

**Process for preparing a free-flowing animal feed
supplement based on a methionine salt and the granular
material obtainable therefrom.**

5 The invention relates to a process for preparing a free-flowing, easy to handle animal feed supplement based on a methionine salt in which a granulated product is obtained starting from a methionine salt solution obtained in a conventional manner and the methioninate granular products
10 obtained therefrom.

Methionine and aqueous solutions of methionine salts, in particular sodium methioninate (DE 31 05 009 C), but also substitutes such as the methionine hydroxy analogue (MHA)
15 are used all over the world as feed additives for rearing poultry, pigs and other economically useful animals and mainly promotes the production of animal protein. With regard to the increasing population of the world and increasing nutritional problems, methionine, as one of the
20 essential amino acids in the animal growth process, and its different forms, and thus also its cost effective production, are very important. Solid or liquid forms may be preferred, depending on the requirements.

25 Commercially available sodium methioninate solution has a concentration of 40 wt.% methionine and its biological value corresponds to that of solid methionine, in contrast to the substitute MHA, compared on an equimolar basis. There are several suitable methods for preparing these
30 types of sodium methioninate solutions, e.g.:

1. Dissolution of isolated methionine in caustic soda solution.
- 35 2. Alkaline hydrolysis of 5-(β -methylmercaptoethyl)-hydantoin with NaOH and/or Na₂CO₃.
3. Alkaline hydrolysis of methionine amide.

Although method 1 provides the purest product it is more costly and thus less economic than the production of methionine itself, due to an additional process step in comparison to production of the solid. In contrast,

5 methods 2 and 3 are used at an earlier point in the production of methionine and thus there is no need to isolate the solid during the production of DL-methionine, depending on capacity.

- 10 The preparation of 5-(β -methylmercaptoethyl)-hydantoin is performed in a known manner by direct synthesis from the conventional starting materials methylmercapto-propionaldehyde (MMP) and hydrocyanic acid in the presence of ammonia and carbon dioxide. Methionine amide is
- 15 prepared in a known manner by hydrolysis of methionine nitrile, which again is obtained by direct synthesis from the conventional starting materials MMP, hydrocyanic acid or ammonium cyanide and ammonia.
- 20 Depending on special requirements, it may be expedient to use a solid or a liquid form of the animal feed supplement.

The decision about which form to produce depends, *inter*

25 *alia*, on the mixing apparatus which is available and the specific preferences of the particular manufacturer.

When preparing mixed feeds, the different feedstuffs and additives are initially present as separate components

30 which, depending on their characteristics, are prepared by milling, shredding, drying or purifying. If the separate components have the characteristics required, the actual mixing process is performed in a mixing unit suitable for this process. Individual mixed batches differ, depending

35 on the size of the unit. The essential amino acid methionine is used as a supplement for mixed feeds in concentrations of the order of magnitude of 0.01 to

1.0 wt.%. These amounts are added directly to the mixed feed by appropriate weighing and metering systems.

DE 31 05 009 describes the fact that aqueous solutions of sodium or potassium methioninate have the same methionine activity as solid methionine when used as an animal feed additive.

However, a result of the low-temperature stability of methioninate solutions, which has to be guaranteed by suppliers, it has hitherto been possible to supply only solutions with a concentration of up to 40 wt.% of methioninate. Thus commercial products contain up to about 60 wt.% of water which leads to an approximately 2.5-fold increase in transport costs as compared with the transport of solid methionine. This has prevented liquid supplements based on methionine penetrating the market.

The use of crystalline sodium methioninate has not been considered due to the strongly hygroscopic nature of this compound.

However, it would be very useful to provide an additive for animal feeds which satisfies the following requirements:

1. It has precisely the same nutritive efficacy as solid crystalline methionine.
2. It can be converted into a liquid form at the desired concentration by the feedstuff mixer itself, without having to handle, for example, alkalis.
3. As little as possible "dead volume" in the form of water is carried during transport, so that the active substance content of the transported material is high.

4. The product can be adapted to the specific requirements of the individual users and optionally may also be used as a solid.

5 In view of these problems, the object of the invention is to provide a process such that the problems listed above can be solved by the product obtained. The invention also provides a new and improved solid methioninate product for animal feed supplements.

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The invention provides a process for preparing a free-flowing, easy to handle animal feed supplement based on methionine, in which the starting material is an aqueous methionine salt solution (methioninate solution) generally
15 obtained in a conventional manner, which is characterised in that the methionine salt solution is converted into a granular material in one or more stages.

This process may be performed continuously or batchwise.

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The solutions are generally 10 to 70 wt.% strength, preferably 20 to 60 wt.% strength, in particular 25 to 45 wt.% strength, with respect to methionine.

25 Sodium and/or potassium methioninate solutions are preferably used, wherein the molar ratio of methionine to K or Na ions is preferably 1.1:1 to 1:1.1, preferably 1:1.

It has also been found to be advantageous to first treat
30 the solutions to be sprayed and/or granulated with active carbon.

In one embodiment the methionine salt solution is spray dried in a spray apparatus with a centrifugal atomiser,
35 wherein the temperature difference between the inlet temperature (120 - 200°C) and the outlet temperature (60 - 100°C) should be as large as possible. The powder obtained in this way is then converted into a granular

material. This is achieved using a granulating plate, a granulating drum or a mixer. The granular mixture is preferably prepared in an Eirich mixer using an inserted, strongly shearing mixing device (cutter head insert).

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The procedure in general is such that the spray dried powder is granulated in the mixing device together with a preferably saturated solution of the methionine salt.

- 10 The ratio by weight of powder to saturated solution, with respect to solid substance, is preferably in the range from 1:0.01 to 1:0.5.

The powder obtained by spray drying generally has a bulk
15 density of 350 to 500 kg/m³, and a dust fraction of at least 1 to 5 % (Dr. Groschopp's dust test).

The granular material has a bulk density of greater than 650 kg/m³, preferably greater than 700 kg/m³ and a particle
20 size distribution of 63 to 5000 µm, preferably 100 to 3000 µm, in particular 100 to 1400 µm, wherein about 90 % has a particle size fraction > 100 µm.

The proportion with a particle size < 63 µm is generally
25 at most 2 %, preferably 1 %, the Dr Groschopp's dust fraction is < 1 %, preferably < 0.5 %.

Another process variant for preparing the granular material according to the invention is granulation in a
30 fluidised bed. In this case spraying the sodium methioninate solution and building up the feed additive granular material is performed in only one process step. The fluidised reactor being used may contain one or more crushing devices to regulate the particle size.

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Here again preferably saturated methioninate solutions are used although less concentrated solutions may also be used.

The increase in weight in the fluidised bed under steady state conditions is compensated for by continuous withdrawal of the granular material. By means of a specific mode of operation, a granular material with the
5 desired particle size can be extracted from the discharge pipe, and this may optionally be passed through a cooling zone during discharge. The fine dust extracted with the drying air from the drying chamber is separated and returned to the granulation process as nuclei for the
10 formation of granules. When preparing granular material according to the invention the temperature in the drying section of the fluidised bed is generally 100 to 200°.

Temperature management and optionally the use of one or
15 more crushing devices in the fluidised bed determines the particle sizes which can be achieved. The preferred granular material with a particle size distribution between 63 and 5000 μm , preferably between 100 and 3000 μm , in particular between 100 and 1400 μm , wherein
20 about 90 % has a particle size greater than 100 μm , is produced according to the invention with the optional addition of additives. The dryer is designed, with respect to the amounts of air used (rate of flow of air), in such a way that on the one hand the granular material is not
25 broken down and on the other hand fine dust is extracted below a given low particle size.

The granular material prepared in this way is preferably produced in the form of spheres and has a bulk density of
30 > 650 kg/m^3 , preferably > 700 kg/m^3 and a dust fraction of < 1 %, preferably < 0.5 % (Dr. Groschopp's dust test).

Other shaping processes, such as e.g. extrusion (Bextruder) may optionally be used to prepare granular
35 material according to the invention. The equipment may then be connected in series with another process. Thus, for example, it is possible to combine an intensive mixer

with a Bextruder and a fluidised bed drier both for continuous and batchwise processes.

In order to improve the ease of handling of the granular material being prepared it is recommended that the methionine salt solutions be sprayed and granulated in the presence of additives based on siliceous materials.

These include hydrophilic and hydrophobic silicas, of a pyrogenic nature or prepared by precipitation of 5 to 300 m²/g (sic), preferably spray dried silicas. Finely divided zeolites e.g. zeolite A or bentonites may also be used.

These additives may either be suspended in the solution being sprayed or preferably be introduced with the air stream into the equipment in which the solution is sprayed and optionally granulated.

The amount of other additives is 0.1 to 10 wt.%, preferably 0.1 to 5 wt.%, with respect to the granulated solid. Obviously these additive include, in addition to the siliceous compounds, preferred substances which are authorised for use in animal feedstuffs, in particular fatty acids and their salts, preferably alkali metal or alkaline earth salts.

The fatty acids include in particular stearic acid and palmitic acid and mixtures of fatty acids containing 16 to 18 carbon atoms or their above-mentioned salts.

Whereas non-granulated sodium methioninate cakes easily and loses its free-flowing properties due to its hygroscopic nature, unexpectedly this does not occur with the granular materials according to the invention. They remain free-flowing and easy to handle even when exposed to the weather and, in comparison to spray dried powders,

exhibit obvious improvements to their properties with regard to:

- a) free-flowing character and ease of handling
- b) reduced dust content,
- 5 c) reduced tendency to cake when exposed to the weather
- d) high bulk density.

Whereas spray dried products cake after being stored for
10 7 days at 55 % relative humidity, granular material according to the invention remains free-flowing and easy to meter out.

The process according to the invention can be performed
15 due only to the unexpected fact that methioninate does not decompose, even with inlet temperatures of more than 100°C, in the spray drier or equivalent apparatus.

Decomposition of these compounds, which is rendered
20 obvious e.g. by the presence of yellow discoloration, would actually be expected due to the known instability of these compounds in the presence of alkalis.

These granular materials prepared for the first time are
25 also subjects of the invention.

Useful developments of the production process and the product itself are the objects of the dependent Claims.

30 Experimental section

To assess the granular materials according to the invention, the following tests were performed:

35 1. Hygroscopicity test

To assess the hygroscopicity at room temperature, the following atmospheric humidities were established in

several desiccators (ϕ 160 mm) using saturated solutions (with excess solute present):

55 % relative humidity: $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

76 % relative humidity: NaCl.

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5 g of each test substance are distributed uniformly in a weighing bottle (ϕ 50 mm) and the weighing bottles are stored open in the desiccator (at the desired humidity) at room temperature. The weighing bottles are taken out of the desiccator after 1, 2, 3, 5 and 7 days, assessed visually and the increase in weight recorded. In a few cases the water content can also be determined using a Karl-Fischer titration.

15 2. Caking test

Screen printing pads which have each been filled with 20 g of the particular test substance and are provided with an applied weight of 1.2 kg are each placed in a desiccator at room temperature at a relative humidity of 55 or 76 % (established using saturated salt solutions, see point 1). After 3 days the compressed products obtained in this way are laid carefully in a horizontally-rotating roller sieve (55 rpm). After switching on the rotating sieve the abrasion time in seconds after which a defined amount (10 g) of abrasion has occurred on the roller sieve is determined (weight below the roller sieve). The shorter the abrasion time the lower the tendency to cake.

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3. Dr. Groschopp's dust measurement

100 g of test substance are placed in the vibrating chute (2) via the feed funnel (1). The frequency of the vibrating chute is adjusted via the controller so that the powder flows slowly and uniformly into the funnel. The powder falls through the funnel (3) and inlet tube (4) into the inner cylinder (5) in the test apparatus

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which is placed underneath the funnel, while the dust falls outside this vessel onto the base plate (6) of the outer cylinder (7) (see figure 1).

5 After completing the addition of powder, the residues of powder remaining in the vibrating chute and in the funnel are transferred to the test apparatus using a brush. After a waiting time of 5 minutes, the dust deposited on the bright polished base plate is collected
10 and weighed. The dust content is expressed as a percent with respect to the amount initially weighed out.

15 **Example**

A spray dried sodium methioninate (NaMet; molar ratio Met:Na = 1:1) was used for the granulation process wherein the methioninate solution was pre-treated with active
20 carbon.

Analysis for NaMet (spray dried)

- bulk density (kg/m³) 500
 - compacted density (kg/m³) 600
 - 25 • particle size distribution (%) <200 µm >90 %
 - dust fraction (%) approx. = 4
- (Dr. Groschopp's dust test, figure 1: dust test equipment)

30 The spray dried product is granulated in an Eirich mixer under the following conditions (table 1):

Table 1: Granulating conditions in the Eirich mixer

Product	Granulate A	Granulate B
Weight of NaMet (spray dried) used [kg]	2.5	1.66 (+83 g stearic acid as additive)
Volume of granulating liquid [ml] Liquimeth (60% Met)	530	390
Speed of fluidiser (rpm)	3000	3000

- 5 The general handling properties of the granular material were checked (table 2).

Table 2: Handling properties of the granular material

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Product	Granulate A	Granulate B
Bulk density (kg/m ³)	740	800
Compacted density (kg/m ³)	840	900
Particle size distribution (%)		
< 100 μ m	7	9
100 - 500 μ m	51	53
500 - 1000 μ m	23	23
1000 - 1400 μ m	6	5
1400 - 3150 μ m	9	8
3150 - 5000 μ m	4	2
Dust fraction (%)	0.2	0.1

Data on the hygroscopic characteristics and tendency to cake of sodium methioninate in the spray dried and granular form respectively are particularly relevant (see
15 table 3).

When comparing the various product forms it can be seen that a much smaller increase in weight (equal to absorption of water) takes place with granular material. The differences between spray dried product and granules is particularly noticeable at a relative humidity of 55 %. With a relative humidity of 76 % (although the numerical differences are smaller) the visual appearance of the granular form is much better.

- 10 Increases in weight of up to about 18 % produce a thicker or thinner surface incrustation on the product. Whereas in the case of the granular material a short, sharp blow to the glass vessel was sufficient to obtain a free-flowing product, the spray dried powder had to be crushed after
15 "weathering" in order to obtain a free-flowing material.

This subjective impression is also confirmed by the results on assessing the tendency to cake (table 3). The lower tendency to cake of sodium methioninate in granular
20 form is clearly demonstrated by the shorter abrasion times.

Table 3: Hygroscopicity and tendency to cake of sodium methioninate in the spray dried form and as a granular material.

Product	NaMet (spray dried)	Granulate A	Granulate B
55% relative humidity			
Increase in weight (%)			
after 1 day	8.4	5.8	4.0
2 days	11.8	6.7	4.6
3 days	12.1	7.1	5.3
4 days	11.4	7.7	5.4
5 days	13.4	7.8	5.6
Tendency to cake			
Abrasion time (s)	60	20	13
76% relative humidity			
Increase in weight (%)			
after 1 day	12.4	10.1	8.9
2 days	17.7	13.6	11.4
3 days	23.6	15.0	14.5
4 days	25.7	26.3	24.7
5 days	31.0	33.6	31.2
Tendency to cake			
Abrasion time (s)	295	145	147

Claims

1. Process for preparing a free-flowing, animal feed supplement based on a methionine salt, characterised in that a methionine salt solution is converted into a granular material.
2. Process according to Claim 1, characterised in that the methionine salt solution is spray dried and the powder obtained in this way is then granulated.
3. Process according to Claim 1, characterised in that the methionine salt solution is simultaneously spray dried and granulated in a fluidised bed.
4. Process according to one or more of Claims 1 to 3, characterised in that the methionine salt solution is converted into a granular material by means of a shaping process, optionally by extrusion) (sic).
5. Process according to one or more of Claims 1 to 4, characterised in that the methionine salt solution is treated with active carbon before spray drying and/or granulation.
6. Process according to one or more of Claims 1 to 5, characterised in that the methionine salt solution is sprayed and/or granulated in the presence of additives based on siliceous material.
7. Process according to Claim 6, characterised in that a hydrophilic or hydrophobic silica, prepared by precipitation or of a pyrogenic nature, is used as the additive in an amount of 0.1 to 10 wt.%, with respect to the solid.
8. Process according to Claim 6, characterised in that a finely divided zeolite or bentonite is used as the



additive in an amount of 0.1 to 10 wt.%, with respect to the solid.

- 5 9. Process according to Claim 6, characterised in that fatty acids and/or their alkali metal/alkaline earth metal salts are used as the additive in an amount of 0.1 to 10 wt.%, with respect to the solid.
- 10 10. Process according to one or more of the preceding Claims, characterised in that a 10 to 70 % strength solution, with respect to a methionine base, is used.
- 15 11. Process according to Claim 10, characterised in that a 25 to 50 % strength solution is used.
- 20 12. Process according to one of the preceding Claims, characterised in that a Na and/or K methioninate solution is used.
- 25 13. Process according Claim 12, characterised in that a sodium methioninate solution is used.
- 30 14. Process according to one or more of the preceding Claims, characterised in that a powder with a bulk density in the range 350 to 500 kg/m³ and a dust fraction in the range 1 to 5 % is obtained after spray drying and that this is granulated.
- 35 15. Process according to one or more of the preceding Claims, characterised in that the spray dried powder is granulated together with a saturated solution of the methionine salt in a mixer with a strong shear action.
16. Process according to Claim 15, characterised in that the ratio by weight of powder to saturated solution of methioninate, with respect to the solid substance, is in the range from 1:0.01 to 1:0.5.



17. Process according to one or more of the preceding
Claims, characterised in that granulation is
performed in a fluidised bed, optionally with
5 inserted crushing devices.
18. Process according to one or more of the Claims (sic),
characterised in that an extrusion shaping process is
used to obtain the granulated material, optionally
10 combined with an intensive mixer or a fluidised bed
drier.
19. Methioninate granular material which is very free-
flowing characterised by
15 a) a bulk density of $> 650 \text{ kg/m}^3$,
b) a particle size distribution of 63 to 5000 μm ,
c) a dust content of $< 1 \%$.

