulties of adhesion or appearance of viscous mass during the preparation, and without using the base of the vessel to produce the product.

Another object of the invention is to provide a process for the preparation of complexes between an acid and a metal, continuously.

The subject of the invention is thus a particle comprising:

- A nucleus consisting essentially of a salt of formula (I) below:



in which :

A represents an anion selected from the group consisting of 2-hydroxy-4-methylthiobutanoate, methionate and cysteine,

M represents a divalent or trivalent metal,

5 n being equal to 2 when said metal is divalent and to 3 when said metal is trivalent, and

- A layer comprising a compound B selected from the group consisting of 2-hydroxy-4-methyl-thio-butanoic acid (HMTBA), methionine, cysteine, their mixtures, their salts and complexes ,

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said layer coating said core,

the weight percentage of said compound B relative to the salt of formula (I) of the ring being from about 10% to about 50%,

15 said compound B not being, or not solely, in the form of a salt of formula (I), the content of sulfur-containing organic compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88 %, 89% or 90% by weight, based on the total mass of said particle.

The content of organic sulfur compounds corresponds to TOS (Total Organic Sulfur).

20 When the particle comprises HMTBA, the HMTBA content is measured by TOS measurement.

Surprisingly, the particle obtained is stable and remains in pulverulent form, despite high TOS. It is neither viscous nor sticky.

The term "particle" is understood to mean a small element of matter which, with the naked eye, appears in one piece and not constituted by a juxtaposition of smaller elements.

25 The term "core consisting essentially of a salt of formula (I)" is understood in particular to mean a core comprising more than 70% by weight of said salt of formula (I).

The percentage by weight of said compound B included in said layer is given with respect to the mass of salt of formula (I) of the core, and not with respect to the total mass of said particle.

30 By "said compound B is not, or not solely, in the form of a salt of formula (I)", it is meant that compound B is in a form other than a salt of formula (I), in free form or in the form of a complex of formula (II) as described below, or in the form of a mixture comprising a salt of formula (I) and at least one other form such as the free form or a complex of formula (II).

According to an advantageous embodiment, the present invention relates to a particle as defined above, in which said compound B is in the form:

- free, selected from 2-hydroxy-4-methylthio-butanoic acid (HMTBA), methionine and cysteine, and / or
 - 5 - said said salt of formula (I) as defined above, and / or
 - a complex of formula (A) 4M (II) in which A and M are as defined above, A preferably representing 2-hydroxy-4-methylthio-butanoic acid (HMTBA)
- said compound B not being, or not solely, in the form of a salt of formula (I),
- 10 said compound B being in particular in the form:
- free,
 - of the complex of formula (II),
 - of a mixture of the free form and the complex of formula (II),
 - a mixture of the free form and the salt of formula (I),
 - 15 - of a mixture of the salt of formula (I) and of the complex of formula (II), or
 - of a mixture of the free form, of the salt of formula (I) and of the complex of formula (II).

According to an advantageous embodiment, the present invention relates to a particle as defined above, in which said compound B is in the form of:

- the complex of formula (II),
- a mixture of the free form and the complex of formula (II),
- a mixture of the salt of formula (I) and of the complex of formula (II), or
- a mixture of the free form, the salt of formula (I) and the complex of formula (II),

25 said compound B being in particular in the form of the complex of formula (II).

According to an advantageous embodiment, the present invention relates to a particle as defined above, comprising less than 3%, in particular less than 2% or 1.5%, of water by weight.

According to an advantageous embodiment, the present invention relates to a particle as defined above, the calcium content of which is between 6 and 11% by weight, in particular 30 6.5 to 10%, more particularly 7 to 9 %, even more particularly of 7.5%, 8.0% or 8.5%, the calcium content being in particular about 8%.

According to an advantageous embodiment, the present invention relates to a particle as defined above, in which the weight percentage of said compound B relative to the salt of

formula (I) of the ring is between about 10% and about 40% , more preferably from about 15% to about 35%, more preferably from about 20% to about 32%, most preferably from 21%, 22%, 23%, 24%, 25%, 26%, 27% 28%, 29%, 30% or 31%.

According to an advantageous embodiment, the present invention relates to a particle
5 as defined above, in which said metal is chosen from the group comprising Mg, Be, Ca, Sr, Ba, Mn, Fe, Co, Ni, Cu, Zn, Pt, B, Al, Ga, In, in particular Mg, Ca, Fe, Mn, Al, Cu, Zn.

According to an advantageous embodiment, the present invention relates to a particle
as defined above, in which said metal and n are such that M^{n+} represents Mg^{2+} , Be^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Co^{3+} , Ni^{3+} , Cu^{2+} , Zn^{2+} , P^{2+} , Al^{3+} , Ga^{3+} or In^{3+} , especially
10 Mg^{2+} , Fe^{2+} , Fe^{3+} , Al^{3+} , Mn^{2+} , Cu^{2+} or Zn^{2+} .

According to an advantageous embodiment, the present invention relates to a particle
as defined above, wherein said salt of formula (I) is $(HMTBA)_2Ca$, $(HMTBA)_2Mg$,
 $(HMTBA)_2Fe$, $(HMTBA)_2Mn$, $(HMTBA)_2Zn$, $(HMTBA)_2Cu$, $(HMTBA)_3Fe$, $(HMTBA)_3Al$,
 $(Methionine)_2Ca$, $(Methionine)_2Mg$, $(Methionine)_2Fe$, $(Methionine)_2Mn$, $(Methionine)_2Zn$,
15 $(Methionine)_2Cu$, $(Methionine)_3Fe$, $(Methionine)_3Al$, $(Cysteine)_2Ca$, $(Cysteine)_2Mg$,
 $(Cysteine)_2Fe$, $(Cysteine)_2Mn$, $(Cysteine)_2Zn$, $(Cysteine)_2Cu$, $(Cysteine)_3Fe$, $(Cysteine)_3Al$, in
particular a salt of formula $(HMTBA)_2Ca$, $(HMTBA)_2Mg$, $(HMTBA)_2Fe$, $(HMTBA)_2Mn$,
 $(HMTBA)_2Zn$, $(HMTBA)_2Cu$, $(Methionine)_2Ca$, $(Methionine)_2Mg$, $(Methionine)_2Fe$,
 $(Methionine)_2Mn$, $(Methionine)_2Zn$, $(Methionine)_2Cu$, $(Cysteine)_2Ca$, $(Cysteine)_2Mg$,
20 $(Cysteine)_2Fe$, $(Cysteine)_2Mn$, $(Cysteine)_2Zn$, $(Cysteine)_2Cu$.

According to an advantageous embodiment, the present invention relates to a particle
as defined above, in which said anion A^- is 2-hydroxy-4-methyl-thio-butanoate.

According to an advantageous embodiment, the present invention relates to a particle
as defined above, in which said compound B included in said layer is 2-hydroxy-4-
25 methylthio-butanoic acid (HMTBA), or one of its salts or complexes.

According to an advantageous embodiment, the present invention relates to a particle
as defined above, in which said anion A^- is 2-hydroxy-4-methylthiobutanoate, and said
compound B included in said layer is 2-hydroxy-4-methylthio-butanoic acid (HMTBA), or a
salt or complex thereof.

30 According to an advantageous embodiment, the present invention relates to a particle
as defined above, in which the compound A forming said anion A^- and said compound B if B
is in free form, or the compound forming compound B, if B is in the form of salt or complex,
are different.

According to an advantageous embodiment, the present invention relates to a particle as defined above, in which said 2-hydroxy-4-methylthio-butanoic acid (HMTBA) is in monomeric form with more than 60% by weight.

According to an advantageous embodiment, the present invention relates to a particle comprising:

- a nucleus consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, and
- a layer comprising a compound B selected from the group consisting of 2-hydroxy-4-methyl-thio-butanoic acid (HMTBA), methionine, cysteine, their mixtures, their salts and complexes,

said layer coating said core,

the weight percentage of said compound B relative to the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$ of the ring being from about 10% to about 50%,

said compound B not being, or not solely, in the form of the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, the content of sulfur-containing organic compounds (TOS) in said particle being greater than 87% to 88%, 89% or 90% by weight, based on the total mass of said particle.

According to an advantageous embodiment, the present invention relates to a particle comprising:

- a nucleus consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, and
- a layer comprising 2-hydroxy-4-methyl-thio-butanoic acid (HMTBA), said layer coating said core,

the weight percentage of the HMTBA of said layer relative to the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$ of the core being from about 10% to about 50%,

the HMTBA of said layer not being, or not only, in the form of the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$,

the content of organic sulfur compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said particle.

According to an advantageous embodiment, the present invention relates to a particle comprising:

- a nucleus consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, and
- a layer comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA) and calcium, the atomic ratio S/Ca being between 2.7 and 3.7,

said layer coating said core,

the weight percentage of the HMTBA of said layer relative to the salt of formula (I) (HMTBA)₂Ca of the core being from about 10% to about 50%,
the content of organic sulfur compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said
5 particle.

According to an advantageous embodiment, the present invention relates to a particle comprising:

- a nucleus consisting essentially of a salt of formula (I) (HMTBA)₂Ca, and
- a layer comprising complex of formula (II) (HMTBA)₄Ca,

10 said layer coating said core,

the mass percentage of HMTBA of said layer relative to to the salt of formula (I) (HMTBA)₂Ca of the ring being from about 10% to about 50%,
the content of organic sulfur compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said
15 particle.

The invention also relates to a pulverulent composition consisting or comprising particles as defined above.

By "pulverulent particle composition" is meant a solid, in a fractioned state, ie, particulate, according to the present invention.

20 According to an advantageous embodiment, the present invention relates to a composition as defined above, in which the granulometric size of said particles varies from 10 to 3000 µm, in particular from 20 to 300 µm, in particular from 100 to 250 µm, in mean particle size distribution [Dv (0.5)].

By mean particle size distribution [Dv (0.5)] is meant the average particle size
25 diameter measured by laser diffraction, 50% of the particles of said composition having a diameter greater than said average diameter and 50% of the particles of said composition having a diameter lower than said mean diameter.

According to an advantageous embodiment, the present invention relates to a composition as defined above, the uncapped density of which is greater than 350 g / l, in
30 particular greater than 400 g / l.

The uncapped (or aerated) density of said pulverulent composition can be measured using a 250 ml test piece graduated every 2 ml. This method is described in the standard AFNOR NF X 04-344. The procedure consists in pouring the powder composition into the test piece so as to be close to the maximum graduation of the receptacle and then measuring

the mass as well as the volume occupied by said pulverulent composition. The uncapped density is then calculated by the ratio of the mass of powder to the volume occupied by the pulverulent composition.

According to an advantageous embodiment, the present invention relates to a composition as defined above, the bulk density of which after 10 motions is greater than 400 g / l, in particular greater than 450 g / l.

The compacted density of said pulverulent composition can be measured using a 250 ml test piece graduated every 2 ml and a Dual Autotap volumeter type conforming to the ASTM B527 and D4164 standards. The procedure consists in pouring the pulverulent composition into the test piece so as to be close to the maximum graduation of the receptacle. The test specimen is then gently placed on the Autotap plate to undergo the desired number of vertical shocks as a function of the target packed density (D10 = ten packed density, D500 = density packed at 500 strokes). The compacted density is then calculated by the ratio of the mass of packed powder to the volume occupied by the said packed powder in the said test piece.

According to an advantageous embodiment, the present invention relates to a composition as defined above, the angle of inclination of which is between 34° and 40°, in particular of 36° to 38°.

The angle of slope of said pulverulent composition can be measured by determining the angle at the base of the slide cone obtained by passing the sample through a special funnel (stainless steel funnel whose base diameter (d) inside is 6 mm) at a conventional height, above a perfectly flat and horizontal marble plate. The procedure, performed four times, consists of:

- adjust the height (H) between the plate and base of the funnel to 40 mm,
- check the center of the funnel with the marble plate,
- place a sheet of paper on the plate by centering it with the funnel,
- pour the powder into the funnel,
- stop the feed when the top of the cone touches the base of the funnel,
- inscribe the base of the cone, in the form of a circle, in a square,
- measures the distance D separating two opposite sides of said square.

The angle of slide slope α is expressed in degrees and is given by the formula

$$\alpha = \arctan\left(\frac{2 \cdot H}{D - d}\right)$$

with

H: the cone height in mm (H = 40),

d: inside diameter of the base of the funnel in mm (d = 6 mm),

D: arithmetic mean of the 4 measurements in mm.

According to an advantageous embodiment, the present invention relates to a composition as defined above, comprising, in addition to said particles, oil, especially vegetable oil.

The vegetable oil is in particular chosen from soybean oil, sunflower oil, rapeseed oil, groundnut oil and mixtures thereof.

The invention also relates to a method for preparing a particle comprising:

- a nucleus consisting essentially of a salt of formula (I) below:



in which :

A⁻ represents an anion selected from the group consisting of 2-hydroxy-4-methylthiobutanoate, methionate and cysteine,

M represents a divalent or trivalent metal,

15 n being equal to 2 when said metal is divalent and to 3 when said metal is trivalent, and

- a layer comprising a compound B selected from the group consisting of 2-hydroxy-4-methyl-thio-butanoic acid (HMTBA), methionine, cysteine, their mixtures, their salts and complexes,

20 said layer coating said core,

the weight percentage of said compound B relative to the salt of formula (I) of the ring being from about 10% to about 50%

said compound B not being, or not solely, in the form of a salt of formula (I),

the content of sulfur-containing organic compounds (TOS) in said particle being greater than 25 87% by mass, in particular greater than 88 %, 89% or 90% by weight,

said method comprising a step of spraying on a solid consisting essentially of a salt of formula (I) as defined above, of a composition comprising a compound B selected from the group consisting of 2-hydroxy-4-methylthio-butanoic acid (HMTBA), methionine, cysteine, 30 mixtures thereof, salts and complexes, the mass of said compound B being from about 10% to about 50% of the mass of the salt of formula (I) of the solid, to obtain said particle.

According to an advantageous embodiment, the present invention relates to a process as defined above, in which said composition comprises a compound B selected from the

group consisting of 2-hydroxy-4-methylthio-butanoic acid (HMTBA) methionine and cysteine, in free form.

According to an advantageous embodiment, the present invention relates to a process as defined above, in which said spraying step is carried out:

- 5 - in a fluidized bed of air in a batch or continuously,
or
- in atomization tower by copulverization.

By sputtering is meant the spraying together of a liquid and a powder.

10 According to an advantageous embodiment, the present invention relates to a process as defined above, in which said spraying step is carried out continuously.

According to an advantageous embodiment, the present invention relates to a process as defined above, in which said spraying step is carried out on a vibrofluidizer.

 According to an advantageous embodiment, the present invention relates to a process
15 as defined above, in which said spraying step is carried out under an inert atmosphere, in particular under nitrogen, the inert gas being more particularly recycled.

According to an advantageous embodiment, the present invention relates to a process as defined above, in which said composition is in liquid form.

 According to an advantageous embodiment, the present invention relates to a process
20 as defined above, in which said composition additionally comprises water, the percentage by weight of water of said composition being comprised between 0.5 and 50.

According to an advantageous embodiment, the present invention relates to a process as defined above, in which the core consisting essentially of a salt of formula (I) is obtained by reactive atomization.

25 By reactive atomization is meant the atomization of a reaction mixture, said mixture being the combination of two or more compounds which can react chemically together when mixed, the contacting of the compounds of the reaction mixture being followed immediately by spraying by atomization.

 According to an advantageous embodiment, the present invention relates to a process
30 as defined above, in which the core consisting essentially of a salt of formula (I) is obtained as a fluidized air bed, a granulator, a rotary granulator, mixer.

According to an advantageous embodiment, the present invention relates to a process as defined above, in which the core consisting essentially of a salt of formula (I) is obtained by reactive extrusion.

The reactive extrusion can be carried out by techniques well known to those skilled in the art. In particular, the salt of formula (I) can be obtained by the reactive extrusion as described in application FR 2 964 968.

5 According to an advantageous embodiment, the present invention relates to a process as defined above, in which the core consisting essentially of a salt of formula (I) is obtained using a static or dynamic mixer.

According to an advantageous embodiment, the present invention relates to a process as defined above, in which the core consisting essentially of a salt of formula (I) is obtained by reactive atomization under an inert atmosphere, in particular under nitrogen, the inert gas
10 being in particular recycled when the core consisting essentially of a salt of formula (I) is not obtained by reactive extrusion.

According to an advantageous embodiment, the present invention relates to a process as defined above, in which said compound B included in said layer is in the form:

- free, selected from 2-hydroxy-4-methylthio-butanoic acid (HMTBA), methionine and
15 cysteine, and / or
- said salt of formula (I) as defined above, and / or
- a complex of formula (A)₄M (II) in which A and M are as defined above, A preferably representing 2-hydroxy-4-methylthio-butanoic acid (HMTBA)

said compound B not being, or not solely, in the form of a salt of formula (I),

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said compound B being in particular in the form:

- free,
- the complex of formula (II),
- a mixture of the free form and the complex of formula (II),
- 25 - a mixture of the free form and the salt of formula (I),
- a mixture of the salt of formula (I) and the complex of formula (II), or
- a mixture of the free form, of the salt of formula (I) and of the complex of formula (II).

30 According to an advantageous embodiment, the present invention relates to a process as defined above, in which said particle comprises less than 3%, 2% or 1.5% of water by mass

According to an advantageous embodiment, the present invention relates to a process as defined above, in which the said particle has a calcium content of between 6 and 11% by

weight, in particular of 6.5 to 10%, more particularly of 7 to 9%, the calcium content being in particular about 8%.

According to an advantageous embodiment, the present invention relates to a process as defined above, in which the weight percentage of said compound B relative to the salt of formula (I) of the ring is from about 10% to about 40% , particularly from about 15% to about 35%, more preferably from about 20% to about 32%.

According to an advantageous embodiment, the present invention relates to a process as defined above, in which said metal is chosen from the group comprising Mg, Be, Ca, Sr, Ba, Mn, Fe, Co, Ni, Cu, Zn, Pt, B, Al, Ga, In, in particular Mg, Ca, Fe, Mn, Al, Cu, Zn.

According to an advantageous embodiment, the present invention relates to a process as defined above, in which said metal and n are such that M^{n+} represents Mg^{2+} , Be^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Co^{3+} , Ni^{3+} , Cu^{2+} , Zn^{2+} , P^{2+} , Al^{3+} , Ga^{3+} or In^{3+} , especially Mg^{2+} , Fe^{2+} , Fe^{3+} , Al^{3+} , Mn^{2+} , Cu^{2+} or Zn^{2+} .

According to an advantageous embodiment, the present invention relates to a process as defined above, in which said salt of formula (I) is $(HMTBA)_2Ca$, $(HMTBA)_2Mg$, $(HMTBA)_2Fe$, $(HMTBA)_2Mn$, $(HMTBA)_2Zn$, $(HMTBA)_2Cu$, $(HMTBA)_3Fe$, $(HMTBA)_3Al$, $(Methionine)_2Ca$, $(Methionine)_2Mg$, $(Methionine)_2Fe$, $(Methionine)_2Mn$, $(Methionine)_2Zn$, $(Methionine)_2Cu$, $(Methionine)_3Fe$, $(Methionine)_3Al$, $(Cysteine)_2Ca$, $(Cysteine)_2Mg$, $(Cysteine)_2Fe$, $(Cysteine)_2Mn$, $(Cysteine)_2Zn$, $(Cysteine)_2Cu$, $(Cysteine)_3Fe$, $(Cysteine)_3Al$, in particular a salt of formula $(HMTBA)_2Ca$, $(HMTBA)_2Mg$, $(HMTBA)_2Fe$, $(HMTBA)_2Mn$, $(HMTBA)_2Zn$, $(HMTBA)_2Cu$, $(Methionine)_2Ca$, $(Methionine)_2Mg$, $(Methionine)_2Fe$, $(Methionine)_2Mn$, $(Methionine)_2Zn$, $(Methionine)_2Cu$, $(Cysteine)_2Ca$, $(Cysteine)_2Mg$, $(Cysteine)_2Fe$, $(Cysteine)_2Mn$, $(Cysteine)_2Zn$, $(Cysteine)_2Cu$.

According to an advantageous embodiment, the present invention relates to a process as defined above, in which said anion A^- is 2-hydroxy-4-methyl-thio-butanoate.

According to an advantageous embodiment, the present invention relates to a process as defined above, in which said compound B included in said layer is 2-hydroxy-4-methylthio-butanoic acid (HMTBA), or one of its salts or complexes.

According to an advantageous embodiment, the present invention relates to a process as defined above, in which said anion A^- is 2-hydroxy-4-methylthiobutanoate, and said compound B included in said layer is 2-hydroxy-4-methylthio-butanoic acid (HMTBA), or a salt or complex thereof.

According to an advantageous embodiment, the present invention relates to a process as defined above, in which said 2-hydroxy-4-methylthio-butanoic acid (HMTBA) is in monomeric form with more than 60% by weight.

According to an advantageous embodiment, the present invention relates to a process
5 for preparing a particle comprising:

- a nucleus consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, and
- a layer comprising a compound B selected from the group consisting of 2-hydroxy-4-methyl-thio-butanoic acid (HMTBA), methionine, cysteine, their mixtures, their salts and complexes,

10 said layer coating said core,

the weight percentage of said compound B relative to the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$ of the ring being from about 10% to about 50%,

said compound B not being, or not only, in the form of the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said
15 particle,

said process comprising a step of spraying on a solid consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, of a composition comprising a compound B selected from the group consisting of 2-hydroxy-4-methylthio (HMTBA), methionine, cysteine, mixtures thereof, salts
20 and complexes, the weight of said compound B being from about 10% to about 50% of the weight of the salt of formula (I) of the solid, to obtain said particle.

According to an advantageous embodiment, the present invention relates to a process for preparing a particle comprising:

- 25
- a nucleus consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, and
 - a layer comprising a compound B selected from the group consisting of 2-hydroxy-4-methyl-thio-butanoic acid (HMTBA), methionine, cysteine, their mixtures, their salts and complexes,

said layer coating said core,

30 the weight percentage of said compound B relative to the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$ of the ring being from about 10% to about 50%,

said compound B not being, or not only, in the form of the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$,

the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said particle,

said process comprising a step of spraying in a fluidized bed of air in a batch or continuously on a solid consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, of a composition comprising a compound B selected from the group consisting of 2-hydroxy-4-methylthio-butanoic acid (HMTBA), methionine, cysteine, their mixtures, their salts and complexes, the mass of said compound B being from about 10% about 50% of the mass of the salt of formula (I) of the solid,

to obtain said particle.

According to an advantageous embodiment, the present invention relates to a process for preparing a particle comprising:

- a nucleus consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, and
- a layer comprising a compound B selected from the group consisting of 2-hydroxy-4-methyl-thio-butanoic acid (HMTBA), methionine, cysteine, their mixtures, their salts and complexes,

said layer coating said core, wherein the weight percentage of said compound B relative to the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$ of the ring is from about 10% to about 50%

said compound B not being, or not only, in the form of the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$,

the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said particle,

said process comprising a step of spraying in a fluidized bed of air in a batch or continuously on a solid consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, said solid being obtained by reactive atomization of a composition comprising a compound B group selected from the group consisting of 2-hydroxy-4-methylthio-butanoic acid (HMTBA), methionine, cysteine, their mixtures, their salts and complexes, the mass of said compound B being from about 10% to about 50% of the mass of the salt of formula (I) of the solid,

to obtain said particle.

According to an advantageous embodiment, the present invention relates to a process for preparing a particle comprising:

- a nucleus consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, and

- a layer comprising a compound B selected from the group consisting of 2-hydroxy-4-methyl-thio-butanoic acid (HMTBA), methionine, cysteine, their mixtures, their salts and complexes,

said layer coating said core,

5 the weight percentage of said compound B relative to the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$ of the ring being from about 10% to about 50%,

said compound B not being, or not only, in the form of the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said
10 particle,

said process comprising a step of spraying in atomization tower by copulverization onto a solid consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, of a composition comprising a compound B selected from the group consisting of 2- hydroxy-4-methylthiobutanoic acid (HMTBA), methionine, cysteine, mixtures thereof, salts and
15 complexes, the weight of said compound B being from about 10% to about 50% of the mass of the salt of formula (I) of the solid,
to obtain said particle.

According to an advantageous embodiment, the present invention relates to a process for preparing a particle comprising:

- a nucleus consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, and
- a layer comprising a compound B selected from the group consisting of 2-hydroxy-4-methyl-thio-butanoic acid (HMTBA), methionine, cysteine, their mixtures, their salts and complexes,

said layer coating said core,

25 the weight percentage of said compound B relative to the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$ of the ring being from about 10% to about 50%,

said compound B not being, or not only, in the form of the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said
30 particle,

said process comprising a step of spraying in atomization towers by copulverization onto a solid consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, said solid being obtained by reactive atomization in said atomization tower of a composition comprising a compound B selected from the group consisting of 2-hydroxy-4-methylthio-butanoic acid (HMTBA),

methionine, cysteine, their mixtures, their salts and complexes, compound B being from about 10% to about 50%) of the mass of the salt of formula (I) of the solid, to obtain said particle.

According to an advantageous embodiment, the present invention relates to a process for preparing a particle comprising:

- a core consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, and
- a layer comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA),

said layer coating said core,

the weight percentage of the HMTBA of said layer relative to the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$ of the ring being from about 10% to about 50%,

the HMTBA of said layer not being, or not only, in the form of the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$,

the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said particle,

said method comprising a step of spraying on a solid consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, a composition comprising 2-hydroxy-4-methyl-thio-butanoic acid (HMTBA) of said compound B being from about 10% to about 50% of the mass of the salt of formula (I) of the solid,

to obtain said particle.

According to an advantageous embodiment, the present invention relates to a process for preparing a particle comprising:

- a core consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, and
- a layer comprising 2-hydroxy-4-methyl-thio-butanoic acid (HMTBA),

said layer coating said core,

the weight percentage of the HMTBA of said layer relative to the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$ of the core being from about 10% to about 50%,

the HMTBA of said layer not being, or not only, in the form of the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$,

the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said particle,

said process comprising a step of spraying a fluidized bed of air in a batch or continuously on a solid consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, of a composition comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA), the mass of said compound B being from about 10% to about 50% of the weight of the salt of formula (I) of the solid,

5 to obtain said particle.

According to an advantageous embodiment, the present invention relates to a process for preparing a particle comprising:

- a core consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, and
- a layer comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA), or one of its salts or complexes,

10

said layer coating said core,

the weight percentage of the HMTBA of said layer relative to the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$ of the core being from about 10% to about 50%,

the HMTBA of said layer not being, or not only, in the form of the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$,

15

the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said particle,

said process comprising a step of spraying in a bed of fluidized air in a batch or continuously on a solid consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, said solid being obtained by reactive atomization of a composition comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA), the mass of said HMTBA of said layer being from about 10% to about 50% of the mass of the salt of formula (I) of the solid,

20

to obtain said particle.

25 According to an advantageous embodiment, the present invention relates to a process for preparing a particle comprising:

- a core consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, and
- a layer comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA), or one of its salts or complexes, said layer coating said core,

30 the weight percentage of the HMTBA of said layer relative to the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$ of the core being from about 10% to about 50%,

the HMTBA of said layer not being, or not only, in the form of the salt of formula (I) $(\text{HMTBA})_2\text{Ca}$,

the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said particle,

said process comprising a step of spraying in atomization tower by copulverization onto a solid consisting essentially of a salt of formula (I) (HMTBA)₂Ca, of a composition comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA), the mass of said HMTBA of said layer being from about 10% to about 50% of the mass of the salt of formula (I) of the solid,
to obtain said particle.

According to an advantageous embodiment, the present invention relates to a process for preparing a particle comprising:

- a nucleus consisting essentially of a salt of formula (I) (HMTBA)₂Ca, and
- a layer comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA), or one of its salts or complexes, said layer coating said core,

the weight percentage of the HMTBA of said layer relative to the salt of formula (I) (HMTBA)₂Ca of the core being from about 10% to about 50%,

the HMTBA of said layer not being, or not only, in the form of the salt of formula (I) (HMTBA)₂Ca,

the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said particle,

said process comprising a step of spraying in atomization towers by copulverization onto a solid consisting essentially of a salt of formula (I) (HMTBA)₂Ca, said solid being obtained by reactive atomization in said atomization tower of a composition comprising of 2-hydroxy-4-

methylthio-butanoic acid (HMTBA), the mass of said

HMTBA of said layer being from about 10% to about 50% of the mass of the salt of formula (I) of the solid, of the solid,

to obtain said particle.

According to an advantageous embodiment, the present invention relates to a process for preparing a particle comprising:

- a nucleus consisting essentially of a salt of formula (I) (HMTBA)₂Ca, and
- a layer comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA) or one of its salts or complexes, and calcium, the atomic ratio S / Ca being between 2.7 and 3.7,

said layer coating said core,

the weight percentage of HMTBA of said layer relative to the salt of formula (I) of the core being from about 10% to about 50%;

the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said particle.

said method comprising a step of spraying on a solid consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, a composition comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA) of said HMTBA of said layer being from about 10% to about 50% of the weight of the salt of formula (I) of the solid, to obtain said particle.

According to an advantageous embodiment, the present invention relates to a process for preparing a particle comprising:

- a nucleus consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, and
- a layer comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA) or one of its salts or complexes, and calcium, the atomic ratio S / Ca being between 2.7 and 3.7,

said layer coating said core,

the weight percent of the HMTBA of said layer relative to the salt of formula (I) of the ring being from about 10% to about 50%,

the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said particle.

said process comprising a step of spraying a fluidized bed of air in a batch or continuously on a solid consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, of a composition comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA), the mass of said HMTBA of said layer being from about 10% to about 50% of the weight of the salt of formula (I) of the solid, to obtain said particle.

According to an advantageous embodiment, the present invention relates to a process for preparing a particle comprising:

- a nucleus consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, and

- a layer comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA) or one of its salts or complexes, and calcium, the S / Ca atomic ratio being from 2.7 to 3.7,

said layer coating said core,

the weight percent of the HMTBA of said layer relative to the salt of formula (I) of the ring
5 being from about 10% to about 50%,

the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said particle.

10 said process comprising a step of spraying in a bed of fluidized air in a batch or continuously on a solid consisting essentially of a salt of formula (I) (HMTBA)₂Ca, said solid being obtained by reactive atomization of a composition comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA), the mass of said HMTBA of said layer being from about 10% to about 50% of the mass of the salt of formula (I) of the solid, to obtain said particle.

15 According to an advantageous embodiment, the present invention relates to a process for preparing a particle comprising:

- a nucleus consisting essentially of a salt of formula (I) (HMTBA)₂Ca, and
- a layer comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA) or one of its salts or complexes, and calcium, the atomic ratio S / Ca being between 2.7 and 3.7,

20 said layer coating said core,

the weight percent of the HMTBA of said layer relative to the salt of formula (I) of the ring being from about 10% to about 50%,

the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said
25 particle.

said process comprising a step of spraying in atomization tower by copulverization onto a solid consisting essentially of a salt of formula (I) (HMTBA)₂Ca, of a composition comprising 2-hydroxy-4-methylthio- butanoic acid (HMTBA), the mass of said HMTBA of said layer being from about 10% to about 50% of the mass of the salt of formula (I) of the
30 solid, to obtain said particle.

According to an advantageous embodiment, the present invention relates to a process for preparing a particle comprising:

A nucleus consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, and a layer comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA) or one of its salts or complexes, and calcium, the S / Ca atomic ratio being from 2.7 to 3.7, said layer coating said core, the weight percent of the HMTBA of said layer relative to the salt of formula (I) of the ring
5 being from about 10% to about 50%,
the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said particle.

said process comprising a step of spraying in atomization towers by copulverization onto a
10 solid consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, said solid being obtained by reactive atomization in said atomization tower of a composition comprising (HMTBA), the mass of said HMTBA of said layer being from about 10% to about 50% of the mass of the salt of formula (I) of the solid,
to obtain said particle.

15 According to an advantageous embodiment, the present invention relates to a process for preparing a particle comprising:

- a nucleus consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, and
- a layer comprising complex of formula (II) $(\text{HMTBA})_4\text{Ca}$,

said layer coating said core,
20 the weight percent of the HMTBA of said layer relative to the salt of formula (I) of the ring being from about 10% to about 50%,
the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said particle.

25 said method comprising a step of spraying on a solid consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, a composition comprising 2-hydroxy-4-methyl-thio-butanoic acid (HMTBA) of said HMTBA of said layer being from about 10% to about 50% of the mass of the salt of formula (I) of the solid,
to obtain said particle.

30 According to an advantageous embodiment, the present invention relates to a process for preparing a particle comprising:

- a nucleus consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, and
- a layer comprising complex of formula (II) $(\text{HMTBA})_4\text{Ca}$,

said layer coating said core,

the weight percent of the HMTBA of said layer relative to the salt of formula (I) of the ring being from about 10% to about 50%,

the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said particle.

said process comprising a step of spraying a fluidized bed of air in a batch or continuously on a solid consisting essentially of a salt of formula (I) (HMTBA)₂Ca, of a composition comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA), the mass of said HMTBA of said layer being from about 10% to about 50% of the weight of the salt of formula (I) of the solid, to obtain said particle.

According to an advantageous embodiment, the present invention relates to a process for preparing a particle comprising:

- a nucleus consisting essentially of a salt of formula (I) (HMTBA)₂Ca, and
- a layer comprising complex of formula (II) (HMTBA)₄Ca,

said layer coating said core,

the weight percent of the HMTBA of said layer relative to the salt of formula (I) of the ring being from about 10% to about 50%,

the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said particle.

said process comprising a step of spraying in a bed of fluidised air in a batch or continuously on a solid consisting essentially of a salt of formula (I) (HMTBA)₂Ca, said solid being obtained by reactive atomization of a composition comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA), the mass of said HMTBA of said layer being from about 10% to about 50% of the weight of the salt of formula (I) obtaining said particle.

According to an advantageous embodiment, the present invention relates to a process for preparing a particle comprising:

- a nucleus consisting essentially of a salt of formula (I) (HMTBA)₂Ca, and
- a layer comprising complex of formula (II) (HMTBA)₄Ca,

said layer coating said core,

the weight percent of the HMTBA of said layer relative to the salt of formula (I) of the ring being from about 10% to about 50%,

the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said particle.

said process comprising a step of spraying in atomization tower by copulverization onto a solid consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, of a composition comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA), the mass of said HMTBA of said layer being from about 10% to about 50% of the mass of the salt of formula (I) of the solid, to obtain said particle.

According to an advantageous embodiment, the present invention relates to a process for preparing a particle comprising:

- A nucleus consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, and
- A layer comprising complex of formula (II) $(\text{HMTBA})_4\text{Ca}$,

said layer coating said core,

the weight percent of the HMTBA of said layer relative to the salt of formula (I) of the ring being from about 10% to about 50%,

the content of Sulfur Organic Compounds (TOS) in said particle being greater than 87% by mass, in particular greater than 88%, 89% or 90% by mass, relative to the total mass of said particle.

said process comprising a step of spraying in atomization towers by copulverization onto a solid consisting essentially of a salt of formula (I) $(\text{HMTBA})_2\text{Ca}$, said solid being obtained by reactive atomization in said atomization tower of a composition comprising 2-hydroxy-4-methylthio-butanoic acid (HMTBA), the mass of said HMTBA of said layer being from about 10% to about 50% of the mass of the salt of formula (I) of the solid, to obtain said particle.

According to an advantageous embodiment, the present invention relates to a process for the preparation of a particle in which the compound A forming said anion A^- and said compound B if B is in free form or the compound forming compound B, if B is in salt or complex form, are different.

According to an advantageous embodiment, the present invention relates to a process for the preparation of a particle in which the compound A forming said anion A^- and said

compound B if B is in free form or the compound forming compound B, if B is in salt or complex form, are different,

said method comprising a step of spraying on a solid consisting essentially of a salt of formula (I) $(A^-)_nM^{n+}$ as defined above, of a composition comprising a compound B selected from the

5 group consisting of 2-hydroxy-4-methyl-thio-butanoic acid

(HMTBA), methionine and cysteine, mixtures thereof, salts and complexes, the weight of said compound B being from about 10% to about 50% of the weight of the salt of formula I) of the solid,

to obtain said particle.

10 According to an advantageous embodiment, the present invention relates to a process for the preparation of a particle in which the compound A forming said anion A^- and said compound B if B is in free form or the compound forming compound B, if B is in salt or complex form, are different.

According to an advantageous embodiment, the present invention relates to a process
15 for the preparation of a particle in which the compound A forming said anion A^- and said compound B if B is in free form or the compound forming compound B, if B is in salt or complex form, are different,

said process comprising a step of spraying a fluidized bed of air in a discontinuous or continuous manner on a solid consisting essentially of a salt of formula (I) $(A^-)_nM^{n+}$ as
20 defined above, of a composition comprising a compound B selected from the group consisting of 2-hydroxy-4-methylthio-butanoic acid (HMTBA), methionine and cysteine, mixtures thereof, salts and complexes. mass of said compound B being from about 10% to about 50% of the mass of the salt of formula (I) of the solid,
to obtain said particle.

25 According to an advantageous embodiment, the present invention relates to a process for the preparation of a particle in which the compound A forming said anion A^- and said compound B if B is in free form or the compound forming compound B, if B is in salt or complex form, are different.

According to an advantageous embodiment, the present invention relates to a process
30 for the preparation of a particle in which the compound A forming said anion A^- and said compound B if B is in free form or the compound forming compound B, if B is in salt or complex form, are different,

said process comprising a step of spraying a fluidized bed of air in a discontinuous or continuous manner on a solid consisting essentially of a salt of formula (I) $(A^-)_nM^{n+}$ as

defined above, said solid being obtained by reactive atomization, of a composition comprising a compound B selected from the group consisting of 2-hydroxy-4-methylthio-butanoic acid (HMTBA), methionine and cysteine, mixtures thereof, their salts and complexes, the mass of said compound B being from about 10% to about 50% of the mass of the salt of formula (I) of the solid

to obtain said particle.

According to an advantageous embodiment, the present invention relates to a process for the preparation of a particle in which the compound A forming said anion A^- and said compound B if B is in free form or the compound forming compound B, if B is in salt or complex form, are different.

According to an advantageous embodiment, the present invention relates to a process for the preparation of a particle in which the compound A forming said anion A^- and said compound B if B is in free form or the compound forming compound B, if B is in salt or complex form, are different,

said process comprising a step of spraying in atomization towers by copulverization onto a solid consisting essentially of a salt of formula (I) $(A^-)_nM^{n+}$ as defined above, of a composition comprising a compound B group selected from the group consisting of 2-hydroxy-4-methylthio-butanoic acid (HMTBA), methionine and cysteine, their mixtures, their salts and complexes, the mass of said compound B being from about 10% to about 50% of the mass of the salt of formula (I) of the solid,

to obtain said particle.

According to an advantageous embodiment, the present invention relates to a process for the preparation of a particle in which the compound A forming said anion A^- and said compound B if B is in free form or the compound forming compound B, if B is in salt or complex form, are different.

According to an advantageous embodiment, the present invention relates to a process for the preparation of a particle in which the compound A forming said anion A^- and said compound B if B is in free form or the compound forming compound B, if B is in salt or complex form, are different,

said process comprising a step of spraying in atomization towers by copulverization onto a solid consisting essentially of a salt of formula (I) $(A^-)_nM^{n+}$ as defined above, said solid being obtained by reactive atomization in said spray tower, with a composition comprising a compound B selected from the group consisting of 2-hydroxy-4-methylthio-butanoic acid (HMTBA), methionine and cysteine, mixtures thereof, their salts and complexes, the mass of

said compound B being from about 10% to about 50% of the mass of the salt of formula (I) of the solid,
to obtain said particle.

5 DESCRIPTION OF THE FIGURES

FIG. 1A is an optical microscopy plate relating to the powder obtained at the end of Example 1.

FIG. 1B is an optical microscopy shot relating to the powder obtained at the end of Example 12.

FIG. 2A is a scanning optical microscopy photo relative to the powder obtained at the end of Example 1.

FIG. 2B is a scanning optical microscopy photo relative to the powder obtained at the end of Example 12.

FIG. 3A shows the X-ray powder analysis spectrum of sample A between $2\theta = 1^\circ$ and $2\theta = 24^\circ$ obtained using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$).

FIG. 3B shows the X-ray powder analysis spectrum of sample B between $2\theta = 1^\circ$ and $2\theta = 24^\circ$ obtained by means of a radiation Mo-K α ($\lambda = 0.71073 \text{ \AA}$).

FIG. 3C shows the X-ray powder analysis spectrum of sample C between $2\theta = 1^\circ$ and $2\theta = 24^\circ$ obtained using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$).

Sample A corresponds to the salt powder of formula (I) (HMTBA)₂Ca obtained in the first part of Example 9.

Sample B corresponds to the powder obtained at the end of Example 1.

Sample C corresponds to the powder obtained at the end of Example 12.

FIG. 4 shows a scanning electron microscope (SEM) analysis coupled to X-ray emission spectrometry, performed at the core (A) and at the surface (B) of the same particle according to Example 3.

FIG. 5 is a block diagram of a method according to the invention, implemented in a multi-effects tower.

An aqueous medium containing an acid, symbolized by the circle A, optionally passes through a heater 130 and feeds the contact device 134 by a pump 131. An aqueous medium containing a metal or metal cation symbolized by the circle B optionally passes through a heater 132 and feeds by a pump 133 the contacting device 134. The aqueous phase resulting

from the mixture between the aqueous medium A and the aqueous medium B is sprayed into the atomization tower via the spraying device 104 intended for the production of monodisperse or polydisperse aerosols.

5 An aqueous medium containing an acid, symbolized by the circle A ', optionally passes through a heater 144 and feeds by a pump 145 the spraying device 147 intended for the production of aerosols.

An aqueous medium containing an acid, symbolized by the circle A ", optionally passes through a heater 151 and feeds by a pump 152 the spraying device 148 intended for the production of aerosols.

10 The circle C represents a complementary spraying device for anti-caking agent via a powder meter 136, if necessary.

The circle D represents the introduction of the hot carrier gas, **in particular air and / or inert gas**, into the spray-drying version, via the fan 124.

15 The circle E represents the introduction of the secondary carrier gas, for drying and / or final cooling of the final stabilized composition obtained, solid or solidifying via a fan 137.

The circle J represents the introduction of the carrier gas onto the external vibrated fluidized bed 139, for the final drying or / and cooling of the final stabilized composition obtained, solid or solidified via the fan 146.

20 A cyclone 138 separates all or part of the final product F, that is to say the pulverulent composition which is recovered, and the carrier gas G which is evacuated.

The external vibrated fluidized bed 139 allows the recovery of all or part of the final product H, that is to say the pulverulent composition, from the bottom of the tower.

25 The introduction of the secondary air E takes place through a permeable bottom 142 of the tower 135 to bring the pulverulent material into a fluidized bed. The spent air is evacuated by one or more orifices 143 provided through the upper wall of the enclosure 101.

The introduction of the secondary air J takes place through a permeable bottom 149 of the vibrated fluidized bed 139 to bring the pulverulent material into a fluidized bed. The waste air is evacuated via the line 150 connected to the inlet of the cyclone 138.

30 In this example, the spent air then passes through the cyclone 138 which produces on one side of the product particles F and on the other side the air to be evacuated G. The majority of the particles are collected just above the permeable wall 142. FIG. 1 illustrates that the particles are collected either directly in F or via the external fluidized bed 139 at H. FIG.

The addition of a powdered substance, in particular fine particles of the pulverulent composition recovered at the outlet of the cyclone 138, product F, or of the powdered composition, can also be provided, represented by the circle I, in the spraying zone. which is injected by means of the device 141 consisting mainly of a powder dispenser.

5 **FIG. 6** is a block diagram of a method according to the invention, implemented in a multi-effects tower and as described in FIG. 5, with $A = A' = A''$.

FIG. 7 is a block diagram of a method according to the invention, implemented in a multi-effects tower.

10 An aqueous medium containing an acid, symbolized by the circle A, is transferred into a reactor C equipped with a thermostatically controlled jacket 161. An aqueous medium containing a metal or metal cation symbolized by the circle B is added gradually to the reactor C with stirring. The aqueous phase K resulting from the mixture between the aqueous medium A and the aqueous medium B is fed by the delivery pump 162 to be sprayed into the atomization tower via the spraying device 104 intended for the production of monodisperse
15 aerosols or polydispersed.

An aqueous medium containing an acid, symbolized by the circle A', optionally passes through a heater 144 and feeds by a pump 145 the spraying device 147 intended for the production of aerosols.

20 An aqueous medium containing an acid, symbolized by the circle A'', optionally passes through a heater 151 and feeds by a pump 152 the spraying device 148 intended for the production of aerosols.

The circle C represents a complementary spraying device for anti-caking agent via a powder meter 136, if necessary.

25 The circle D represents the introduction of the hot carrier gas, in particular air and / or inert gas, into the spray-drying version, via the fan 124.

The circle E represents the introduction of the secondary carrier gas, for drying and / or final cooling of the final stabilized composition obtained, solid or solidifying via a fan 137.

30 The circle J represents the introduction of the carrier gas onto the external vibrated fluidized bed 139, for the final drying or / and cooling of the final stabilized composition obtained, solid or solidified via the fan 146.

A cyclone 138 separates all or part of the final product F, that is to say the pulverulent composition which is recovered, and the carrier gas G which is evacuated.

The external vibrated fluidized bed 139 allows the recovery of all or part of the final product H, that is to say the pulverulent composition, from the bottom of the tower.

The introduction of the secondary air E takes place through a permeable bottom 142 of the tower 135 in order to put the pulverulent material in the form of a fluidized bed. The spent air is evacuated through an orifice 143 provided through the upper wall of the enclosure 101. The introduction of the secondary air J takes place through a permeable bottom 149 of the vibrated fluidized bed 139 to bring the pulverulent material into a fluidized bed. The waste air is evacuated via the line 150 connected to the inlet of the cyclone 138.

In this example, the spent air then passes through the cyclone 138 which produces on one side of the product particles F and on the other side the air to be evacuated G. The majority of the particles are collected just above the permeable wall 142. FIG. 1 illustrates that the particles are collected either directly in F or via the external fluidized bed 139 at H. FIG.

The addition of a powdered substance, in particular fine particles of the pulverulent composition recovered at the outlet of the cyclone 138, product F, or of the powdered substance represented by the circle I, can be provided in the spraying zone. which is injected by means of the device 141 consisting mainly of a powder metering device.

FIG. 8 is a schematic diagram of a method according to the invention, implemented in a fluidized air bed.

A powder composition of salt type $(\text{HMTBA})_2\text{Ca}$, symbolized by the circle B is incorporated in a fluidized air bed 170. An aqueous medium containing an acid, symbolized by the circle A, optionally passes through a heater 171 and feeds by a pump 172 a spraying device 173 intended for the production of aerosols.

The circle D represents the introduction of the carrier gas for drying and / or final cooling of the final stabilized composition obtained, solid or solidified via a fan 174.

The introduction of the gas D takes place through a permeable bottom 175 of the fluidized bed in order to put the pulverulent material B in the form of a fluidized bed. The spent air is evacuated through filter (s) through an orifice 176 provided through the upper wall of the enclosure 177.

The final pulverulent composition H is recovered at the end of the batch when the fluidized bed is emptied.

EXAMPLES

The following Examples 1 to 12 illustrate the invention.

Example 1: Preparation of a powder having a TOS of 88.3 wt.%.

One kilogram of salt (HMTBA)₂Ca at 85.5% TOS, 11.7% calcium and 2.3% moisture was incorporated in a fluidized air bed of a useful volume of 5 liters. 300 g of a solution of HMTBA containing 88% dry matter was sprayed at a rate of 450 g / hr, a spraying pressure of 1.5 bar and an inlet temperature on the d air mixture of 60 ° C. At the end of the spraying, the product was dried for 5 min.

The product obtained had a TOS of 88.3%, a calcium content of 9.2% and a moisture content of 1.3%). The average particle size of this product is 191 µm, the unflatted density of 390 g / l and the packed density at 480 g / l.

Example 2: Preparation of a powder having a TOS of 89.3% by weight

One kilogram of salt (HMTBA)₂Ca at 84.6% TOS, 11.5% calcium and 1.9% moisture was incorporated into a fluidized air bed of a useful volume of 5 liters. To this powder, 504 g of a HMTBA solution containing 88% dry matter was sprayed at a flow rate of 250 g / H, a spraying pressure of 1.5 bar and an inlet temperature on the bed of fluidized air of 60 ° C. At the end of the spraying, the product was dried for 5 min.

The product obtained had a TOS of 89.3%, a calcium content of 8% and a moisture content of 1.6%.

Example 3: Preparation of a powder having a TOS of 88.2% by mass

Two kilograms of salt (HMTBA)₂Ca at 85.5% TOS, 11.7% calcium and 2.3% moisture were incorporated into a fluidized air bed of a useful volume of 12 liters. On this powder, 670 g of a HMTBA solution containing 88% dry matter was sprayed at a flow rate of 600 g / H, a spray pressure of 1 bar and an inlet temperature of the air bed fluidized bed of 55 ° C. At the end of the spraying, the product was dried for 5 min.

The product obtained had a TOS of 88.2%, a calcium content of 8.8%, and a moisture content of 2.2%. The average particle size of this product is 150 µm, the uncut density of 370 g / l, and the packed density of 400 g / l.

Example 4 :Preparation of a powder having a TOS of 88.1% by mass

A grinding stage on a knife mill is carried out on two kilograms of a salt (HMTBA)₂Ca in the form of extrudates obtained according to patent FR2964968. The powder obtained after grinding has a TOS of 74%, a calcium content of 11.2%, a water content of 11% and an average particle size of 150 µm. One kilogram of this product is incorporated into a fluidized bed of a useful volume of 5 liters. 400 g of an HMTBA solution containing 88% dry matter is sprayed onto this powder at a flow rate of 300 g / H, a spraying pressure of 1.5

bar and an inlet temperature of the air bed fluidized bed of 60 ° C. The product is then dried for 30 minutes.

The product obtained had a TOS of 88.1%, a calcium content of 9.2% and a moisture content of 1.4%. The average particle size of this product is 250 µm and the bulk density is 510 g / L.

5 **Example 5:** Preparation of a powder having a TOS of 88.4 mass%

One kilogram of salt (HMTBA)₂Ca at 85.5% TOS, 11.7% calcium and 2.3% moisture is incorporated in a fluidized air bed. 275 g of a 95.47% HMTBA solution of dry matter heated at a temperature of 60 ° C. is sprayed onto this powder at a flow rate of 300 g / H, a spraying pressure of 1.5 bar and a fluidized bed air inlet temperature of 60 ° C. The product is
10 then dried for 5 minutes.

The product obtained had a TOS of 88.4%, a calcium content of 8.9%, and a moisture content of 1.5%. The average particle size of this product is 680 µm, the uncut density of 380 g / l, and the bulk density of 410 g / l.

Example 5 bis: Preparation of a powder having a TOS of 88.2% by mass

15 Three kilograms of salt (HMTBA)₂Ca at 85.5% TOS, 11.7% calcium and 2.3% moisture are incorporated in a rotary granulator with a useful volume of 5 liters of GLATT GRC3 type. On this powder, 1 kg of a HMTBA solution containing 88% dry matter is sprayed at a flow rate of 600 g / H, a spraying pressure of 1.5 bar, an inlet temperature of the granulator of 60 ° C and a disk rotation speed of 200 rpm. The product is then dried for 5 minutes.

20 The product obtained had a TOS of 88.2%, a calcium content of 9.1% and a moisture content of 1.7%. The average particle size of this product is 230 µm and the bulk density is 540 g / l.

Example 6: Preparation of a powder having a TOS of 88.1% by weight

A salt powder (HMTBA)₂Ca containing 85.2% TOS, 1.8% calcium and 1.8% moisture was continuously fed to a multiple atomisation tower at a flow rate of 200 kg / H.
25 At the bottom of the drying tower was continuously sprayed a solution of HMTBA with 88% dry matter. This solution was sprayed on the one hand on the static bed of the industrial plant at a flow rate of 60 kg / h and a spraying pressure of 4 bar and on the vibrofluidizer at a flow rate of 16 kg / h and a spray pressure of 1.5 bar.

The temperatures applied were 100 ° C. for the static bed temperature, 70 ° C. for the first part
30 of the vibrofluidizer and 30 ° C. for the second part of the vibrofluidizer.

The product obtained had a TOS of 88.1%, a calcium content of 9.1%, and a moisture content of 1.4%. The average particle size of this product is 196 µm, the bulk density 530 g / l and the packed density at 10 strokes of 560 g / l.

Example 7: Preparation of a powder having a TOS of 88.5% by mass

A salt powder (HMTBA)₂Ca with 85.18% TOS, 11.78% calcium and 1.79% moisture is continuously fed into a multiple effect tower at a flow rate of 200 kg / H. At the bottom of the drying tower is continuously sprayed a solution of HMTBA with 96% dry matter, heated to a temperature of 60 ° C. so as to lower its viscosity to below 200 centipoises. This solution is sprayed on the one hand on the static bed of the industrial plant at a flow rate of 48 kg / h and a spraying pressure of 3.5 bar, and on the other hand to the vibrofluidizer at a flow rate of 13 kg / H and a spraying pressure of 1.5 bar.

The temperatures of the liquid feed lines are thermostated at 60 ° C. so as to ensure a satisfactory spraying of the concentrated HMTBA solution.

The temperatures applied are 100 ° C. for the static bed temperature, 70 ° C. for the first part of the vibrofluidizer and 30 ° C. for the second part of the vibrofluidizer.

The product obtained had a TOS of 88.5%, a calcium content of 8.8%, and a moisture content of 1.3%. The average particle size of this product is 250 µm and the bulk density is 550 g / L.

Example 8 Preparation of a powder having a TOS of 88.3% by weight.

A lime milk prepared with 30% dry matter and a solution of HMTBA with 88% dry matter are continuously mixed according to the conditions of the patent FR2988091.

The feed rates are respectively 95 kg / H for lime milk and 130 kg / H for the HMTBA solution.

The reaction mixture is sprayed with a nozzle according to the knowledge of those skilled in the art into a multi-effect atomization tower having an inlet temperature of 180 ° C. and an outlet temperature of 102 ° C.

At the bottom of the tower, a solution of HMTBA with 88% of EST is sprayed on the one hand on the static bed of the MSD tower at a flow rate of 35 kg / h and a spraying pressure of 3 bars, on the vibrofluidizer at a flow rate of 10 kg / h and a spraying pressure of 1.5 bar.

The temperatures applied are 70 ° C. for the static bed temperature, 60 ° C. for the first part of the vibrofluidizer and 30 ° C. for the second part of the vibrofluidizer.

The product obtained had a TOS of 88.3%, a calcium content of 8.9%, and a humidity of 1.6%. The average grain size of this product is 180 µm and the bulk density of 420 g / l.

Example 9: Preparation of a powder having a TOS of 88.6% by weight

A lime milk prepared with 30% dry matter and an HMTBA solution containing 88% dry matter were continuously mixed in an atomizing turbine (of the NIRO Atomizer type). The feed rates were respectively 3.5 kg / h for lime milk and 4.5 kg / h for the HMTBA solution.

The reaction mixture was atomized in a single-effect spray tower at an inlet temperature of 140° C. Outlet temperature of 85° C.

The product was then taken up in a fluidized air bed to simulate a multiple effect tower.

330 g of a solution of HMTBA containing 88% dry matter was sprayed onto 1 kg of powder
5 previously manufactured at a flow rate of 300 g / h, a spraying pressure of 1.5 bar and an inlet temperature of fluidized air bed of 60 ° C. At the end of the spraying, the product was dried for 5 min.

The product obtained had a TOS of 88.6%, a calcium content of 8.7% and a moisture content of 1.5%.

10 **Example 10:** Preparation of a powder having a TOS of 88.6% by mass

A lime milk prepared with 37% dry matter and a solution of HMTBA with 88% dry matter are continuously mixed according to the conditions of patent FR2988091.

The feed rates are respectively 90 kg / H for the milk of lime and 150 kg / H for the HMTBA solution.

15 The mixture is sprayed with a nozzle according to the knowledge of those skilled in the art in a multi-effect atomization tower with an inlet temperature of 180 ° C. and an outlet temperature of 105 ° C.

At the bottom of the tower, a solution of HMTBA concentrated with 96% dry matter is sprayed on the one hand on the static bed of the MSD tower at a flow rate of 31 kg / h and a
20 spraying pressure of 3 bar, and d on the other hand on the vibrofluidizer at a flow rate of 16 kg / h and a spraying pressure of 1.5 bar.

The temperatures of the liquid supply lines are thermostatically controlled at 60 ° C.

The temperatures applied are 70 ° C. for the static bed temperature, 60 ° C. for the first part of the vibrofluidizer and 30 ° C. for the second part of the vibrofluidizer.

25 The product obtained had a TOS of 88.6%, a calcium content of 8.7%, and a moisture content of 1.3%). The average particle size of this product is 210 µm and the bulk density of 430 g / l.

Example 11: Preparation of a powder having a TOS of 88.2% by mass

A lime milk prepared with 30% dry matter and a solution of HMTBA with 88% dry matter are continuously mixed according to the conditions of patent FR2988091.

30 The feed rates are 75 kg / h for lime milk and 102 kg / h for the HMTBA solution, respectively.

The reaction mixture is sprayed with a nozzle according to the knowledge of those skilled in the art, into a multiple effect atomization tower with an inlet temperature of 160 ° C. and an

outlet temperature of 85 ° C. The drying is carried out under nitrogen in a tower equipped with a closed-circuit gas recycling system.

At the bottom of the tower, a solution of 88% HMTBA of EST is sprayed on the one hand on the static bed of the MSD tower at a flow rate of 20 kg / h and a spraying pressure of 3 bar, and d on the other hand on the vibrofluidizer at a flow rate of 15 kg / h and a spraying pressure of 1.5 bar. The temperatures applied are 60 ° C. for the static bed temperature, 50 ° C. for the first part of the vibrofluidizer and 20 ° C. for the second part of the vibrofluidizer. The product obtained had a TOS of 88.2%, a calcium content of 9%, and a humidity of 1%. The average grain size of this product is 240 µm and the bulk density 480 g / L.

Example 12: Preparation of a Powder comprising HMTBA according to a Method Not Applicable to the Present Invention and Comparison of the Product Obtained with a Product According to the Invention

The preparation was carried out batchwise in a Z-arm mixer open to the atmosphere. 372 g of a crystalline HMTBA₂(Ca) powder was incorporated in the mixer and then heated to 85 ° C. by means of the jacket of the material.

A solution of HMTBA with 88% dry matter was added 4 times and at 15 minutes intervals in the mixer in operation. The amounts added were 93 g, 92 g, 94 g and 96 g. At the end of the last addition, the preparation was kept under stirring for 37 min at a temperature of 73-82 ° C. The recovered paste was then subjected to a drying operation for 24 hours in an oven at 70 ° C.

The product obtained after drying was then ground to obtain coarse particles.

A comparative analysis of the products made according to Example 12 and Example 1 of the present application was carried out.

The table below shows the physical and chemical properties of powders.

	Example 1	Example 12
	Process belonging to the present invention	Process not belonging to the present invention
Physical properties		
Grain size, µm	Homogeneous grain size. Gauss curve with a median at 200 µm	Heterogeneous grain size agglomeration with a size from several mm to cm
Bulk density, g/l	370	680
Chemical properties		
Humidity, %	1,5	1
Calcium, %	10,1	9,4

TOS, %	88,4	89,9
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These results clearly indicate a significant difference in the physical properties of these powders. Example 12 results in the obtaining of heterogeneous granules in size with a density of 650 g / l whereas Example 1 of the present application leads to obtaining a homogeneous powder in size with a density close to 400 g / l.

- 5 Other analyzes distinguish the two types of products. Thus, the visual appearance of the powders was studied with an optical microscope (FIG. 1) and with a scanning optical microscope (FIG. 2).

The particles produced according to Example 1 are small spherical particles with a fairly narrow granular size distribution and a cream color.

- 10 The particles of Example 12 are compact aggregates which may be angular, heterogeneous in size and shape, brown in color and smooth in surface.

X-ray analysis also revealed differences in the degree of crystallinity of the particles obtained according to the process (FIG. 3), related to the intensity of the peak at $2\theta = 9^\circ$.

These results make it possible to propose a classification in ascending order of crystallinity

- 15 $A < B < C$

The sample A corresponds to the salt powder of formula (I) $(\text{HMTBA})_2\text{Ca}$ obtained in Example 9, before spraying: it is the salt nucleus of formula (I) $(\text{HMTBA})_2\text{Ca}$, without an outer layer.

Sample B corresponds to the powder obtained at the end of Example 1.

- 20 Sample C corresponds to the powder obtained at the end of Example 12.

The powder A (the salt core of formula (I) without an outer layer) and the powder B (subject of the present invention) are therefore less crystalline than the powder C.

Example 13: SEM analysis coupled to emission spectrometry X of the particles obtained according to Example 3

- 25 A SEM analysis coupled with X-ray emission spectrometry was carried out on a particle manufactured according to Example 3 in order to demonstrate the difference in chemical composition between the core of the outside of the particle (FIG. 4).

The internal quantification (FIG. 4A) is as follows:

Element	% Weight	% At
C	44,11	62,47
O	17,88	19,01
S	22,58	11,98
Ca	15,42	6,54

Total	100,00	100,00
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The atomic ratio S / Ca is, within the particle (in the core), about 1.8.

The external quantification (FIG. 4B) is as follows:

Element	% Weight	% At
C	53,01	67,39
O	22,74	21,7
S	17,6	8,38
Ca	6,65	2,53
Total	100,00	100,00

5

The atomic ratio S / Ca is, on the outside of the particle (at its surface), about 3.3.

This analysis makes it possible to demonstrate a difference in the chemical composition between the core of the particle and the outside of the particle, in particular as regards the percentage of calcium

- 10 The theoretical chemical composition of the salt of formula (I) (HMTBA)₂Ca and the complex of formula (II) (HMTBA)₄Ca is as follows:

Salt form of formula (I) = 338 g / mol

15

Atoms	Numbers	Total molecular weight, g/mol	Ratio of the atom on the total molecular weight
Carbon	10	120	35,5
Oxygen	6	96	28,4
Sulfur	2	64	18,9
Hydrogen	18	18	5,32
Calcium	1	40	11,8

The theoretical atomic ratio S / Ca is, for the salt of formula (I), about 1.6.

Complex form of formula (II) = 636 g / mol

20

Atomes	Numbers	Total molecular weight, g/mol	Ratio of the atome on the total molecular weight
Carbon	20	240	37,7
Oxygen	12	192	30,1

Sulfur	4	128	20,1
Hydrogen	36	36	5,6
Calcium	1	40	6,28

The theoretical atomic ratio S / Ca is, for the salt of formula (I), about 3.2.

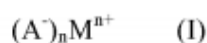
The comparison between the theoretical values and the measured values for sulfur% and calcium% indicates the presence of a salt of formula (I) of HMBTA within the particle and a

5 complex of formula (II) on the outside.

CLAIMS

1. A particle comprising:

a core consisting essentially of a salt of the following formula (I):



wherein A^- represents an anion selected from the group consisting of 2-hydroxy-4-methylthio-butanoate, methioniate and cysteinate,

M is a divalent or trivalent metal,

n being 2 when said metal is divalent and 3 when said metal is trivalent, and

a layer comprising a compound B selected from the group consisting of 2-hydroxy-4-methylthio-butanoic acid (HMTBA), methionine, cysteine, mixtures thereof, salts and complexes,

said layer coating said core,

the weight percentage of said compound B relative to the salt of formula (I) of the ring being from about 10% to about 50%,

said compound B not being, or not solely, in the form of a salt of (I),

the content of organic sulfur compounds (TOS) in said particle being greater than 87% by weight, particularly more than 88%, 89% or 90% by weight, based on the total weight of said particle.

2. A particle according to claim 1 wherein said compound B is in the form:

-free, selected from 2-hydroxy-4-methylthio-butanoic acid (HMTBA), methionine and cysteine, and / or

-said salt of formula (I) as defined in claim 1, and / or

-of a complex of formula $(A)_4M$ (II) in which A and M are as defined in claim 1, A representing preferably 2-hydroxy-4-methylthio-butanoic acid (HMTBA), said compound B not being, or not solely, in the form of a salt of formula (I),

said compound B being in particular in the form:

-free,

-of a complex of formula (II),

-of a mixture of the free form and the complex of formula (II),

-of a mixture of the free form and the salt of formula (I),

-of a mixture of the salt of formula (I) and the complex of formula (II), or

-of a mixture of the free form, the salt of formula (I) and the complex of formula (II).

3. Particle according to any one of claims 1 to 2, in which:

-the water content is less than 3%, in particular less than 2% or 1.5%, by weight,

-the calcium content is from 6 to 11% by weight, in particular 6.5 to 10%, more particularly 7 to 9%, the calcium content being in particular approximately 8%, or

-the percentage by weight of said compound B relative to the salt of formula (I) ranges from about 10% to about 40%, particularly from about 15% to about 35%, more preferably from about 20% to about 32%.

4. A particle according to any one of claims 1 to 3 wherein said metal is selected from the group comprising Mg, Be, Ca, Sr, Ba, Mn, Fe, Co, Ni, Cu, Zn, Pt, B, Al, Ga, In, in particular Mg, Ca, Fe, Mn, Al, Cu, Zn,

said salt of formula (I) being in particular (HMTBA)₂Ca, (HMTBA)₂Mg,

(HMTBA)₂Fe, (HMTBA)₂Mn, (HMTBA)₂Zn, (HMTBA)₂Cu, (HMTBA)₃Fe,

(HMTBA)₃Al, (Methionine)₂Ca, (Methionine)₂Mg, (Methionine)₂Fe,

(Methionine)₂Mn, (Methionine)₂Zn, (Methionine)₂Cu, (Methionine)₃Fe,

(Methionine)₃Al, (Cysteine)₂Ca, (Cysteine)₂Mg, (Cysteine)₂Fe, (Cysteine)₂Mn,

(Cysteine)₂Zn, (Cysteine)₂Cu, (Cysteine)₃Fe, (Cysteine)₃Al, in particular a salt of

formula (HMTBA)₂Ca, (HMTBA)₂Mg, (HMTBA)₂Fe, (HMTBA)₂Mn, (HMTBA)₂Zn,

(HMTBA)₂Cu, (Methionine)₂Ca, (Methionine)₂Mg, (Methionine)₂Fe,

(Methionine)₂Mn, (Methionine)₂Zn, (Methionine)₂Cu, (Cysteine)₂Ca, (Cysteine)₂Mg,

(Cysteine)₂Fe, (Cysteine)₂Mn, (Cysteine)₂Zn, (Cysteine)₂Cu.

5. A particle according to any one of claims 1 to 3, wherein:

-said anion A⁻ is 2-hydroxy-4-methyl-thio-butanoate,

and / or

-said compound B included in said layer is 2 -hydroxy-4-methylthio-butanoic acid

(HMTBA), or a salt or complex thereof.

6. Pulverulent composition consisting of or comprising particles as defined in any one of claims 1 to 5.

7. Pulverulent particle composition according to claim 7, wherein the particle size distribution of said particles varies from 10 to 3000 μm , in particular from 20 to 300 μm , more particularly from 100 to 250 μm , with a mean particle size distribution [Dv(0.5)].

5

8. Pulverulent composition according to any one of Claims 6 to 7, of which:

-the uncapped density is greater than 350 g/L, in particular greater than 400 g/L, or

-the packed density is greater than 400 g/L, in particular greater than 450 g/L.

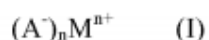
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9. Pulverulent composition according to any one of claims 6 to 8, comprising, in addition to said particles, oil, especially vegetable oil.

10. A process for the preparation of a particle comprising:

15

a core consisting essentially of a salt of the following formula (I):



wherein:

20

A⁻ represents an anion selected from the group consisting of 2-hydroxy-4-methylthiobutanoate, methioniate and cysteinate,

M is a divalent or trivalent metal,

n being 2 when said metal is divalent and 3 when said metal is trivalent, and

a layer comprising a compound B selected from the group consisting of 2-hydroxy-4-methylthio-butanoic acid (HMTBA), methionine and cysteine,

25

said layer coating said core,

the percentage by weight of said compound B with respect to the salt of formula (I) of the ring being from about 10% to about 50%,

said compound B being not, or not only, in the form of a salt of formula (I)

30

content of sulfur-containing organic compound (TOS) of said particle being greater than 87% by weight, in particular greater than 88%, 89% or 90% by weight, relative to the total weight of said particle,

said method comprising a step of spraying on a solid consisting essentially of a salt of formula (I) composition comprising a compound B selected from the group consisting of 2-hydroxy-4-methylthio-butanoic acid (HMTBA), methionine and

cysteine, the weight of said compound B being from about 10% to about 50% of the weight of the salt of formula (I) of the solid, in order to obtain said particle, in particular said composition additionally comprising water, the percentage by weight of water of said composition being from 0.5 to 50.

5

11. A method according to claim 10, wherein said spraying step is carried out:

- in a fluidized bed of batchwise or
- continuous flow, or –
- on a vibrofluidizer, or
- 10 - in atomization tower by copulverization,

said spraying step being in particular carried out continuously.

12. A process according to any one of claims 10 to 11, wherein the core consisting essentially of a salt of formula (I) is obtained:

15

- by reactive atomization,
- fluidized air bed, granulator, rotary granulator, in a mixer, by reactive extrusion, or
- by means of a static or dynamic mixer.

20