

Amorphous submicron particles

The invention relates to pulverulent amorphous solids having a very small median particle size and a narrow particle size distribution, a process for the preparation thereof and the use thereof.

Prior art

Finely divided, amorphous silica and silicates have been produced industrially for decades. As a rule, the very fine milling is carried out in spiral jet mills or opposed jet mills using compressed air as milling gas, e.g. EP 0139279.

It is known that the achievable particle diameter is proportional to the square root of the inverse of the impact velocity of the particles. The impact velocity in turn is predetermined by the jet velocity of the expanding gas jets of the respective milling medium from the nozzles used. For this reason, superheated steam can preferably be used for generating very small particle sizes, since the acceleration power of steam is about 50% greater than that of air. However, the use of steam has the disadvantage that condensation may occur in the entire milling system, particularly during the startup of the mill, which as a rule results in the formation of agglomerates and crusts during the milling process.

The median particle diameters d_{50} achieved with the use of conventional jet mills in the milling of amorphous silica, silicates or silica gels have therefore been substantially above 1 μm to date. Thus, for example, US 3,367,742 describes a process for milling aerogels, in which aerogels having a median particle diameter of 1.8 to 2.2 μm are obtained. Milling to a median particle diameter of less than 1 μm is, however, not possible with this technique. Furthermore, the particles of US 3,367,742 have a broad particle size distribution with particle diameters of 0.1 to 5.5 μm and a fraction of 15 to 20% of particles $> 2 \mu\text{m}$. A large fraction of large particles,

i.e. $> 2 \mu\text{m}$, is disadvantageous for applications in coating systems since as a result thin coats having a smooth surface cannot be produced. US 2,856,268 describes the combined milling and drying of silica gels in vapour jet mills. However, the
5 median particle diameters achieved thereby were substantially above $2 \mu\text{m}$.

An alternative possibility for milling is wet comminution, e.g. in ball mills. This leads to very finely divided suspensions of the products to be milled, cf. for example WO 200002814. It is
10 not possible with the aid of this technology to isolate a finely divided, agglomerate-free dry product from these suspensions, in particular without changing the porosymmetric properties.

It was therefore an object of the present invention to provide
15 novel finely divided, pulverulent, amorphous solids and a process for the preparation thereof.

Further objects not specified in detail arise from the overall context of the description and of the claims and examples.

The inventors have surprisingly found that it is possible to
20 mill amorphous solids by means of a very special process specified in more detail in Claims 1 to 19 to a median particle size d_{50} of less than $1.5 \mu\text{m}$ and in addition to achieve a very narrow particle distribution.

The object is thus achieved by the process as defined in more
25 detail in the claims and the following description and the amorphous solids specified in more detail there.

The invention consequently relates to a process for milling amorphous solids by means of a milling system (milling apparatus), preferably comprising a jet mill, characterized in that
30 the mill is operated in the milling phase with an operating medium selected from a group consisting of gas and/or vapour, preferably steam, and/or a gas containing steam, and in that the milling chamber is heated in a heat-up phase, i.e. before

the actual operation with the operating medium, in such a way that the temperature in the milling chamber and/or at the mill exit is higher than the dew point of the vapour and/or operating medium.

- 5 Other subject matter comprises amorphous solids having a median particle size d_{50} of $< 1.5 \mu\text{m}$ and/or a d_{90} value of $< 2 \mu\text{m}$ and/or a d_{99} value of $< 2 \mu\text{m}$.

The amorphous solids may be gels but also those having a different structure, such as, for example, particles comprising
10 agglomerates and/or aggregates. They are preferably solids containing or consisting of at least one metal and/or at least one metal oxide, in particular amorphous oxides of metals of the 3rd and 4th main group of the Periodic Table of the Elements. This applies both to the gels and to the other
15 amorphous solids, in particular those containing particles comprising agglomerates and/or aggregates. Precipitated silicas, pyrogenic silicas, silicates and silica gels are particularly preferred, silica gels comprising hydrogels as well as aerogels as well as xerogels.

- 20 The present invention furthermore relates to the use of the amorphous solids according to the invention, having a median particle size d_{50} of $< 1.5 \mu\text{m}$ and/or a d_{90} value of $< 2 \mu\text{m}$ and/or a d_{99} value of $< 2 \mu\text{m}$, for example, in surface coating systems.

With the process according to the invention, it is possible for
25 the first time to prepare pulverulent amorphous solids having a median particle size d_{50} of $< 1.5 \mu\text{m}$ and a narrow particle size distribution, expressed by the d_{90} value of $< 2 \mu\text{m}$ and/or the d_{99} value of $< 2 \mu\text{m}$.

The milling of amorphous solids, in particular those containing
30 a metal and/or metal oxide, for example of metals of the 3rd and 4th main group of the Periodic Table of the Elements, such as, for example, precipitated silicas, pyrogenic silicas, silicates and silica gels, for achieving such small median

particle sizes was possible to date only by means of wet milling. However, only dispersions could be obtained thereby. The drying of these dispersions led to reagglomeration of the amorphous particles so that the effect of the milling was

- 5 partly cancelled out and median particle sizes d_{50} of $< 1.5 \mu\text{m}$ and particle size distribution d_{90} value of $< 2 \mu\text{m}$ could not be achieved in the case of the dried, pulverulent solids. In the case of the drying of gels, the porosity was also adversely affected.
- 10 Compared with the processes of the prior art, in particular the wet milling, the process according to the invention has the advantage that it comprises dry milling which leads directly to pulverulent products having very small median particle size, which particularly advantageously may also have a high poro-
- 15 sity. The problem of reagglomeration during drying is eliminated since no drying step downstream of the milling is required.

A further advantage of the process according to the invention in one of its preferred embodiments is that the milling can

20 take place simultaneously with the drying so that, for example, a filter cake can be directly further processed. This saves an additional drying step and simultaneously increases the space-time yield.

In its preferred embodiments, the process according to the invention also has the advantage that no condensate or only

25 very small amounts of condensate form in the milling system, in particular in the mill, when starting up the milling system. Consequently, no condensate forms in the milling system even during cooling and the cooling phase is substantially shortened. The effective machine run times can therefore be

30 increased.

Finally, because no condensate or only very little condensate is formed in the milling system during startup, an already dried material to be milled is prevented from becoming wet

again, with the result that the formation of agglomerates and crusts during the milling process can be prevented.

Owing to the very special and unique median particle sizes and particle size distributions, the amorphous pulverulent solids prepared by means of the process according to the invention have particularly good properties when used in surface coating systems, for example as rheology auxiliaries, in paper coating and in paints or finishes.

For example, because of the very small median particle size and in particular the low d_{90} value and d_{99} value, the products according to the invention make it possible to produce very thin coatings.

The present invention is described in detail below. Some terms used in the description as well as in the claims are defined beforehand.

The terms powder and pulverulent solids are used synonymously in the context of the present invention and designate in each case finely comminuted, solid substances comprising small dry particles, dry particles meaning that they are externally dry particles. Although these particles generally have a water content, this water is bound to the particles or in the capillaries thereof so strongly that it is not released at room temperature and atmospheric pressure. In other words, they are particulate substances detectable by optical methods and not suspensions or dispersions. Furthermore, they may be both surface-modified and non-surface-modified solids. The surface modification is preferably effected with carbon-containing coating materials and can take place both before and after the milling.

The solids according to the invention may be present as a gel or as particle-containing agglomerates and/or aggregates. Gel means that the solids are composed of a stable, three-

dimensional, preferably homogeneous network of primary particles. Examples of these are silica gels.

Particle-containing aggregates and/or agglomerates in the context of the present invention have no three-dimensional
5 network or at least no network of primary particles which extends over all the particles. Instead, they have aggregates and agglomerates of primary particles. Examples of this are precipitated silicas and pyrogenic silicas.

A description of the structural difference of silica gels
10 compared with precipitated SiO_2 is to be found in Iler R.K., "The Chemistry of Silica", 1979, ISBN 0-471-02404-X, Chapter 5, page 462, and in Figure 3.25. The content of this publication is hereby incorporated in the description of this invention.

The process according to the invention is carried out in a
15 milling system (milling apparatus), preferably in a milling system comprising a jet mill, particularly preferably comprising an opposed jet mill. For this purpose, a feed material to be comminuted is accelerated in expanding gas jets of high velocity and comminuted by particle-particle impacts.
20 Very particularly preferably used jet mills are fluidized-bed opposed jet mills or dense-bed jet mills or spiral jet mills. In the case of the very particularly preferred fluidized-bed opposed jet mill, two or more milling jet inlets are present in the lower third of the milling chamber, preferably in the form
25 of milling nozzles, which are preferably present in a horizontal plane. The milling jet inlets are particularly preferably arranged at the circumference of the preferably round milling chambers so that the milling jets all meet at one point in the interior of the milling chamber. Particularly
30 preferably, the milling jet inlets are distributed uniformly over the circumference of the milling chamber. In the case of three milling jet inlets, the space would therefore be 120° in each case.

In a special embodiment of the process according to the invention, the milling system (milling apparatus) comprises a classifier, preferably a dynamic classifier, particularly preferably a dynamic paddle wheel classifier, especially
5 preferably a classifier according to Figures 2 and 3.

In a particularly preferred embodiment, a dynamic air classifier according to Figures 2a and 3a is used. This dynamic air classifier contains a classifying wheel and a classifying wheel shaft and a classifier housing, a classifier gap being formed
10 between the classifying wheel and the classifier housing and a shaft lead-through being formed between the classifying wheel shaft and the classifier housing, and is characterized in that flushing of classifier gap and/or shaft lead-through with compressed gases of low energy is effected.

15 When using a classifier in combination with the jet mill operated under the conditions according to the invention, a limit is imposed on the oversize particles, the product particles ascending together with the expanded gas jets being passed from the centre of the milling container through the
20 classifier, and the product which has a sufficient fineness then being discharged from the classifier and from the mill. Particles which are too coarse return to the milling zone and are subjected to further comminution.

In the milling system, a classifier can be connected as a
25 separate unit downstream of the mill, but an integrated classifier is preferably used.

An essential feature of the process according to the invention is that a heat-up phase is included upstream of the actual milling step, in which heat-up phase it is ensured that the
30 milling chamber, particularly preferably all substantial components of the mill and/or of the milling system on which water and/or steam could condense, is/are heated up so that its/their temperature is above the dew point of the vapour. The heating up can in principle be effected by any heating method.

However, the heating up is preferably effected by passing hot gas through the mill and/or the entire milling system so that the temperature of the gas is higher at the mill exit than the dew point of the vapour. Particularly preferably, it is ensured
5 that the hot gas preferably sufficiently heats up all substantial components of the mill and/or of the entire milling system which come into contact with the steam.

The heating gas used can in principle be any desired gas and/or gas mixtures, but hot air and/or combustion gases and/or inert
10 gases are preferably used. The temperature of the hot gas is above the dew point of the steam.

The hot gas can in principle be introduced at any desired point into the milling chamber. Inlets or nozzles are preferably present for this purpose in the milling chamber. These inlets
15 or nozzles may be the same inlets or nozzles through which the milling jets are also passed during the milling phase (milling nozzles). However, it is also possible for separate inlets or nozzles (heating nozzles) through which the hot gas and/or gas mixture can be passed to be present in the milling chamber. In
20 a preferred embodiment, the heating gas or heating gas mixture is introduced through at least two, preferably three or more, inlets and nozzles which are arranged in a plane and are arranged at the circumference of the preferably round mill container in such a way that the jets all meet at one point in
25 the interior of the milling chamber. Particularly preferably, the inlets or nozzles are distributed uniformly over the circumference of the milling chamber.

During the milling, a gas and/or a vapour, preferably steam and/or a gas/steam mixture, is let down through the milling jet
30 inlets, preferably in the form of milling nozzles, as operating medium. This operating medium has as a rule a substantially higher sound velocity than air (343 m/s), preferably at least 450 m/s. Advantageously, the operating medium comprises steam and/or hydrogen gas and/or argon and/or helium. It is particu-
35 larly preferably superheated steam. In order to achieve very

fine milling, it has proved particularly advantageous if the operating medium is let down into the mill at a pressure of 15 to 250 bar, particularly preferably of 20 to 150 bar, very particularly preferably 30 to 70 bar and especially preferably
5 40 to 65 bar. The operating medium also particularly preferably has a temperature of 200 to 800°C, particularly preferably 250 to 600°C and in particular 300 to 400°C.

In the case of steam as an operating medium, i.e. particularly when the vapour feed pipe is connected to a steam source, it
10 proves to be particularly advantageous if the milling or inlet nozzles are connected to a vapour feed pipe which is equipped with expansion bends.

Furthermore, it has proved to be advantageous if the surface of the jet mill has as small a value as possible and/or the flow
15 paths are at least substantially free of projections and/or if the components of the jet mill are designed for avoiding accumulations. By these measures, deposition of the material to be milled in the mill can additionally be prevented.

The invention is explained in more detail merely by way of
20 example with reference to the below-described preferred and special embodiments of the process according to the invention and the preferred and particularly suitable versions of jet mills and the drawings and descriptions of the drawings, i.e. it is not limited to these working examples and use examples or
25 to the respective combinations of features within individual working examples.

Individual features which are stated and/or shown in relation to specific working examples are not limited to these working examples or the combination with the other features of these
30 working examples but can be combined, within the technical possibilities, with any other variants, even if they are not separately discussed in the present documents.

Identical reference numerals in the individual figures and images of the drawings designate identical or similar components or components having an identical or similar effect. The diagrams in the drawing also clarify those features which are
5 not provided with reference numerals, regardless of whether such features are described below or not. On the other hand, features which are contained in the present description but not visible or shown in the drawing, are also readily understandable for a person skilled in the art.

10 As already indicated above, a jet mill, preferably an opposed jet mill, comprising integrated classifier, preferably an integrated dynamic air classifier, can be used for the production of very fine particles in the process according to the invention. Particularly preferably, the air classifier contains
15 a classifying wheel and a classifying wheel shaft and a classifier housing, a classifier gap being formed between the classifying wheel and the classifier housing and a shaft lead-through being formed between the classifying wheel shaft and the classifier housing, and is operated in such a way that
20 flushing of classifier gap and/or shaft lead-through with compressed gases of low energy is effected.

Preferably, the flushing gas is used at a pressure of not more than at least approximately 0.4 bar, particularly preferably not more than at least about 0.3 bar and in particular not more
25 than about 0.2 bar above the internal pressure of the mill. The internal pressure of the mill may be at least about in the range from 0.1 to 0.5 bar.

Furthermore, it is preferable if the flushing gas is used at a temperature of about 80 to about 120°C, in particular approximately 100°C, and/or if the flushing gas used is low-energy
30 compressed air, in particular at about 0.3 bar to about 0.4 bar.

The speed of a classifying rotor of the air classifier and the internal amplification ratio $V (= D_i/D_F)$ can be chosen or set

or can be regulatable so that the circumferential speed of the operating medium (B) at a dip tube or outlet nozzle coordinated with the classifying wheel reaches up to 0.8 times the sound velocity of the operating medium. In the formula $V (= D_i/DF)$,
5 D_i is the internal diameter of the classifying wheel (8), i.e. the distance between the inner edges of the blades (34), and DF is the internal diameter of the dip tube (20). In a particularly preferred embodiment, the internal diameter of the classifying wheel D_i is 280 mm and the internal diameter of the
10 dip tube DF is 100 mm. For the definition of the amplification ratio, cf. also Dr R. Nied, "Strömungsmechanik und Thermodynamik in der mechanischen Verfahrenstechnik [Flow mechanics and thermodynamics in mechanical process engineering]", available from management consultant
15 Dr Roland Nied, 86486 Bonstetten, Germany. Also available from NETZSCH-CONDUX Mahltechnik GmbH, Rodenbacher Chaussee 1, 63457 Hanau, Germany.

This can be further developed if the speed of a classifying rotor of the air classifier and the internal amplification
20 ratio $V (= D_i/DF)$ are chosen or set or are regulatable so that the circumferential speed of the operating medium (B) at the dip tube or outlet nozzle reaches up to 0.7 times and particularly preferably up to 0.6 times the sound velocity of the operating medium.

25 In particular, it is furthermore possible advantageously to ensure that the classifying rotor has a height clearance which increases with decreasing radius, that area of the classifying rotor through which flow takes place preferably being at least approximately constant. Alternatively or in addition, it may be
30 advantageous if the classifying rotor has an interchangeable, corotating dip tube. In an even further variant, it is preferable to provide a fines outlet chamber which has a widening cross section in the direction of flow.

Furthermore, the jet mill according to the invention can
35 advantageously contain in particular an air classifier which

contains the individual features or combinations of features of the wind classifier according to EP 0 472 930 B1. The entire disclosure content of EP 0 472 930 B1 is hereby fully incorporated by this reference in order to avoid simply adopting
5 identical subject matter. In particular, the air classifier may contain means for reducing the circumferential components of flow according to EP 0 472 930 B1. It is possible in particular to ensure that an outlet nozzle which is coordinated with the classifying wheel of the air classifier and is in the form of a
10 dip tube has, in the direction of flow, a widening cross section which is preferably designed to be rounded for avoiding eddy formations.

Preferred and/or advantageous embodiments of the milling system which can be used in the process according to the invention or
15 of the mill are evident from Figures 1 to 3a and the associated description, it once again being emphasized that these embodiments merely explain the invention in more detail by way of example, i.e. said invention is not limited to these working examples and use examples or to the respective combinations of
20 features within individual working examples.

Fig. 1 shows, in the form of a diagram, a working example of a jet mill in a partly cutaway schematic drawing,

Fig. 2 shows a working example of an air classifier of a jet mill in vertical arrangement and as a schematic
25 middle longitudinal section, the outlet tube for the mixture of classifying air and solid particles being coordinated with the classifying wheel,

Fig. 2a shows a working example of an air classifier analogous to Figure 2 but with flushing of classifier gap 8a and shaft lead-through 35b,
30

Fig. 3 shows, in schematic representation and as a vertical section, a classifying wheel of an air classifier,

Fig. 3a shows, in schematic representation and as a vertical section, the classifying wheel of an air classifier analogous to Figure 3 but with flushing of classifier gap 8a and shaft lead-through 35b,

5 Figure 4 shows the particle distribution of silica 1 (unmilled)

Figure 5 shows a TEM of Example 1,

Figure 6 shows a histogram of the equivalent diameter of Example 1,

10 Figure 7 shows a TEM of Example 2,

Figure 8 shows a histogram of the equivalent diameter of Example 2,

Figure 9 shows a TEM of Example 3a,

15 Figure 10 shows a histogram of the equivalent diameter of Example 3a,

Figure 11 shows a TEM of Example 3b,

Figure 12 shows a histogram of the equivalent diameter of Example 3b

20 Individual features which are stated and/or shown in relation to specific working examples are not limited to these working examples or the combination with the other features of these working examples but can be combined within the technical possibilities with any other variants, even if they are not
25 separately discussed in the present documents.

Identical reference numerals in the individual figures and images of the drawings designate identical or similar

components and components having an identical or similar effect. The diagrams in the drawing also clarify those features which are not provided with reference numerals, regardless of whether such features are described below or not. On the other
5 hand, features which are contained in the present description but aren't visible or shown in the drawing are also readily understandable for a person skilled in the art.

Fig. 1 shows a working example of a jet mill 1 comprising a cylindrical housing 2, which encloses a milling chamber 3, a
10 feed 4 for material to be milled, approximately at half the height of the milling chamber 3, at least one milling jet inlet 5 in the lower region of the milling chamber 3 and a product outlet 6 in the upper region of the milling chamber 3. Arranged there is an air classifier 7 having a rotatable classifying
15 wheel 8 with which the milled material (not shown) is classified in order to remove only milled material below a certain particle size through the product outlet 6 from the milling chamber 3 and to feed milled material having a particle size above the chosen value to a further milling process.

20 The classifying wheel 8 may be a classifying wheel which is customary in air classifiers and the blades of which (cf. below, for example in relation to Fig. 3) bound radial blade channels, at the outer ends of which the classifying air enters and particles of relatively small particle size or mass are
25 entrained to the central outlet and to the product outlet 6 while larger particles or particles of greater mass are rejected under the influence of centrifugal force. Particularly preferably, the air classifier 7 and/or at least the classifying wheel 8 thereof are equipped with at least one design
30 feature according to EP 0 472 930 B1.

It is possible to provide only one milling jet inlet 5, for example consisting of a single, radially directed inlet opening or inlet nozzle 9, in order to enable a single milling jet 10 to meet, at high energy, the particles of material to be milled
35 which reach the region of the milling jet 10 from the feed 4

for material to be milled, and to divide the particles of material to be milled into smaller particles which are taken in by the classifying wheel 8 and, if they have reached an appropriately small size or mass, are transported to the outside through the product outlet 6. However, a better effect is achieved with milling jet inlets 5 which are diametrically opposite one another in pairs and form two milling jets 10 which strike one another and result in more intense particle division than is possible with only one milling jet 10, in particular if a plurality of milling jet pairs are produced.

Preferably two or more milling jet inlets, preferably milling nozzles, in particular 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12 milling jet inlets, which are arranged in the lower third of the preferably cylindrical housing of the milling chamber, are used. These milling jet inlets are ideally arranged distributed in a plane and uniformly over the circumference of the milling chamber so that the milling jets all meet at one point in the interior of the milling chamber. Particularly preferably, the inlets or nozzles are distributed uniformly over the circumference of the milling chamber. In the case of three milling jets, this would be an angle of 120° between the respective inlets or nozzles. In general, it may be said that the larger the milling chamber, the more inlets or milling nozzles are used.

In a preferred embodiment of the process according to the invention, the milling chamber can, in addition to the milling jet inlets, contain heating openings 5a, preferably in the form of heating nozzles, through which hot gas can be passed into the mill in the heat-up phase. These nozzles or openings can - as already described above - be arranged in the same plane as the milling openings or nozzles 5. One heating opening or nozzle 5a, but preferably also a plurality of heating openings or nozzles 5a, particularly preferably 2, 3, 4, 5, 6, 7 or 8 heating openings or nozzles 5a, may be present.

In a very particularly preferred embodiment, the mill contains two heating nozzles or openings and three milling nozzles or openings.

For example, the processing temperature can furthermore be
5 influenced by using an internal heating source 11 between feed
4 for material to be milled and the region of the milling jets
10 or a corresponding heating source 12 in the region outside
the feed 4 for material to be milled, or by processing
particles of material to be milled which is in any case already
10 warm and avoids heat losses in reaching the feed 4 for material
to be milled, for which purpose a feed tube 13 is surrounded by
a temperature-insulating jacket 14. The heating source 11 or
12, if it is used, can in principle be of any desired form and
therefore usable for the particular purpose and chosen accord-
15 ing to availability on the market so that further explanations
in this context are not required.

In particular, the temperature of the milling jet or of the
milling jets 10 is relevant to the temperature, and the
temperature of the material to be milled should at least
20 approximately correspond to this milling jet temperature.

For the formation of the milling jets 10 introduced through
milling jet inlets 5 into the milling chamber 3, superheated
steam is used in the present working example. It is to be
assumed that the heat content of the steam after the inlet
25 nozzle 9 of the respective milling jet inlet 5 is not substan-
tially lower than before this inlet nozzle 9. Because the
energy necessary for impact comminution is to be available
primarily as flow energy, the pressure drop between the inlet
15 of the inlet nozzle 9 and the outlet 16 thereof will be
30 considerable in comparison (the pressure energy will be very
substantially converted into flow energy) and the temperature
drop too will not be inconsiderable. This temperature drop in
particular should be compensated by the heating of the material
to be milled, to such an extent that material to be milled and
35 milling jet 10 have the same temperature in the region of the

centre 17 of the milling chamber 3 when at least two milling jets 10 meet one another or in the case of a multiplicity of two milling jets 10.

Regarding the design of and procedure for preparing the milling jet 10 comprising superheated steam, in particular in the form of a closed system, reference is made to DE 198 24 062 A1, the complete disclosure content of which in this regard is hereby incorporated by reference in order to avoid simply adopting identical subject matter. For example, milling of hot slag as material to be milled is possible with optimum efficiency by a closed system.

In the diagram of the present working example of the jet mill 1, any feed of an operating medium B is typified by a reservoir or generation device 18, which represents, for example, a tank 18a, from which the operating medium B is passed via pipe devices 19 to the milling jet inlet 5 or the milling jet inlets 5 to form the milling jet 10 or the milling jets 10.

In particular, starting from a jet mill 1 equipped with an air classifier 7, the relevant working examples being intended and understood herein only as exemplary and not as limiting, a process for producing very fine particles is carried out with this jet mill 1 using an integrated dynamic air classifier 7. Apart from the fact that the milling phase is preceded by a heat-up phase in which all parts which come into contact with the vapour are heated to a temperature above the dew point of the vapour and the fact that a preferably integrated classifier is used, the innovation compared with conventional jet mills is that the speed of the classifying rotor or classifying wheel 8 of the air classifier 7 and the internal amplification ratio V ($= D_i/DF$) are preferably chosen, set or regulated so that the circumferential speed of an operating medium B at a dip tube or outlet nozzle 20 coordinated with the classifying wheel 8 reaches up to 0.8 times, preferably up to 0.7 times and particularly preferably up to 0.6 times the sound velocity of the operating medium B.

With reference to the previously explained variant with superheated steam as operating medium B or as an alternative thereto, it is particularly advantageous to use, as operating medium, gases or vapours B which have a higher and in particular substantially higher sound velocity than air (343 m/s). Specifically, gases or vapours B which have a sound velocity of at least 450 m/s are used as operating medium. This substantially improves the production and the yield of very fine particles compared with processes using other operating media, as are conventionally used according to practical knowledge, and hence optimizes the process overall.

A fluid, preferably the abovementioned steam, but also hydrogen gas or helium gas, is used as operating medium B.

In a preferred embodiment, the jet mill 1, which is in particular a fluidized-bed jet mill or a dense-bed jet mill or a spiral jet mill, is formed or designed with the integrated dynamic air classifier 7 for producing very fine particles or provided with suitable devices so that the speed of the classifying rotor or classifying wheel 8 of the air classifier 7 and the internal amplification ratio $V (= D_i/DF)$ are chosen or set or regulatable or controllable so that the circumferential speed of the operating medium B at the dip tube or outlet nozzle 20 reaches up to 0.8 times, preferably up to 0.7 times and particularly preferably up to 0.6 times the sound velocity of the operating medium B.

Furthermore, the jet mill 1 is preferably equipped with a source, for example the reservoir or generation device 18 for steam or superheated steam or another suitable reservoir or generation device, for an operating medium B, or such an operating medium source is coordinated with it, from which, for operation, an operating medium B is fed at a higher and in particular substantially higher sound velocity than air (343 m/s), such as, preferably, a sound velocity of at least 450 m/s. This operating medium source, such as, for example, the reservoir or generation device 18 for steam or superheated

steam, contains gases or vapours B for use during operation of the jet mill 1, in particular the abovementioned steam but hydrogen gas and helium gas are also preferred alternatives.

Particularly with the use of hot steam as operating medium B,
5 it is advantageous to provide pipe devices 19 which are equipped with expansion bends (not shown), and are then also to be designated as vapour feed pipe, to the inlet or milling nozzles 9, i.e. preferably when the vapour feed pipe is connected to a steam source as a reservoir or generation device
10 18.

A further advantageous aspect in the use of steam as operating medium B consists in providing the jet mill 1 with a surface which is as small as possible, or in other words in optimizing the jet mill 1 with regard to as small a surface as possible.
15 Particularly in relation to steam as operating medium B, it is particularly advantageous to avoid heat exchange or heat loss and hence energy loss in the system. This purpose is also served by the further alternative or additional design measures, namely designing the components of the jet mill 1 for
20 avoiding accumulations or optimizing said components in this respect. This can be realized, for example, by using flanges which are as thin as possible in the pipe devices 19 and for connection of the pipe devices 19.

Energy loss and also other flow-relevant adverse effects can
25 furthermore be suppressed or avoided if the components of the jet mill 1 are designed or optimized for avoiding condensation. Even special devices (not shown) for avoiding condensation may be present for this purpose. Furthermore, it is advantageous if the flow paths are at least substantially free of projections
30 or optimized in this respect. In other words, the principle of avoiding as much as possible or everything which can become cold and where condensation may therefore arise is implemented by these design variants individually or in any desired combinations.

Furthermore, it is advantageous and therefore preferable if the classifying rotor has a height clearance increasing with decreasing radius, i.e. towards its axis, in particular that area of the classifying rotor through which flow takes place being at least approximately constant. Firstly or alternatively, it is possible to provide a fines outlet chamber which has a widening cross section in the direction of flow.

A particularly preferred embodiment in the case of the jet mill 1 consists in the classifying rotor 8 having an interchangeable, corotating dip tube 20.

Further details and variants of preferred designs of the jet mill 1 and its components are explained below with reference to Figs. 2 and 3.

The jet mill 1 preferably contains, as shown in the schematic diagram in Fig. 2, an integrated air classifier 7 which is, for example in the case of designs of the jet mill 1 as a fluidized-bed jet mill or as a dense-bed jet mill or as a spiral jet mill, a dynamic air classifier 7 which is advantageously arranged in the centre of the milling chamber 3 of the jet mill 1. Depending on the volume flow rate of milling gas and classifier speed, the desired fineness of the material to be milled can be influenced.

In the air classifier 7 of the jet mill 1 according to Fig. 2, the entire vertical air classifier 7 is enclosed by a classifier housing 21 which substantially comprises the upper part 22 of the housing and the lower part 23 of the housing. The upper part 22 of the housing and the lower part 23 of the housing are provided at the upper and lower edge, respectively, with in each case an outward-directed circumferential flange 24 and 25, respectively. The two circumferential flanges 24, 25 are present one on top of the other in the installation or operational state of the air classifier 8 and are fixed by suitable means to one another. Suitable means for fixing are,

for example, screw connections (not shown). Clamps (not shown) or the like can also serve as detachable fixing means.

At virtually any desired point of the flange circumference, two circumferential flanges 24 and 25 are connected to one another
5 by a joint 26 so that, after the flange connecting means have been released, the upper part 22 of the housing can be swivel-
led upwards relative to the lower part 23 of the housing in the direction of the arrow 27 and the upper part 22 of the housing is accessible from below and the lower part 23 of the housing
10 from above. The lower part 23 of the housing in turn is formed in two parts and substantially comprises the cylindrical
classifying chamber housing 28 with the circumferential flange 25 at its upper open end and a discharge cone 29 which tapers
conically downwards. The discharge cone 29 and the classifying
15 chamber housing 28 rest one on top of the other with flanges 30, 31 at the upper and lower end, respectively, and the two
flanges 30, 31 of discharge cone 29 and classifying chamber housing 28 are connected to one another by detachable fixing
means (not shown) like the circumferential flanges 24, 25. The
20 classifier housing 21 assembled in this manner is suspended in or from support arms 28a, a plurality of which are distributed
as far as possible uniformly spaced around the circumference of the classifier or compressor housing 21 of the air classifier 7
of the jet mill 1 and grip the cylindrical classifying chamber
25 housing 28.

A substantial part of the housing internals of the air classifier 7 is in turn the classifying wheel 8 having an upper cover
disc 32, having a lower cover disc 33 axially a distance away
and on the outflow side and having blades 34 of expedient
30 contour which are arranged between the outer edges of the two
cover discs 32 and 33, firmly connected to these and distributed
uniformly around the circumference of the classifying wheel 8. In the case of this air classifier 7, the classifying wheel 8
is driven via the upper cover disc 32 while the lower cover
35 disc 33 is the cover disc on the outflow side. The mounting of
the classifying wheel 8 comprises a classifying wheel shaft 35

which is positively driven in an expedient manner, is led out of the classifier housing 21 at the upper end and, with its lower end inside the classifier housing 21, supports the classifying wheel 8 non-rotatably in an overhung bearing. The classifying wheel shaft 35 is led out of the classifier housing 21 in a pair of worked plates 36, 37 which close the classifier housing 21 at the upper end of a housing end section 38 in the form of a truncated cone at the top, guide the classifying wheel shaft 35 and seal this shaft passage without hindering the rotational movements of the classifying wheel shaft 35. Expediently, the upper plate 36 can be coordinated in the form of a flange non-rotatably with the classifying wheel shaft 35 and supported nonrotatably via rotary bearing 35a on the lower plate 37, which in turn is coordinated with a housing end section 38. The underside of the cover disc 33 on the outflow side is in the common plane between the circumferential flanges 24 and 25 so that the classifying wheel 8 is arranged in its totality within the hinged upper part 22 of the housing. In the region of the conical housing end section 38, the upper part 22 of the housing also has a tubular product feed nozzle 39 of the feed 4 for material to be milled, the longitudinal axis of which product feed nozzle is parallel to the axis 40 of rotation of the classifying wheel 8 and its drive or classifying wheel shaft 35 and which product feed nozzle is arranged radially outside on the upper part 22 of the housing, as far as possible from this axis 40 of rotation of the classifying wheel 8 and its drive or classifying wheel shaft 35.

In a particularly preferred embodiment according to Figures 2a and 3a, the integrated dynamic air classifier 1 contains a classifying wheel 8 and a classifying wheel shaft 35 and a classifier housing, as was already explained. A classifier gap 8a is defined between the classifying wheel 8 and the classifier housing 21, and a shaft lead-through 35b is formed between the classifying wheel shaft and the classifier housing 21 (cf. in this context Figs. 2a and 3a). In particular, starting from a jet mill 1 equipped with such an air classifier 7, the relevant working examples being understood here as being

only exemplary and not limiting, a process for producing very fine particles is carried out using this jet mill 1, comprising an integrated dynamic air classifier 7. In addition to the fact that the milling chamber is heated before the milling phase to
5 a temperature above the dew point of the vapour, the innovation compared with conventional jet mills consists in flushing of classifier gap 8a and/or shaft lead-through 35b with compressed gases of low energy. The peculiarity of this design is precisely the combination of the use of these compressed low-
10 energy gases with the high-energy superheated steam, with which the mill is fed through the milling jet inlets, in particular milling nozzles or milling nozzles present therein. Thus, high-energy media and low-energy media are simultaneously used.

In the embodiment according to both figures 2 and 3 on the one
15 hand and 2a and 3a on the other hand, the classifier housing 21 receives the tubular outlet nozzle 20 which is arranged axially identically with the classifying wheel 8 and rests with its upper end just below the cover disc 33 of the classifying wheel 8, which cover disc is on the outflow side, but without being
20 connected thereto. Mounted axially in coincidence at the lower end of the outlet nozzle 20 in the form of a tube is an outlet chamber 41 which is likewise tubular but the diameter of which is substantially larger than the diameter of the outlet nozzle 20 and in the present working example is at least twice as
25 large as the diameter of the outlet nozzle 20. A substantial jump in diameter is therefore present at the transition between the outlet nozzle 20 and the outlet chamber 41. The outlet nozzle 20 is inserted into an upper cover plate 42 of the outlet chamber 41. At the bottom, the outlet chamber 41 is
30 closed by a removable cover 43. The assembly comprising outlet nozzle 20 and outlet chamber 41 is held in a plurality of support arms 44 which are distributed uniformly in a star-like manner around the circumference of the assembly, connected firmly at their inner ends in the region of the outlet nozzle
35 20 to the assembly and fixed with their outer ends to the classifier housing 21.

The outlet nozzle 20 is surrounded by a conical annular housing 45, the lower, larger external diameter of which corresponds at least approximately to the diameter of the outlet chamber 41 and the upper, smaller external diameter of which corresponds
5 at least approximately to the diameter of the classifying wheel 8. The support arms 44 end at the conical wall of the annular housing 45 and are connected firmly to this wall, which in turn is part of the assembly comprising outlet nozzle 20 and outlet chamber 41.

- 10 The support arms 44 and the annular housing 45 are parts of the flushing air device (not shown), the flushing air preventing the penetration of material from the interior of the classifier housing 21 into the gap between the classifying wheel 8 or more exactly the lower cover disc 3 thereof and the outlet nozzle
15 20. In order to enable this flushing air to reach the annular housing 45 and from there the gap to be kept free, the support arms 44 are in the form of tubes, with their outer end sections led through the wall of the classifier housing 21 and connected via an intake filter 46 to a flushing air source (not shown).
- 20 The annular housing 45 is closed at the top by a perforated plate 47 and the gap itself can be adjustable by an axially adjustable annular disc in the region between perforated plate 47 and lower cover disc 33 of the classifying wheel 8.

The outlet from the outlet chamber 41 is formed by a fines
25 discharge tube 48 which is led from the outside into the classifier housing 21 and is connected tangentially to the outlet chamber 41. The fines discharge tube 48 is part of the product outlet 6. A deflection cone 49 serves for cladding the entrance of the fines discharge tube 48 at the outlet chamber
30 41.

At the lower end of the conical housing end section 38, a classifying air entry spiral 50 and a coarse material discharge 51 are coordinated in horizontal arrangement with the housing end section 38. The direction of rotation of the classifying
35 air entry spiral 50 is in the opposite direction to the

direction of rotation of the classifying wheel 8. The coarse material discharge 51 is detachably coordinated with the housing end section 38, a flange 52 being coordinated with the lower end of the housing end section 38 and a flange 53 with the upper end of the coarse material discharge 51, and both flanges 52 and 53 in turn being detachably connected to one another by known means when the air classifier 7 is ready for operation.

The dispersion zone to be designed is designated by 54. Flanges worked (bevelled) on the inner edge, for clean flow, and a simple lining are designated by 55.

Finally, an interchangeable protective tube 56 is also mounted as a closure part on the inner wall of the outlet nozzle 20, and a corresponding interchangeable protective tube 57 can be mounted on the inner wall of the outlet chamber 41.

At the beginning of operation of the air classifier 7 in the operating state shown, classifying air is introduced via the classifying air entry spiral 50 into the air classifier 7 under a pressure gradient and with an entry velocity chosen according to the purpose. As a result of introducing the classifying air by means of a spiral, in particular in combination with the conicity of the housing end section 38, the classifying air rises spirally upwards in the region of the classifying wheel 8. At the same time, the "product" comprising solid particles of different mass is introduced via the product feed nozzle 39 into the classifier housing 21. Of this product, the coarse material, i.e. the particle fraction having a greater mass, moves in a direction opposite to the classifying air into the region of the coarse material discharge 51 and is provided for further processing. The fines, i.e. the particle fraction having a lower mass, is mixed with the classifying air, passes radially from the outside inwards through the classifying wheel 8 into the outlet nozzle 20, into the outlet chamber 41 and finally via a fines outlet tube 48 into a fines outlet 58, and from there into a filter in which the operating medium in the

form of a fluid, such as, for example air, and fines are separated from one another. Coarser constituents of the fines are removed radially from the classifying wheel 8 by centrifugal force and mixed with the coarse material in order to
5 leave the classifier housing 21 with the coarse material or to circulate in the classifier housing 21 until it has become fines having a particle size such that it is discharged with the classifying air.

Owing to the abrupt widening of the cross section from the
10 outlet nozzle 20 to the outlet chamber 41, a substantial reduction in the flow velocity of the fines/air mixture takes place there. This mixture will therefore pass at a very low flow velocity through the outlet chamber 41 via the fines outlet tube 48 into the fines outlet 58 and produce only a
15 small amount of abraded material on the wall of the outlet chamber 41. For this reason, the protective tube 57 is also only a very precautionary measure. The high flow velocity in the classifying wheel 8 for reasons relating to a good separation technique, also prevails, however, in the discharge or
20 outlet nozzle 20, and the protective tube 56 is therefore more important than the protective tube 57. Particularly important is the jump in diameter with a diameter increase at the transition from the outlet nozzle 20 into the outlet chamber 41.

The air classifier 7 can besides in turn be readily maintained
25 as a result of the subdivision of the classifier housing 21 in the manner described and the coordination of the classifier components with the individual part-housings, and components which have become damaged can be changed with relatively little effort and within short maintenance times.

30 While the classifying wheel 8 with the two cover discs 32 and 33 and the blade ring 59 arranged between them and having the blades 34 is shown in the schematic diagram of Fig. 2 and 2a in the already known, customary form with parallel cover discs 32 and 33 having parallel surfaces, the classifying wheel 8 is

shown in Fig. 3 and 3a for a further working example of the air classifier 7 of an advantageous further development.

This classifying wheel 8 according to Fig. 3 and 3a contains, in addition to the blade ring 59 with the blades 34, the upper
5 cover disc 32 and the lower cover disc 33 an axial distance away therefrom and located on the outflow side, and is rotatable about the axis 40 of rotation and thus the longitudinal axis of the air classifier 7. The diametral dimension of the classifying wheel 8 is perpendicular to the axis 40 of
10 rotation, i.e. to the longitudinal axis of the air classifier 7, regardless of whether the axis 40 of rotation and hence said longitudinal axis are perpendicular or horizontal. The lower cover disc 33 on the outflow side concentrically encloses the outlet nozzle 20. The blades 34 are connected to the two cover
15 discs 33 and 32. The two cover discs 32 and 33 are now, in contrast to the prior art, conical, preferably such that the distance of the upper cover disc 32 from the cover disc 33 on the outflow side increases from the ring 59 of blades 34 inwards, i.e. towards the axis 40 of rotation, and does so
20 preferably continuously, such as, for example, linearly or non-linearly, and more preferably so that the area of the cylinder jacket through which flow takes place remains approximately constant for every radius between blade outlet edges and outlet nozzle 20. The outflow velocity which decreases owing to the
25 decreasing radius in known solutions remains at least approximately constant in this solution.

In addition to that variant of the design of the upper cover disc 32 and of the lower cover disc 33 which is explained above and in Fig. 3 and 3a, it is also possible for only one of these
30 two cover discs 32 or 33 to be conical in the manner explained and for the other cover disc 33 or 32 to be flat, as is the case for both cover discs 32 and 33 in relation to the working example according to Fig. 2. In particular, the shape of the cover disc which does not have parallel surfaces can be such
35 that the area of the cylinder jacket through which flow takes

place remains at least approximately constant for every radius between blade outlet edges and outlet nozzle 20.

The invention, in particular the process according to the invention, is described merely by way of example in the description and in the drawing by way of the working examples and not limited thereto but comprises all variations, modifications, substitutions and combinations which the person skilled in the art can derive from the present documents, in particular from the claims and the general presentations in the introduction of this description and the description of the working examples and the diagrams thereof in the drawing and can combine with his professional knowledge and the prior art. In particular, all individual features and design possibilities of the invention and their variants can be combined.

With the process described in more detail above, it is possible to mill any desired particles, in particular amorphous particles, so that pulverulent solids having a medium particle size d_{50} of $< 1.5 \mu\text{m}$ and/or a d_{90} value of $< 2 \mu\text{m}$ and/or a d_{99} value of $< 2 \mu\text{m}$ are obtained. In particular, it is possible to achieve these particle sizes or particle size distributions by dry milling.

The amorphous solids according to the invention are distinguished in that they have a median particle size (TEM) d_{50} of $< 1.5 \mu\text{m}$, preferably $d_{50} < 1 \mu\text{m}$, particularly preferably d_{50} of 0.01 to $1 \mu\text{m}$, very particularly preferably d_{50} of 0.05 to $0.9 \mu\text{m}$, particularly preferably d_{50} of 0.05 to $0.8 \mu\text{m}$, especially preferably of 0.05 to $0.5 \mu\text{m}$ and very especially preferably of 0.08 to $0.25 \mu\text{m}$ and/or a d_{90} value of $< 2 \mu\text{m}$, preferably d_{90} of $< 1.8 \mu\text{m}$, particularly preferably d_{90} of 0.1 to $1.5 \mu\text{m}$, very particularly preferably d_{90} of 0.1 to $1.0 \mu\text{m}$ and particularly preferably d_{90} of 0.1 to $0.5 \mu\text{m}$ and/or a d_{99} value of $< 2 \mu\text{m}$, preferably $d_{99} < 1.8 \mu\text{m}$, particularly preferably $d_{99} < 1.5 \mu\text{m}$, very particularly preferably d_{99} of 0.1 to $1.0 \mu\text{m}$ and particularly preferably d_{99} of 0.25 to $1.0 \mu\text{m}$. All

abovementioned particle sizes are based on the particle size determination by means of TEM analysis and image evaluation.

The amorphous solids according to the invention may be gels but also other types of amorphous solids. They are preferably
5 solids containing or consisting of at least one metal and/or metal oxide, in particular amorphous oxides of metals of the 3rd and 4th main group of the Periodic Table of the Elements. This applies both to the gels and to the amorphous solids having a different type of structure. Precipitated silicas,
10 pyrogenic silicas, silicates and silica gels are particularly preferred, silica gels including hydrogels as well as aerogels as well as xerogels.

In a first special embodiment, the amorphous solids according to the invention are particulate solids containing aggregates
15 and/or agglomerates, in particular precipitated silicas and/or pyrogenic silica and/or silicates and/or mixtures thereof, having a median particle size d_{50} of $< 1.5 \mu\text{m}$, preferably d_{50} of $< 1 \mu\text{m}$, particularly preferably d_{50} of 0.01 to $1 \mu\text{m}$, very particularly preferably d_{50} of 0.05 to $0.9 \mu\text{m}$, particularly
20 preferably d_{50} of 0.05 to $0.8 \mu\text{m}$, especially preferably of 0.05 to $0.5 \mu\text{m}$ and very especially preferably of 0.1 to $0.25 \mu\text{m}$ and/or a d_{90} value of $< 2 \mu\text{m}$, preferably d_{90} of $< 1.8 \mu\text{m}$, particularly preferably d_{90} of 0.1 to $1.5 \mu\text{m}$, very particularly preferably d_{90} of 0.1 to $1.0 \mu\text{m}$, particularly preferably d_{90} of
25 0.1 to $0.5 \mu\text{m}$ and especially preferably d_{90} of 0.2 to $0.4 \mu\text{m}$ and/or a d_{99} value of $< 2 \mu\text{m}$, preferably d_{99} of $< 1.8 \mu\text{m}$, particularly preferably d_{99} of $< 1.5 \mu\text{m}$, very particularly preferably d_{99} of 0.1 to $1.0 \mu\text{m}$, particularly preferably d_{99} of 0.25 to $1.0 \mu\text{m}$ and especially preferably d_{99} of 0.25 to $0.8 \mu\text{m}$.
30 Very particularly preferred here are precipitated silicas since they are substantially more economical in comparison with pyrogenic silicas. All abovementioned particle sizes are based on the particle size determination by means of TEM analysis and image evaluation.

In a second special embodiment, the amorphous solids according to the invention are gels, preferably silica gels, in particular xerogels or aerogels, having a median particle size d_{50} of $< 1.5 \mu\text{m}$, preferably d_{50} of $< 1 \mu\text{m}$, particularly preferably d_{50} of 0.01 to $1 \mu\text{m}$, very particularly preferably d_{50} of 0.05 to $0.9 \mu\text{m}$, particularly preferably d_{50} of 0.05 to $0.8 \mu\text{m}$, especially preferably of 0.05 to $0.5 \mu\text{m}$ and very especially preferably of 0.1 to $0.25 \mu\text{m}$ and/or a d_{90} value of $< 2 \mu\text{m}$, preferably a d_{90} of 0.05 to $1.8 \mu\text{m}$, particularly preferably d_{90} of 0.1 to $1.5 \mu\text{m}$, very particularly preferably d_{90} of 0.1 to $1.0 \mu\text{m}$, particularly preferably d_{90} of 0.1 to $0.5 \mu\text{m}$ and especially preferably d_{90} of 0.2 to $0.4 \mu\text{m}$ and/or a d_{99} value of $< 2 \mu\text{m}$, preferably d_{99} of $< 1.8 \mu\text{m}$, particularly preferably d_{99} of 0.05 to $1.5 \mu\text{m}$, very particularly preferably d_{99} of 0.1 to $1.0 \mu\text{m}$, particularly preferably d_{99} of 0.25 to $1.0 \mu\text{m}$ and especially preferably d_{99} of 0.25 to $0.8 \mu\text{m}$. All abovementioned particle sizes are based on the particle size determination by means of TEM analysis and image evaluation.

A further, even more special embodiment 2a relates to a narrow-pore xerogel which, in addition to the d_{50} , d_{90} and d_{99} values already contained in embodiment 2, also has a pore volume of 0.2 to 0.7 ml/g , preferably 0.3 to 0.4 ml/g .

A further, even more special embodiment 2b relates to a xerogel which, in addition to the d_{50} , d_{90} and d_{99} values already contained in embodiment 2, has a pore volume of 0.8 to 1.4 ml/g , preferably 0.9 to 1.2 ml/g .

A further, even more special embodiment 2c relates to a xerogel which, in addition to the d_{50} , d_{90} and d_{99} values already contained in embodiment 2, also has a pore volume of 1.5 to 2.1 ml/g , preferably 1.7 to 1.9 ml/g .

The reaction conditions and the physicochemical data of the precipitated silicas according to the invention are determined by the following methods:

Particle size determination

In the following examples, particle sizes which were measured by one of the three following methods are mentioned at various points. The reason for this is that the particle sizes

- 5 mentioned there extend over a very wide particle size range (~100 nm to 1000 μm). Depending on the expected particle size of the sample to be investigated, a different method from among the three particle size measurement methods may therefore be suitable in each case.
- 10 Particles having an expected median particle size of about > 50 μm were determined by means of screening. Particles having an expected median particle size of about 1-50 μm were investigated by means of the laser diffraction method, and TEM
- 15 analysis + image evaluation were used for particles having an expected median particle size of < 1.5 μm .

The method used for determining the particle sizes mentioned in the examples is stated in each case in the tables by means of a footnote. The particle sizes which are mentioned in the claims relate exclusively to the determination of the particle size by

20 means of transmission electron microscopy (TEM) in combination with image analysis.

1. Determination of the particle distribution by means of screening

- 25 For determining the particle distribution, the sieve fractions are determined by means of a mechanical shaker (Retsch AS 200 Basic).

For the sieve analysis, the test sieves having a defined mesh size are stacked one on top of the other in the following

30 sequence:

Dust tray, 45 μm , 63 μm , 125 μm , 250 μm , 355 μm , 500 μm .

The resulting sieve tower is fastened to the sieving machine. For screening, 100 g of solid are weighed accurately to 0.1 g and added to the uppermost sieve of the sieve tower. Shaking is effected for 5 minutes at an amplitude of 85.

- 5 After the screening has been switched off automatically, the individual fractions are reweighed accurately to 0.1 g. The fractions must be weighed directly after shaking since moisture losses may otherwise falsify the results.

The summed weights of the individual fractions should give at
10 least 95 g in order to be able to evaluate the result.

2. Determination of the particle size distribution by means of laser diffraction (Horiba LA 920)

The determination of the particle distribution is effected by
15 the laser diffraction principle on a laser diffractometer (from Horiba, LA-920).

First, the sample of the amorphous solid is dispersed in 100 ml of water without addition of dispersing additives in a 150 ml beaker (diameter: 6 cm) so that a dispersion having a propor-
20 tion by weight of 1% by weight of SiO_2 forms. This dispersion is then thoroughly dispersed (300 W, unpulsed) using an ultrasound finger (Dr Hielscher UP400s, Sonotrode H7) over a period of 5 min. For this purpose, the ultrasound finger should be attached so that the lower end thereof dips to about 1 cm above the
25 bottom of the beaker. Immediately after the dispersing, the particle size distribution of a partial sample of the dispersion subjected to ultrasound is determined using the laser diffractometer (Horiba LA-920). A refractive index of 1.09 should be chosen for the evaluation using the Horiba LA-920
30 standard software supplied.

All measurements are effected at room temperature. The particle size determination and the relevant sizes, such as, for

example, the particle sizes d_{90} and d_{99} , are automatically calculated by the device and plotted as a graph. The information and the operating instructions should be noted.

5 **3. Determination of the particle size by means of**
 transmission electron microscopy (TEM) and image analysis

The preparation of the transmission electron micrographs (TEM) is effected on the basis of ASTM D 3849-02.

10 For the measurements based on image analysis, a transmission electron microscope (from Hitachi, H-7500, having a maximum acceleration voltage of 120 kV) is used. The digital image processing is effected by means of software from Soft Imaging Systems (SIS, Münster, Westphalia). The program version iTEM 5.0 is used.

15 For the determinations, about 10-15 mg of the amorphous solid are dispersed in an isopropanol/water mixture (20 ml of isopropanol/10 ml of distilled water) and treated for 15 min with ultrasound (ultrasound processor UP 100, from Dr Hielscher GmbH, HF power 100 W, HF frequency 35 kHz). Thereafter, a small
20 amount of (about 1 ml) is taken from the prepared dispersion and then applied to the support grid. The excess dispersion is absorbed using filter paper. The grid is then dried.

The choice of magnification is described in ITEM WK 5338 (ASTM) and is dependent on the primary particle size of the amorphous
25 solid to be investigated. Usually, the electron-optical magnification 50,000 : 1 and the final magnification 20,000 : 1 are chosen in the case of silicas. For the digital recording system, ASTM D 3849 specifies the suitable resolution in
30 nm/pixel, depending on the primary particle size of the amorphous solid to be measured.

The recording conditions must be combined so that the reproducibility of the measurements can be ensured.

The individual particles to be characterized on the basis of the transmission electron micrographs must be imaged with sufficiently crisp contours. The distribution of the particles should not be too dense. The particles should as far as possible be separated from one another. There should be as few overlaps as possible.

After sampling various image sections of a TEM preparation, suitable regions are correspondingly selected. It should be ensured here that the ratio of small, medium and large particles for the respective sample is representative and characteristic and there is no selective preference of small or large particles by the operator.

The total number of aggregates to be measured depends on the scatter of the aggregate sizes: the larger this is, the more particles have to be measured in order to arrive at an adequate statistical conclusion. In the case of silicas, about 2500 individual particles are measured.

The determination of the primary particle sizes and size distributions is effected on the basis of transmission electron micrographs prepared specially for this purpose; the latter are analysed by means of a particle size analyser TGZ3 according to Endter and Gebauer (sold by Carl Zeiss). The entire measuring process is supported by the analysis software DASyLab 6.0-32.

First, the measuring ranges are calibrated according to the size range of the particles to be investigated (determination of the smallest and largest particles), after which the measurements are effected. An enlarged transparency of a transmission electron micrograph is positioned on the evaluation desk so that the centre of gravity of a particle is approximately in the centre of the measuring mark. Thereafter, by turning the hand wheel on the TGZ3, the diameter of the circular measuring mark is changed until its area is as close as possible to that of the image object to be analysed.

Frequently, the structures to be analysed are not circular. In this case, those area sections of the particle which project beyond the measuring mark have to be matched with those area sections of the measuring mark which lie outside the particle boundary. Once this match has been made, the actual counting process is triggered by pressing a foot switch. The particle in the region of the measuring mark is perforated by a marking pin striking downwards.

Thereafter, the TEM transparency is moved again on the evaluation desk until a new particle is adjusted under the measuring mark. A new matching and counting procedure is effected. This is repeated until all particles required according to the evaluation statistics have been characterized.

The number of particles to be counted depends on the scatter of the particle size: the greater this is, the more particles have to be counted in order to arrive at an adequate statistical conclusion. In the case of silicas, about 2500 individual particles are measured.

After the end of the evaluation, the values of the individual counters are logged.

The median value of the equivalent diameters of all particles evaluated is stated as the median particle size d_{50} . For determining the particle sizes d_{90} and d_{99} , the equivalent diameters of all evaluated particles are divided into classes of in each case 25 nm (0-25 nm, 25-50 nm, 50-100 nm, ... 925-950 nm, 950-975 nm, 975-1000 nm) and the frequencies of the respective classes are determined. From the cumulative plot of this frequency distribution, it is possible to determine the particle sizes d_{90} (i.e. 90% of the evaluated particles have a smaller equivalent diameter) and d_{99} .

Determination of the specific surface area (BET)

- The specific nitrogen surface area (referred to below as BET surface area) of the pulverulent solids is determined on the basis of ISO 5794-1/Annex D using the TRISTAR 3000 device
- 5 (Micromeritics) by multipoint determination according to DIN ISO 9277.

Determination of the N₂ pore volume and the pore radius distribution of mesoporous solids by nitrogen sorption

- 10 The principle of measurement is based on nitrogen sorption at 77 K (volumetric method) and can be used for mesoporous solids (2 nm to 50 nm pore diameter).

- The determination of the pore size distribution is carried out according to DIN 66134 (determination of the pore size
- 15 distribution and of the specific surface area of mesoporous solids by nitrogen sorption; method according to Barrett, Joyner and Halenda (BJH)).

- Drying of the amorphous solids is effected in a drying oven. The sample preparation and measurement are effected using the
- 20 ASAP 2400 device (from Micromeritics). Nitrogen 5.0 and helium 5.0 are used as measuring gases. Liquid nitrogen serves as a refrigerating bath. Sample weights are determined in [mg] accurately to one place after the decimal point using an analytical balance.

- 25 The sample to be investigated is predried at 105°C for 15-20 h. 0.3 to 1 g thereof is weighed into a sample vessel. The sample vessel is connected to the ASAP 2400 device and thoroughly heated at 200°C for 60 min in vacuo (final vacuum < 10 µm Hg). The sample cools to room temperature in vacuo and is covered
- 30 with a layer of nitrogen and weighed. The difference from the

weight of the nitrogen-filled sample vessel without solid gives the exact sample weight.

The measurement is effected according to the operating instructions of the ASAP 2400.

- 5 For evaluating the N₂ pore volume (pore diameter < 50 nm), the adsorbed volume is determined on the basis of the desorption branch (pore volume for pores having a pore diameter of < 50 nm).

- 10 The pore radius distribution is calculated on the basis of the measured nitrogen isotherm according to the BJH method (E.P. Barrett, L. G. Joyner, P.H. Halenda, J. Amer. Chem. Soc., vol. 73, 373 (1951)) and plotted as a distribution curve.

The average pore size (pore diameter; APD) is calculated according to the Wheeler equation

- 15
$$\text{APD [nm]} = 4000 * \text{mesopore volume [cm}^3\text{/g]} / \text{BET surface area [m}^2\text{/g]}.$$

Determination of the moisture and of the loss on drying

- 20 The moisture of amorphous solids is determined according to DIN EN ISO 787-2 after drying for 2 hours in a through-circulation drying oven at 105°C. This loss on drying predominantly consists of water moisture.

Determination of the pH

- 25 The determination of the pH of the amorphous solids is effected in the form of 5% strength aqueous suspension at room temperature on the basis of DIN EN ISO 787-9. The sample weights were

changed from the specifications of this standard (5.00 g of SiO₂ per 100 ml of demineralized water).

Determination of the DBP absorption

- 5 The DBP absorption (DBP number), which is a measure of the absorbtivity of amorphous solids, is determined on the basis of the standard DIN 53601 as follows:

12.50 g of pulverulent, amorphous solid (moisture content 4 ± 2%) are introduced into the kneader chamber (article number
10 279061) of the Brabender absorptometer "E" (without damping of the outlet filter of the torque transducer). With constant mixing (kneader blades rotating at a speed of 125 rpm), dibutyl phthalate is added dropwise to the mixture at a rate of
15 4 ml/min at room temperature by means of the "Brabender T 90/50 Dosimat". Mixing in requires only a small force and is monitored by means of the digital display. Towards the end of the determination, the mixture becomes pasty, which is indicated by a sharp increase in the force required. When the display shows 600 digits (torque of 0.6 Nm), both the kneader
20 and the DBP metering are switched off by means of an electrical contact. The synchronous motor for the DBP feed is coupled to a digital counter so that the consumption of DBP in ml can be read.

The DBP absorbed is stated in the unit [g/100g] without places
25 after the decimal point and is calculated using the following formula:

$$DBP = \frac{V * D * 100}{E} * \frac{g}{100g} + K$$

where DBP = DBP absorption in g/100g

V = consumption of DBP in ml

30 D = density of DBP in g/ml (1.047 g/ml at 20°C)

E = sample weight of silica in g

K = correction value according to moisture correction table, in g/100g

The DBP absorption is defined for anhydrous, amorphous solids. With the use of moist precipitated silicas or silica gels, the correction value K should be taken into account for calculating the DBP absorption. This value can be determined on the basis of the correction table below: for example, a silica water content of 5.8% would mean an addition of 33 g/(100 g) for the DBP absorption. The moisture of the silica or of the silica gel is determined according to the method "Determination of the moisture or of the loss on drying" described below.

Moisture correction table for dibutyl phthalate absorption - anhydrous

% moisture	.% moisture				
	.0	.2	.4	.6	.8
0	0	2	4	5	7
1	9	10	12	13	15
2	16	18	19	20	22
3	23	24	26	27	28
4	28	29	29	30	31
5	31	32	32	33	33
6	34	34	35	35	36
7	36	37	38	38	39
8	39	40	40	41	41
9	42	43	43	44	44
10	45	45	46	46	47

Determination of the tamped density

- 5 The determination of the tamped density is effected on the basis of DIN EN ISO 787-11.

A defined amount of a previously unscreened sample is introduced into a graduated glass cylinder and subjected to a specified number of tamps by means of a tamping volumeter.

During the tamping, the sample becomes more compact. As a result of the investigation carried out, the tamped density is obtained.

The measurements are carried out on a tamping volumeter having
5 a counter from Engelsmann, Ludwigshafen, type STAV 2003.

First, a 250 ml glass cylinder is tared on a precision balance. 200 ml of the amorphous solid are then introduced into the tared measuring cylinder with the aid of a powder funnel so that no cavities form. The sample amount is then weighed
10 accurately to 0.01 g. The cylinder is then tapped lightly so that the surface of the silica in the cylinder is horizontal. The measuring cylinder is placed in the measuring cylinder holder of the tamping volumeter and tamped 1250 times. The volume of the tamped sample is read accurately to 1 ml after a
15 single tamping cycle.

The tamped density $D(t)$ is calculated as follows:

$$D(t) = m * 1000/V$$

$D(t)$: tamped density [g/l]

V : volume of the silica after tamping [ml]

20 m : mass of the silica [g]

Determination of the alkali number

The alkali number determination (AN) is understood as meaning the consumption of hydrochloric acid in ml (in the case of a
25 50 ml sample volume, 50 ml of distilled water and a hydrochloric acid used which has a concentration of 0.5 mol/l) in a direct potentiometric titration of alkaline solutions or suspensions to a pH of 8.30. The free alkali content of the solution or suspension is determined thereby.

The pH apparatus (from Knick, type: 766 pH meter Calimatic with temperature sensor) and the pH electrode (combined electrode from Schott, type N7680) are calibrated at room temperature with the aid of two buffer solutions (pH = 7.00 and
5 pH = 10.00). The combined electrode is immersed in the measuring solution or suspension thermostatted at 40°C and consisting of 50.0 ml of sample and 50.0 ml of demineralized water. Hydrochloric acid solution having a concentration of 0.5 mol/l is then added dropwise until a constant pH of 8.30 is
10 established. Because the equilibrium between the silica and the free alkali content is established only slowly, a waiting time of 15 min is required before a final reading of the acid consumption. In the case of the chosen amounts of substance and concentrations, the read hydrochloric acid consumption in ml
15 corresponds directly to the alkali number, which is stated without dimensions.

As already mentioned, the examples below serve for illustration and more detailed explanation of the invention, but do not limit it in any way.

20

Starting materials:

Silica 1:

The precipitated silica used as starting material to be milled was prepared according to the following process:

25 The waterglass used at various points in the following method for the preparation of silica 1 and the sulphuric acid are characterized as follows:

Water glass: density 1.348 kg/l, 27.0% by weight of SiO_2 , 8.05
% by weight of Na_2O

30 Sulphuric acid: density 1.83 kg/l, 94% by weight

117 m³ of water are initially introduced into a 150 m³ precipitation vessel having an inclined bottom, inclined-blade MIG stirring system and Ekato fluid sheer turbine and 2.7 m³ of water glass are added. The ratio of water glass to water is
5 adjusted so that an alkali number of 7 results. The initially taken mixture is then heated to 90°C. After the temperature has been reached, water glass, at a metering rate of 10.2 m³/h, and sulphuric acid, at a metering rate of 1.55 m³/h, are metered in simultaneously for the duration of 75 min with stirring.
10 Thereafter, water glass, at a metering rate of 18.8 m³/h, and sulphuric acid, at a metering rate of 1.55 m³/h, are added simultaneously for a further 75 min at 90°C with stirring. During the entire addition time, the metering rate of the sulphuric acid is corrected if required so that an alkali
15 number of 7 is maintained during this period.

The water glass metering is then switched off. Sulphuric acid is then added in the course of 15 min so that a pH of 8.5 is then established. At this pH, the suspension is stirred for the duration of 30 min (= aged). The pH of the suspension is then
20 adjusted to 3.8 by addition of sulphuric acid in the course of about 12 min. During the precipitation, the ageing and the acidification, the temperature of the precipitation suspension is kept at 90°C.

The suspension obtained is filtered using a membrane filter
25 press and the filter cake is washed with demineralized water until a conductivity of < 10 mS/cm is found in the wash water. The filter cake is then present with a solids content of < 25%.

The drying of the filter cake is effected in a spin-flash dryer.

30 The data of silica 1 are stated in Table 1.

Hydrogel preparation

A silica gel (= hydrogel) is prepared from water glass (density 1.348 kg/l, 27.0% by weight of SiO_2 , 8.05% by weight of Na_2O) and 45% strength sulphuric acid.

For this purpose, 45% strength by weight sulphuric acid and
5 soda water glass are thoroughly mixed so that a reactant ratio corresponding to an excess of acid (0.25 N) and an SiO_2 concentration of 18.5% by weight is established. The resulting hydrogel is stored overnight (about 12 h) and then crushed to a particle size of about 1 cm. It is washed with demineralized
10 water at 30 - 50°C until the conductivity of the wash water is below 5 mS/cm.

Silica 2 (hydrogel)

The hydrogel prepared as described above is aged with addition
15 of ammonia at pH 9 and 80°C for 10 - 12 hours and then adjusted to pH 3 with 45% strength by weight sulphuric acid. The hydrogel then has a solids content of 34 - 35%. It is then coarsely milled on a pinned-disc mill (Alpine type 160Z) to a particle size of about 150 μm . The hydrogel has a residual
20 moisture content of 67%.

The data of silica 2 are stated in Table 1.

Silica 3a:

Silica 2 is dried by means of a spin-flash dryer (Anhydro A/S,
25 APV, type SFD47, $T_{\text{in}} = 350^\circ\text{C}$, $T_{\text{out}} = 130^\circ\text{C}$) so that it has a final moisture content of about 2% after drying.

The data of silica 3a are stated in Table 1.

Silica 3b:

The hydrogel prepared as described above is further washed at about 80°C until the conductivity of the wash water is below 2 mS/cm and is dried in a through-circulation drying oven

5 (Fresenberger POH 1600.200) at 160°C to a residual moisture content of < 5%. In order to achieve a more uniform metering behaviour and milling result, the xerogel is precomminuted to a particle size of < 100 µm (Alpine AFG 200).

The data of silica 3b are stated in Table 1.

10

Silica 3c:

The hydrogel prepared as described above is aged with addition of ammonia at pH 9 and 80°C for 4 hours, then adjusted to about pH 3 with 45% strength by weight sulphuric acid and dried in a
15 through-circulation drying oven (Fresenberger POH 1600.200) at 160°C to a residual moisture content of < 5%. In order to achieve a more uniform metering behaviour and milling result, the xerogel is precomminuted to a particle size of < 100 µm (Alpine AFG 200).

20 The data of silica 3c are stated in Table 1.

Table 1 - Physicochemical data of the unmilled starting materials

		Silica 1	Silica 2	Silica 3a	Silica 3b	Silica 3c
Particle size distribution by means of laser diffraction (Horiba LA 920)						
d ₅₀	[µm]	22.3	n.d.	n.d.	n.d.	n.d.
d ₉₉	[µm]	85.1	n.d.	n.d.	n.d.	n.d.

d ₁₀	[μm]	8.8	n.d.	n.d.	n.d.	n.d.
Particle size distribution by means of sieve analysis						
>250 μm	%	n.d.	n.d.	n.d.	0.0	0.2
>125 μm	%	n.d.	n.d.	n.d.	1.06	2.8
> 63 μm	%	n.d.	n.d.	n.d.	43.6	57.8
> 45 μm	%	n.d.	n.d.	n.d.	44.0	36.0
< 45 μm	%	n.d.	n.d.	n.d.	10.8	2.9
Moisture	%	4.8	67%	< 3%	< 5%	< 5%
pH value	-	6.7	n.d.	n.d.	n.d.	n.d.

n.d. = not determined

Examples 1 - 3: Milling according to the invention

For preparation for the actual milling with superheated steam, a fluidized-bed opposed jet mill according to Figures 1, 2a and 5 3a is first heated to a mill exit temperature of about 105°C via the two heating nozzles 5a (only one of which is shown in Figure 1) through which hot compressed air at 10 bar and 160°C is passed.

For depositing the milled material, a filter unit (not shown in 10 Figure 1) is connected downstream of the mill, the filter housing of which filter unit is heated in the lower third indirectly via attached heating coils by means of 6 bar saturated steam, likewise for preventing condensation. All

apparatus surfaces in the region of the mill, of the separation filter and of the supply lines for steam and hot compressed air are specially insulated.

After the desired heat-up temperature has been reached, the
5 supply of hot compressed air to the heating nozzles is switched off and the supply of superheated steam (38 bar(abs), 330°C) to the three milling nozzles is started.

For protecting the filter material used in the separation filter and for establishing a certain residual water content
10 of, preferably, 2 to 6% in the milled material, water is sprayed into the milling chamber of the mill via a compressed-air-operated binary nozzle in the start phase and during the milling, depending on the mill exit temperature.

The product feed is begun when the relevant process parameters
15 (cf. Table 2) are constant. The feed rate is regulated as a function of the resulting classifier stream. The classifier stream regulates the feed rate in such a way that about 70% of the nominal flow cannot be exceeded.

A speed-controlled rotary-vane feeder which meters the feed
20 material from a storage container via a synchronous lock serving as a barometric closure into the milling chamber under superatmospheric pressure acts as feed member (4).

The comminution of the coarse material is effected in the expanding vapour jets (milling gas). Together with the let-down
25 milling gas, the product particles ascend in the centre of the mill container to the classifying wheel. Depending on the set classifier speed and amount of milling vapour (cf. Table 1), the particles which have sufficient fineness pass together with the milling vapour into the fines outlet and from there into
30 the downstream separation system, while particles which are too coarse pass back into the milling zone and are subjected to further comminution. The discharge of the fines separated off

from the separation filter into the subsequent storage and packing is effected by means of a rotary-vane feeder.

The milling pressure of the milling gas which prevails at the milling nozzles and the amount of milling gas resulting therefrom in combination with the speed of the dynamic paddle wheel classifier determine the fineness of the particle distribution function and the oversize limit.

The relevant process parameters are shown in Table 2, and the product parameters in Table 3:

10

Table 2

Example		Example 1	Example 2	Example 3a	Example 3b	Example 3c
Starting material		Silica 1	Silica 2	Silica 3a	Silica 3b	Silica 3c
Nozzle diameter	[mm]	2.5	2.5	2.5	2.5	2.5
Nozzle type		Laval	Laval	Laval	Laval	Laval
Number	[units]	3	3	3	3	3
Internal mill pressure	[bar abs.]	1.306	1.305	1.305	1.304	1.305
Entry pressure	[bar abs.]	37.9	37.5	36.9	37.0	37.0
Entry temperature	[°C]	325	284	327	324	326

Mill exit temperature	[°C]	149.8	117	140.3	140.1	139.7
Classifier speed	[min ⁻¹]	5619	5500	5491	5497	5516
Classifier current	[A%]	54.5	53.9	60.2	56.0	56.5
Dip tube diameter	[mm]	100	100	100	100	100

Table 3

		Example 1	Example 2	Example 3a	Example 3b	Example 3c
d ₅₀ ¹⁾	nm	125	106	136	140	89
d ₉₀ ¹⁾	nm	275	175	275	250	200
d ₉₉ ¹⁾	nm	525	300	575	850	625
BET surface area	m ² /g	122	354	345	539	421
N ₂ pore volume	ml/g	n.d.	1.51	1.77	0.36	0.93
Average pore size	nm	n.d.	17.1	20.5	2.7	8.8
DBP (anhydrous)	g/100g	235	293	306	124	202

Tamped density	g/l	42	39	36	224	96
Loss on drying	%	4.4	6.1	5.5	6.3	6.4

¹⁾ Determination of the particle size distribution by means of transmission electron microscopy (TEM) and image analysis

List of reference numerals

	1	Jet mill
	2	Cylindrical housing
5	3	Milling chamber
	4	Feed for material to be milled
	5	Milling jet inlet
	5a	Heating nozzles
	6	Product outlet
10	7	Air classifier
	8	Classifying wheel
	8a	Classifier gap
	9	Inlet opening or inlet nozzle
15	10	Milling jet
	11	Heating source
	12	Heating source
	13	Feed tube
	14	Temperature-insulating jacket
20	15	Inlet
	16	Outlet

	17	Centre of the milling chamber
	18	Reservoir or generation device
	19	Pipe devices
	20	Outlet nozzles
5	21	Classifier housing
	22	Upper part of housing
	23	Lower part of housing
	24	Circumferential flange
	25	Circumferential flange
10	26	Joint
	27	Arrow
	28	Classifying chamber housing
	28a	Support arms
	29	Discharge cone
15	30	Flange
	31	Flange
	32	Cover disc
	33	Cover disc
	34	Blade
20	35	Classifying wheel shaft

	35a	Rotary bearing
	35b	Shaft lead-through
	36	Upper worked plates
	37	Lower worked plate
5	38	Housing end section
	39	Product feed nozzle
	40	Axis of rotation
	41	Outlet chamber
	42	Upper cover plate
10	43	Removable cover
	44	Support arms
	45	Conical annular housing
	46	Intake filter
	47	Perforated plate
15	48	Fines discharge tube
	49	Deflection cone
	50	Classifying air inlet spiral
	51	Coarse material discharge
	52	Flange
20	53	Flange

- 54 Dispersion zone
- 55 Flanges worked (bevelled) on the inner edge, and lining
- 56 Interchangeable protective tube
- 57 Interchangeable protective tube
- 5 58 Fines outlet
- 59 Blade ring

Patent Claims:

1. Process for milling amorphous solids by means of a milling system (milling apparatus), preferably a milling system comprising a jet mill, characterized in
5 that the mill is operated in the milling phase with an operating medium selected from the group consisting of gas and/or vapour, preferably steam, and/or a gas containing steam, and in that the milling chamber is heated in a heat-up phase, i.e. before the actual
10 operation with the operating medium, in such a way that the temperature in the milling chamber and/or at the mill exit is higher than the dew point of the vapour and/or operating medium.
2. Process according to Claim 1, characterized in that
15 the jet mill is a fluidized-bed opposed jet mill or a dense-bed jet mill or a spiral jet mill.
3. Process according to Claim 1 or 2, characterized in that the milling system or the mill is operated in the heat-up phase with hot gas and/or a gas mixture,
20 preferably with hot air and/or combustion gases and/or inert gases and/or mixtures thereof.
4. Process according to Claim 3, characterized in that the hot gas and/or gas mixture is passed into the milling chamber during the heat-up phase through
25 inlets, preferably nozzles, which differ from those through which the operating medium is let down during the milling phase.
5. Process according to Claim 3, characterized in that the hot gas and/or gas mixture is passed into the
30 milling chamber during the heat-up phase through the inlets, preferably nozzles, through which the

operating medium is also let down during the milling phase.

- 5 6. Process according to any of Claims 3 to 5, characterized in that the inlets for the heating gas, preferably heating nozzles, and/or the inlets for the operating medium (milling gas), preferably milling nozzles, are arranged in a plane in the lower third of the milling chamber in such a way that the heating jets and/or the milling jets all meet at a point in
10 the interior of the milling container.
- 15 7. Process according to one of Claims 1 to 6, characterized in that dry gas and/or a dry gas mixture, preferably dry air and/or combustion gas and/or inert gas and/or a mixture thereof is passed through the mill for cooling.
8. Process according to one of Claims 1 to 7, characterized in that condensation of the steam on assemblies and/or components of the milling system or of the mill is prevented.
- 20 9. Process according to one of Claims 1 to 8, characterized in that the temperature of the operating medium in the milling phase is in the range of 200 to 800°C.
- 25 10. Process according to one of Claims 1 to 9, characterized in that the pressure of the operating medium in the milling phase is in the range of 15 to 250 bar.
11. Process according to one of Claims 1 to 10, characterized in that classification of the milled material is effected, preferably by means of an integrated and/or dynamic classifier.

12. Process according to Claim 11, characterized in that the classification is effected by means of an integrated dynamic paddle wheel classifier and/or air classifier.
- 5 13. Process according to either of Claims 11 and 12, characterized in that a jet mill (1) comprising an integrated dynamic air classifier (7) is used, the speed of a classifying rotor or wheel (8) of the air classifier (7) and the internal amplification ratio V ($= D_i/DF$) being chosen or set so that the circumferential speed of the operating medium (B) at a dip tube or outlet nozzle (20) coordinated with the classifying wheel reaches up to 0.8 times the sound velocity of the operating medium (B).
- 10
- 15 14. Process according to any of Claims 11 to 13, characterized in that a milling system is used in which flushing of the gap between the classifying wheel and the classifier housing (classifier gap) and/or the shaft lead-through between the classifying wheel shaft and the classifier housing is possible and/or is carried out.
- 20
15. Process according to any of Claims 11 to 14, characterized in that a jet mill (1) comprising an integrated dynamic air classifier (7) which contains a classifying wheel (8) and a classifying wheel shaft (35) and a classifying wheel housing (21), a classifier gap (8a) being formed between the classifying wheel (8) and the classifying wheel housing (21) and a shaft lead-through (35b) being formed between the classifying wheel shaft (35) and the classifier housing (21), is used, and in that flushing of classifier gap (8a) and/or shaft lead-through (35b) with compressed gases of low energy content is effected.
- 25
- 30

16. Process according to any of Claims 10 to 15, characterized in that the amount of milling gas which enters the classifier is regulated so that the median particle size (TEM) d_{50} of the milled material obtained is less than $1.5\text{ }\mu\text{m}$ and/or the d_{90} value is $< 2\text{ }\mu\text{m}$ and/or the d_{99} value is $< 2\text{ }\mu\text{m}$.
17. Process according to any of Claims 1 to 16, characterized in that the amorphous solids are gels or particles containing aggregates and/or agglomerates, preferably amorphous solids containing or consisting of at least one metal and/or at least one metal oxide, particularly preferably amorphous oxides of metals of the 3rd and 4th main group of the Periodic Table of the Elements.
18. Process according to any of Claims 1 to 17, characterized in that amorphous particles which have already been subjected to a drying step are milled.
19. Process according to any of Claims 1 to 18, characterized in that a filter cake of amorphous particles or a hydrogel is milled or simultaneously milled and dried.
20. Amorphous pulverulent solids having a median particle size d_{50} (TEM) of $< 1.5\text{ }\mu\text{m}$ and/or a d_{90} value (TEM) of $< 2\text{ }\mu\text{m}$ and/or a d_{99} value (TEM) of $< 2\text{ }\mu\text{m}$.
21. Amorphous solids according to Claim 20, characterized in that they comprise a gel or a particulate solid containing aggregates and/or agglomerates, preferably solids containing or consisting of at least one metal and/or metal oxide, particularly preferably amorphous oxides of metals of the 3rd and 4th main group of the Periodic Table of the Elements.

22. Amorphous solids according to Claim 21, characterized in that they are silica gels which additionally have a pore volume of 0.2 to 0.7 ml/g.
- 5 23. Amorphous solids according to Claim 21, characterized in that they are silica gels which additionally have a pore volume of 0.8 to 1.5 ml/g.
24. Amorphous solids according to Claim 21, characterized in that they are silica gels which additionally have a pore volume of 1.5 to 2.1 ml/g.
- 10 25. Amorphous solids according to Claim 20, characterized in that they are particulate solids containing aggregates and/or agglomerates, preferably solids containing or consisting of at least one metal and/or metal oxide, particularly preferably amorphous oxides of
15 metals of the 3rd and 4th main group of the Periodic Table of the Elements.
26. Use of the amorphous solids according to any of Claims 20 - 25 in coating systems.
- 20 27. Coating material containing at least one amorphous solid according to any of Claims 20 - 26.