

Active-substance concentrate

The invention relates to an active-substance concentrate, the process for its preparation and its use.

It is known to prepare mixtures consisting of choline
5 chloride and precipitated silica by mixing an aqueous
solution of choline chloride together with at least 2 %
hydrophilic silica and at least about 3 % water-repellent
silica, whereby, however, the mixing process is concluded
so long as silica still rises to the surface of the mixture
10 after an interruption of the mixing movement, and by
subsequently spray-drying this mixture (DE-A 22 09 477).

The known mixture consisting of precipitated silica and
aqueous choline-chloride solution has the disadvantage that
a sufficient stability in storage is not ensured without
15 impairing the flowability.

It is furthermore known to prepare powders containing
choline chloride by atomising an aqueous choline-chloride
solution in a spray tower, in which connection a cloud of
finely divided hydrophobic precipitated silica (SIPERNAT
20 D17 produced by Degussa AG) is present in the spray tower.
In the process the hydrophobic precipitated silica is
deposited on the surface of the choline-chloride particles.
The product obtained is dried in a fluidised-bed drier. It
has an active-substance content amounting to 95.8 wt.-%
25 (DE-A 42 18 768).

The known powder that contains choline chloride has the
disadvantage that it is stable in storage only for a few
days. Water is secreted after as little as 24 hours.

The object is consequently to prepare a mixture consisting
30 of silicon-dioxide variants and active-substance solution,
in particular aqueous choline-chloride solution, that is
stable in storage over a relatively long period and remains
flowable.

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The invention provides an active-substance concentrate that is characterised by:

- Active substance: 85 to 98 wt.-%, preferably 93 to 97 wt.-%
- 5 Hydrophobic silicon-dioxide variant: 2 to 15 wt.-%, preferably 3 to 7 wt.-%
- Water (upon discharge from the drier): maximally 0.5 wt.-%
- Stability in storage: at least 1.5 years with an
10 equilibrium water content

Free-flowing powder.

By way of silicon-dioxide variant, precipitated silicas, pyrogenically prepared silicas and/or silicates may be employed.

- 15 These substances are known from Ullmann's Enzyklopädie der technischen Chemie, Volume 21, 4th Edition, pages 462 to 476 (1982).

- In a preferred embodiment of the invention the active-substance concentrate may contain choline chloride by way
20 of active substance.

Further active substances may be hygroscopic substances from the food sector, such as hydrolysed vegetable protein for example, hygroscopic substances from the animal-feedstuff sector, such as iron sulfate for example.

- 25 The invention further provides a process for preparation of the active-substance concentrate, said process being characterised in that a master-batch suspension with a content of 10 to 15 wt.-% hydrophobic silicon-dioxide variant, in particular with the hydrophobic precipitated
30 silica Sipernat D10, and 85 to 90 wt.-% of 40 to 80-% aqueous active-substance solution, in particular 70 to 80-%

aqueous choline-chloride solution, is firstly produced by mixing the constituents in the form of a reversal emulsion, for example with the aid of a dissolver disc which keeps the suspension in motion, and/or intensive mixing with the
5 aid of a bead mill with cooling device (Dyno mill), this master-batch suspension is optionally diluted with water or with further aqueous active-substance solution and is subsequently spray-dried by means of a known device.

A mixing device that subjects the material to be blended to
10 a forced supply and generates a high shear effect can be employed with particular advantage.

By way of hydrophobic precipitated silicas, precipitated silicas that are made water-repellent by known processes may be employed.

15 The water-repellent precipitated silica SIPERNAT D10 may preferably be employed. This precipitated silica is characterised by the following physicochemical characteristic data:

		SIPERNAT D10 (hydrophobic)
appearance		loose white powder
surface according to BET ¹⁾	m ² /g	90
mean particle size	µm	5
compacted bulk density ²⁾	g/l	100
drying loss ³⁾ (2 h at 105 °C)	%	3
annealing loss ^{4) 8)} (2 h at 1,000 °C)	%	7 ⁹⁾
pH value ⁵⁾ (in 5-% dispersion)		10.3 ¹⁰⁾
SiO ₂ ⁷⁾	%	98
Na ₂ O ⁷⁾	%	1.0
SO ₃	%	0.8
C ⁷⁾	%	3.0
methanol wettability	%	about 60
oversize material ⁶⁾ (acc. to Mocker, 45 µm)	%	0.01

1) acc. to ISO 5794/1

2) acc. to DIN ISO 787/11, JIS K 5101/21 not sieved

5 3) acc. to DIN ISO 787/2, ASTM D 280, JIS K 5101/21

4) acc. to ISO 3262/11, ASTM D 1208, JIS K 5101/23

5) acc. to DIN ISO 787/9, ASTM D 1208, JIS K 5101/24

6) acc. to DIN ISO 787/18, JIS K 5101/20

7) relative to the substance annealed for 2 hours at 1,000 °C

10 8) relative to the substance dried for 2 hours at 105 °C

9) contains about 3 % chemically bonded carbon

10) in water : methanol 1 : 1

Instead of the hydrophobic precipitated silica,
hydrophobic, pyrogenically prepared silicas or hydrophobic
15 silicates may also be employed.

Mixing of the constituents with a view to producing the
master-batch suspension is effected with shear forces that
permit a phase reversal - that is to say, a rewetting of
the surface of the precipitated silica - to be achieved.
20 This phase reversal signifies a complete wetting of the
hydrophobic precipitated silica with the aqueous active-
substance solution without addition of wetting agents.

Premixing may preferably be carried out by means of a dissolver disc; the definitive preparation of a premix may be carried out, in particular, by means of a bead mill. Drying is preferably effected by spray drying.

- 5 The active-substance concentrate according to the invention presents the following advantages:

In the course of storage no change occurs in the physical properties such as stability in storage, grain size or flowability, despite a maximum increase in weight amounting
10 to 33 % moisture from the air. The maximum absorption of water in this case is dependent on the atmospheric humidity. In this connection it is a question of an equilibrium content.

The active-substance concentrate according to the invention
15 may be used for the preparation of premixes and mixed feeds, in which connection it serves as a feed supplement.

Example 1

Preparation of a 95-% choline-chloride powder that is stable in storage

- 20 a) Production of a master-batch suspension

A weighed portion of 85 parts by weight of a 75-% choline-chloride solution and 15 parts by weight Sipernat D10 is mixed in a high-shearing mixing unit with cooling device (analytical mill with water cooling, diameter 6 cm; knife
25 5.5 cm; 20,000 rpm) until such time as a pasty homogeneous suspension has formed. The end of the mixing process is reached when a phase reversal has occurred and no more Sipernat D10 is floating.

It is possible for the suspension obtained in this way to
30 be diluted to any desired concentration both with 75-% choline-chloride solution and with water.

b) Preparation of the 95-% choline-chloride powder

To a weighed portion of 100 parts by weight of the master batch (85/15) 295 parts by weight of a 75-% choline-chloride solution are added and are blended with the aid of
5 a low-shearing mixing unit (lab: for example, blade agitator, magnetic stirrer). The dilution that has been formed in this way contains a Sipernat-D10 concentration amounting to 3.8 %. If it is not possible for the
10 suspension to be pumped or atomised by reason of the viscosity, further dilution can be effected with water.

The suspension obtained in this way is atomised in the spray drier with dried air or under N₂ atmosphere.

The end product is a dry 95-% choline-chloride powder that is stable in storage.

15 Example 2

Preparation of a 95-% choline-chloride powder that is stable in storage

a) Production of a master-batch suspension

A weighed portion of 90 parts by weight of a 75-% choline-chloride solution is processed in a bead mill with cooling
20 device ("Dyno Mill" type, continuous operating mode at 2,000 rpm, exit slit 0.3 mm, mixing vessel 300 ml, glass beads 1 mm diameter, blade disc 8 cm diameter) accompanied by dosing of 10 parts by weight Sipernat D10 so as to form
25 a pasty homogeneous suspension. Working may also proceed in a batch process, by the Sipernat D10

a) being dosed into the exchange vessel, whereby the suspension is constantly premixed with the aid of a dissolver disc,

30 b) being dosed through a second opening directly into the continuous suspension.

The end of the mixing process is reached when a phase reversal has occurred and no more Sipernat D10 is floating.

It is possible for the suspension obtained in this way to be diluted to any desired concentration both with 75-%
5 choline-chloride solution and with water with the aid of a simple mixing unit (for example, a propeller mixer).

b) Preparation of the 95-% choline-chloride powder

To a weighed portion of 100 parts by weight of the master batch (90/10) 163 parts by weight of a 75-% choline-
10 chloride solution are dosed and are blended with the aid of a low-shearing mixing unit (for example, a propeller mixer). The dilution that has been formed in this way contains a Sipernat-D10 concentration amounting to 3.8 %.
If it is not possible for the suspension to be pumped or
15 atomised by reason of the viscosity, further dilution can be effected with water.

The suspension obtained in this way is atomised in the spray drier with dried air or under N₂ atmosphere.

The end product is a dry 95-% choline-chloride powder that
20 is stable in storage.

Open storage at room temperature and 50 to 80-% relative humidity is undertaken with this choline-chloride powder. The results of this storage are listed in Table 1.

Table 1

Open storage at RT and 50 - 80 % rel. humidity

Storage time	Flow mark	Poured-cone height
1 day	1	12 mm
2 days	1	12 mm
3 days	1	11 mm
1 week	1	11 mm
2 weeks	1	11 mm
3 weeks	1	11 mm
4 weeks	1	10 mm
1.5 years	1	11 mm

The flow mark and the poured-cone height are determined by
5 the following methods:

Flowability by means of glass outflow vessels

For uniform emptying of a powder silo and exact dosing of
the powder a good flow behaviour (of the respective powder)
is a prerequisite. Powders that are not readily pourable
10 do not flow or only flow through outflow vessels having a
very large outflow opening; hence powders that are readily
pourable are given a low mark.

Test instruments:

measuring vessel 1. = 2.5 mm diameter
15 measuring vessel 2 = 5.0 mm diameter
measuring vessel 3 = 8.0 mm diameter
measuring vessel 4 = 12.0 mm diameter
measuring vessel 5 = 18.0 mm diameter

Manufactured by: Henz, Schulstr. 18, 63549 Ronneburg.

20 Implementation

Beginning with measuring vessel 5, the outflow vessel is
placed onto a sheet of weighing paper and is filled as far
as the upper edge with the powder to be tested by means of
a second weighing paper which serves as a funnel. By

careful lifting the opening is cleared so that the powder can flow out. If the powder flows out through one vessel, the next-smaller vessel is used and the aforementioned procedure is repeated.

5 Evaluation

Mark	Assessment
1	powder flows freely out of vessel No. 1
2	powder flows freely out of vessel No. 2
3	powder flows freely out of vessel No. 3
4	powder flows freely out of vessel No. 4
5	powder flows freely out of vessel No. 5
6	powder does not flow freely out of vessel No. 5

Flowability by means of poured-cone height

- For uniform emptying of a powder silo and exact dosing of the powder a good flow behaviour of the respective powder is a prerequisite. A good assessment criterion for the flow behaviour is the angle of repose. Since, for the same base measurement, the poured-cone height is directly related to the angle of repose and is significantly easier to determine, the poured-cone height is determined.
- 15 Readily pourable powders have a low poured-cone height.

Test instruments

- metal sieve (1 mm)
 vernier height gauge
 solid metal cylinder, $d = 50 \text{ mm}$, $h = 80 \text{ mm}$
 20 scraper

Implementation

The wire sieve is fastened to the support at a distance of about 10 cm above the solid metal cylinder. With a view to setting the definitive height of the sieve, the powder that is expected to be poorest is poured slowly onto the sieve and is carefully passed through the sieve by means of a scraper. The distance of the sieve from the vertex of the poured cone of the powder is set to 2 cm. This height is maintained in all further comparison tests. If the poured cone of the powder is evenly formed, sieving of the powder is concluded and the poured-cone height is read off at the vertex of the cone with the vernier height gauge.

Evaluation:

The poured-cone height is given in mm.



Claims

1. Active-substance concentrate, characterised by:
 - 5 Active substance: 85 to 98 wt.-%
 Hydrophobic silicon- 3 to 7 wt.-%
 dioxide variant:
 Water (upon discharge maximally 0.5 wt.-%
 from the drier):
 - 10 Stability in storage: at least 1.5 years with an
 equilibrium water content
 Free-flowing powder
2. Active-substance concentrate according to Claim 1,
15 characterised in that the active substance is choline
 chloride.
3. Process for preparation of the active-substance
 concentrate according to Claim 1 or 2, characterised in
 that a master-batch suspension with a content of 10 to
 15 wt.-% hydrophobic silicon-dioxide variant and 85 to
20 90 wt.-% of 70 to 80-% aqueous active-substance solution
 is firstly produced by mixing the constituents in the
 form of a reversal emulsion, this master-batch
 suspension is optionally diluted with water or with
 further aqueous active-substance solution and is
25 subsequently spray-dried by means of a known device.
4. Use of the active-substance concentrate according to
 Claim 1 for the preparation of premixes and mixed feeds.